Positron annihilation studies
of heavy-fermion metals
and related compounds

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This thesis has been submitted to the Science Faculty at the University of Bristol in Candidature for the degree of Ph.D
Abstract

A recently implemented spectrometer for the detection of the two-dimensional angular correlation of electron-positron annihilation radiation (2D-ACAR) is described and utilised for measurements of Heavy-Fermion (HF) Cerium compounds.

The 2D-ACAR study of the HF dense Kondo system CeB$_6$ was performed and compared with that of the isostructural reference non f-electron material LaB$_6$. The anisotropies of the measured momentum spectra were very similar and in reasonable agreement with those of model spectra based on the Fermi surface topology of LaB$_6$ and de Haas van Alphen (dHvA) measurements. However, whereas the related k-space density of LaB$_6$, obtained by an LCW analysis, was in reasonable agreement with the calculations and the dHvA findings, the results for CeB$_6$ showed discrepancies with those expected from the Fermi surface topology. The use of a recently developed filter procedure, designed to remove long range distortions that are often encountered in such LCW spectra, provided a k-space density consistent with dHvA experiments and with theoretical models of the FS obtained by treating the f-electrons as localised.

The results of a preliminary 2D-ACAR study of the electronic structure of the heavy-fermion system CeCu$_6$ were compared with those obtained for the isostructural reference non f-electron system LaCu$_6$. The spectra relating to the two compounds displayed extremely similar anisotropic structures. At present, these structures cannot, however, be attributed to Fermi surface or positron wave-function effects or to anisotropies of full valence bands. In the case of LaCu$_6$, data processing prior to the LCW procedure via the new filtering techniques revealed a reasonable agreement between the LCW data and LAPW Fermi surface calculations. However, in the case of CeCu$_6$ it was difficult to relate the results, still of controversial interpretation, to any theoretical model.
Author declaration

This thesis is the presentation of work carried out in the Department of Physics at the University of Bristol between September 1992 and September 1995. No part of this thesis has been submitted elsewhere for any degree or diploma qualification. The substance of this thesis is original, except where specific references are made to the work of other authors.
Acknowledgements

This thesis is dedicated to my wife Nadia, for the great support she gave me during the time of writing this work, and to my children Adriano and Dario who were always interested in the "invisible light" (gamma rays) coming out of the equipment.

I first would like to thank Ashraf Alam and Balash Györffy, for inviting me to Bristol and the head of my department in ENEA (the Italian Agency for Energy Studies) Mario Stefanon who allowed and supported the collaboration. Alfredo Dupasquier (from Milano Politecnico) also collaborated financially and scientifically on the project.

The members of the positron group at Bristol, led by Ashraf Alam, were very helpful, especially at the early stages of the set-up. Andre, John, Julius, Helen, Nigel, Steve (D) and Steve (U) should all be remembered for their kindness. I must thank also Richard, Ken and Ray for their help with machinery.

I am grateful to all the members of the de Haas van Alphen group for the interesting discussions (particularly with Steven Hayden). The contacts with Balash Györffy and the visitors of the condensed matter theory group were extremely stimulating. In particular, the close collaboration with Hisatomo Harima on the analyses of the experiments performed was invaluable. During my stay in Bristol I also benefited from the visit of Roy West, one of the two fathers of the 2D-ACAR technique, who collaborated on the experiments reported here and gave me a lot of good advice.

However, the list of the acknowledgements would be badly incomplete if I did not recall the scientists with whom I worked before my arrival to Bristol. The late Stephan Berko from Brandeis University (Boston) initiated me into the positron annihilation spectroscopy and helped me to set up the lifetime and doppler broadening experiments on my return to Bologna. Allen Mills, Kelvin Lynn and Piero Sferlazzo (at Brookhaven National Laboratory) introduced me to the 2D-ACAR experiments. The implementation of the spectrometer relied largely on their advice.

With friends from so many countries, it is obvious to realise about the international perspective of Physics, probably the most cosmopolitan science, which is what I like most.
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Introduction

The subject of this thesis is the study of the electronic structure of specific rare-earth metallic compounds via the measurement of the two dimensional angular correlation of the positron-annihilation radiation technique (2D-ACAR).

The compounds analysed belong to a class of materials well known for their large, non-linear specific heat and the unusual behaviour of the resistivity below some characteristic temperature $T^*$. The large low-temperature specific heat indicates an exceptionally high density of states at the Fermi energy which results when the conduction electrons behave as if they were very heavy. Heavy-Fermion (HF) is therefore the usual denomination of these compounds. In all HF compounds one of the constituents is a lanthanide or an actinide with a partially filled f-shell. The role played by the f-electrons in determining the high density of states at the Fermi energy is perhaps the most intriguing and challenging question of HF compounds.

The 2D-ACAR experiments have already been applied with success to the study of the electron-positron momentum distribution of elemental, binary alloys and more complex metallic compounds (like the high $T_c$ superconductors) to obtain information on the topology of their Fermi surface (FS)\(^1\). Within the limits of the perturbation caused by the effect of the non uniform positron density, the 2D-ACAR experiment presents two interesting features: i) has direct access to the electron momentum-wave-function amplitude ii) it can be performed at any temperature\(^2\).

The technique is an almost unique tool for monitoring FS topological transitions which follow temperature or composition changes in (substitutionally) disordered alloys\(^3\).

Here, it is used to complement the low temperature de Haas van Alphen measurements of HF systems in different phases of the magnetic phase diagram. The basic question of the HF phenomena regards the contribution of the f-electrons to the Fermi volume and how the finite temperature effects (in particular, at temperatures $T$ greater than $T^*$) affect the electronic structure.

The first chapter reviews briefly the experiments which display the interesting HF phenomena and some theoretical tools which were devised to explain the experimental

\(^1\) The momentum distribution of semiconductor systems was also studied with 2D-ACAR experiments.

\(^2\) The FS is defined at $T=0K$, but its smearing (in simple metals) is much smaller than the typical experimental resolutions even at room temperature.

\(^3\) It is established that in most cases one can define FS-like discontinuities also in disordered alloys.
findings of systems constituted by metallic systems with very dilute magnetic
impurities. The current understanding of HF systems is then described with emphasis
to the many questions which are not yet solved by the theory (in particular regarding
the contribution of the f-electrons to the Fermi volume).

The second chapter describes the theoretical basis of the angular correlation
experiment in metallic systems and the efforts to deduce from the object of the
experiment, the electron-positron momentum density, information about their Fermi
surface.

The technical aspects of the detection system are described in chapter 3. The
spectrometer was implemented and tested in Bologna and transported to Bristol,
where the experiments described in this thesis were performed. Functional checks of
the single detectors (performed in Bologna) and of the overall spectrometer
(performed in Bristol) are described as well.

Chapter 4 is concerned with the operation of the system, and the procedures followed
in the collection and routine analysis of the data. The standard data analysis and the
novel analysis tools implemented recently at Bristol (and Arlington) are discussed.

Chapter 5 reports the results of the experiments on the HF system CeB₆
supplemented by measurements of the reference non f-electron system LaB₆. The
analysis succeeded in supplying quantitative information on the Fermi topology of
both compounds.

In chapter 6 preliminary results of the HF system CeCu₆ are shown and compared
with those obtained for the reference non f-electron system LaCu₆. Although the
analysis of LaCu₆ provides results which are consistent with the main features of the
calculated FS, the results reported for CeCu₆ are of controversial interpretation and
not supporting any current theoretical model.

Chapter 7 summarises the experimental results and discusses their implications for
Heavy-Fermion issues.

Some appendices present aspects of the data analysis.
1 A brief overview of Heavy Fermion systems

The most intriguing phenomena of solids are those characterized by strong electronic correlations which manifest themselves at (relatively) low temperatures. The most striking one is certainly superconductivity (SC) which, after the discovery of the new class of high temperature cuprate superconductors, has entered a new era of experiments and theories. A second class of materials which has appealed to numerous theorists and experimental groups in the last ten years or so has been termed Heavy-Fermion (HF) systems. To define what is a HF system is not an easy task. As far as the composition is concerned, they are primarily intermetallic compounds in which one of the constituents is a lanthanide or actinide ion with a partially filled f-electron shell. Some of the most famous examples are the Ce-based compounds, CeAl$_3$, CeCu$_2$Si$_2$, CeRu$_2$Si$_2$, CeCu$_6$, CeB$_6$, and the U-based systems UBe$_{13}$, UPt$_3$, URu$_2$Si$_2$, UCd$_{11}$.

At least three different sets of experiments contribute to the description of these systems. They are i) thermodynamic, ii) magnetic and iii) transport measurements. The next section shows that to define the common properties of these materials is a fairly hard task as many experimental parameters which characterize them span over a relatively large range.

1.1 Physical properties

i) Specific Heat
At temperatures much below the Debye temperature $\Theta_D$ $^1$, which is of the order of $10^2$ K, the specific heat $C$ of metals may be written as

$$C = \gamma T + \beta T^3$$

1.1

Here the constants $\gamma$ and $\beta$ account for the electronic and phononic contribution to the specific heat $C$ respectively. In the Debye model [Kittel (1986) p106] the constant $\beta$ (for $N$ atoms) is defined as

$$\beta = 234Nk_B / \Theta_D^3$$

1.2

$^1$ $\Theta_D$ is defined as $\Theta_D = \hbar k_D v / k_B$; here $v$ is the sound velocity and $k_D$, the cut off wave vector, is defined as $k_D = (6\pi^2 N/V)^{1/3}$, where $N/V$ is the atomic density.
and in the free-electron model [Kittel (1986) p125] (FEM) the constant $\gamma$ can be expressed as

$$\gamma = \frac{\pi^2 D(E_F) k_B^2}{3} = \frac{41 n[el/atom]}{T_F[K]}[J/moleK^2],$$  \hspace{1cm} (1.3)

where $D(E_F)$ is the density of electronic states at the Fermi energy $E_F$, $n$ is the number of conduction electrons per atom and $T_F = E_F/k_B$ is the Fermi temperature. In plotting the specific heat $C/T$ versus $T^2$ one should therefore observe a straight line with slope $\beta$ and an intercept at $\gamma$. This is what is measured in the case of simple metals. As $T_F$ is of the order of $10^4$ K, it turns out that in most of the metallic systems the values of $\gamma$ are of the order of milli Joules per mole per K$^2$. For instance, applying eqs. 1.2 and 1.3 to Potassium, gives 1.66 mJ / mole K$^2$ and 2.58 mJ / mole K$^4$ for $\gamma$ and $\beta$ respectively, in good agreement with the 2.08 mJ / mole K$^2$ and 2.57 mJ / mole K$^4$ measured experimentally [Kittel (1986), p139]. In other cases the observed values of $\gamma$ are of the expected magnitude but do not agree closely with the value calculated via eq. 1.3.

Because of the linear dependence of $D(E_F)$ on the free electron mass $m_{el}$ in the FEM, it is natural to define an effective thermal mass as

$$m_{el}^* \equiv \frac{\gamma_{observed}}{\gamma_{free}} m_{el},$$  \hspace{1cm} (1.4)

where $\gamma_{observed}$ is the value measured experimentally, $\gamma_{free}$ is the value calculated (via FEM or more sophisticated computational techniques) and the ratio $\gamma_{observed}/\gamma_{free}$ is called mass enhancement. The pictorial definition of heavy-fermions has arisen owing to the massive coefficients of the linear term of the specific heat which they display. The values of $\gamma$ (in units of mJ / mole K$^2$) which have been observed spread continuously over a large range, from $\gamma$~1620 (CeAl$_3$), $\gamma$~1600 (CeCu$_6$) to $\gamma$~420 (UPt$_3$). A lower cut-off above which a system could be defined as a HF used to be set at 400 mJ / mole K$^2$ but was somewhat arbitrary. In fact, many compounds are known which display values of $\gamma$ in the range 20-400 mJ / mole K$^2$ and should belong to the HF group, according to Onuki et al (1991). This is, for instance, the case of CeB$_6$, which will be discussed in this thesis ($\gamma$~250), URu$_2$Si$_2$ ($\gamma$~180), CeCu$_2$ ($\gamma$~82), CeSb ($\gamma$~20) and many other compounds in the range 100÷20 mJ / mole K$^2$.

Often the mass enhancement is obtained by comparing the $\gamma$ constants with those of corresponding isostructural compounds where the f-electrons are absent. For
example, in the case of Ce compounds one can often produce reference La compounds (e.g. LaB$_6$-CeB$_6$, LaCu$_6$-CeCu$_6$, LaSb-CeSb,...).

ii) Magnetic susceptibility

The magnetic properties of the HF systems are determined essentially by the presence of the f electrons on the rare-earth and actinide ions. Above some characteristic temperature, T*, the magnetic susceptibility $\chi$ is described with good approximation by the so-called Curie-Weiss behaviour,

$$\chi = \frac{N p^2 \mu_B^2}{3k_B T}.$$  \hspace{1cm} \text{(1.5)}

Here N is the number of magnetic moments with $p=\frac{g}[J(J+1)]^{1/2}$, $\mu_B$ is the Bohr magneton, $g$ is the Landé' factor\(^2\) and $J$ the total angular momentum. It is well known that the Curie-Weiss behaviour is typical of systems where "local" magnetic moments are present. In the case of HFs, the values of the magnetic moments measured via the Curie plots are often consistent with those calculated via the Hund's rules [Ashcroft (1976) p650] for free atoms assuming that only the f-electrons of the compounds contribute to the magnetic moment. For example, in triply ionized Ce the calculated $p=2.54$ and in CeB$_6$, for a wide temperature range, $p=2.34$ [N Sato et al (1984)].

At lower temperatures, the magnetic susceptibility can behave very differently depending on the compound. In some case (as it would be natural to expect from purely thermodynamic considerations) the magnetic moments order. In this case the susceptibility $\chi$ is described by a $\chi = \text{constant} / (T-\theta)$ law for T>\theta; here $\theta$ is the temperature where the susceptibility diverges ($T_{\text{Curie}}$, ferromagnetism), or simply shows a cusp ($T_{\text{Neel}}$, antiferromagnetism). A classical example is represented by CeB$_6$.

Conversely, in several other HF compounds $\chi$ (surprisingly) departs from its Curie-Weiss behaviour to approach a weakly varying (approximately constant) function of the temperature. A temperature independent Pauli susceptibility is consistent with a picture where the carriers of the magnetic moments are the conduction electrons. In this case, the susceptibility $\chi$ calculated via FEM is $\chi = \mu_B^2 D(E_F)$. In the FEM the ratio $\chi / \gamma$ (called Wilson ratio) is therefore simply $\frac{3\mu_B^2}{\pi^2 k_B}$. The constant $\chi$ value reached by this class of compounds is, similarly to the $\gamma$ constant, very high in value.

\(^2\) $g = \frac{3}{2} + \frac{S(S+1)-L(L+1)}{2J(J+1)}$, where L is the total orbital angular momentum and S is the total spin (in the Russel-Saunders coupling).
Experiments have shown [Lee et al (1986)] that, for many HF materials, \( \chi \) and \( \gamma \) are enhanced by approximately the same amount.

Another quantity which shows a large enhancement with respect to normal metals is the cyclotron mass, which is measured in the de Haas van Alphen (dHvA) experiments by monitoring the damping in the oscillations in the magnetization, induced by an applied external magnetic field, as a function of the temperature. Values observed for HFs span in ranges up to 100 times the bare electron masses [see for example Taillefer et al 1987]).

**iii) Transport measurements**

The behaviour of the resistivity of all the HF compounds differs strongly from the monotonic behaviour shown by simple metals. In this case the contribution to the resistivity \( \rho \) is dominated by the electron phonon interactions. The temperature dependence of the resistivity (Ashcroft (1976) p 525) is linear, \( \rho \propto T \), for \( T \gg \Theta_D \) and \( \rho \propto T^5 \) for \( T \ll \Theta_D \). The resistivity, \( \rho \), then approaches a constant at very low temperature contributed by the impurities (Mathiensen rule).

Figure 1.1 shows the low temperature part of the \( \rho \) vs \( T \) diagram for the series \( \text{Ce}_x\text{La}_{1-x}\text{B}_6 \). (At higher temperatures the resistivity is increasing with increasing temperature.) The resistivity of HFs displays a twofold structure as a function of the temperature:

i) It shows a minimum and then rises as the temperature decreases. This behaviour resembles the one observed in the case of noble metals with very dilute magnetic impurities and is named the **Kondo effect** after the scientist who, after almost 30 years of mystery, was the first to suggest an outline of an explanation [Kondo (1964)].

In that case the total resistivity can be described by the following expression

\[
\rho(T) = \rho_0 + a_1 \ln \frac{a_2}{T} + b T^5 ,
\]
where the physical meaning of the constants $a_1$ and $a_2$ will be discussed later. (In the case of the magnetic impurities, a temperature independent plateau in the resistivity is then observed below some characteristic temperature.)

ii) For very low temperatures (always less than ~10 K) $\rho$ reaches a maximum and then decreases again showing what has been termed as Kondo lattice coherent behaviour. The temperature dependence in this region can be described by an equation of the form

$$\rho(T) = \rho_0 + AT^2.$$  

The $T^2$ behaviour is typical of a resistivity dominated by electron-electron interaction [Ashcroft (1976) p 346]. It is essentially a consequence of the Pauli exclusion principle and in normal metals is usually too weak to be observed except at extremely low temperatures. In the case of HFs the $T^2$ behaviour can be observed because of the very high value of the coefficient $A$. A very important experimental result (figure 1.2) is that for HFs the ratio $A/\gamma^2$ has a common value ($\sim 1 \times 10^{-5}$ $\mu\Omega$ cm (mole K/mJ)^2 [K Kadowaki (1986)]. It is surprising that all HFs, which have very different ground states (magnetically ordered or not) follow this universal relation very closely.

It is interesting to note that superconductivity appears in some HFs (to date CeCu$_2$Si$_2$, UBe$_{13}$ and UPt$_3$) at low temperature ($T<1$K) [see, for example, Steglich (1984)]. A discussion of HF superconductivity is not the aim of this brief survey. The fact that these HFs (in particular UPt$_3$) seem to display "unconventional" superconductivity, particularly as far the the nature of the fermions' pairing is concerned, gives rise to problems which would require a very thorough discussion and will not be pursued here.
1.2 Theoretical models for dilute alloys of magnetic impurities in simple metals

The properties of dilute alloys of transition metals (like Vanadium or Iron) or rare-earths dissolved in a simple metal solvent like copper or gold gave rise to an impressive number of studies in the sixties and the seventies. In the most comprehensive review paper on the field, Tsvelick and Wiegmann (1983) count 1500 (!!) papers plus 20 reviews written specifically on the Kondo problem. Heavy-Fermions, in spite of showing some similarity with the magnetic impurities systems, add further complications which are still hiding exact solutions. In this brief introduction, only topics relevant to the experimental results which will be reported later in this thesis will be mentioned.

To elucidate these problems, the model Hamiltonians which have been devised to explain the experimental findings on magnetic impurities will be briefly discussed. Many of these model Hamiltonians are still widely used (with the required modifications) to describe HFs. It is, in fact, a common belief that lanthanide and actinide ions in HFs play a role similar to the one played in dilute magnetic alloys.

i) The Anderson Hamiltonian

As mentioned above, the high temperature behaviour of the magnetic susceptibility is consistent with a local magnetic moment model. The conditions for the existence of local moments in Magnetic Impurities were discussed by Friedel (1956) and Anderson (1961). The underlying physical assumptions of the Anderson model Hamiltonian were the following:

1) The metallic host is represented by an electron band with Bloch states of energy $\varepsilon_k$ and momentum $k$.

2) The impurity is characterized by an inner local $d$ (or $f$ for rare earths) state in which the Coulomb interaction introduces a repulsion, $U$, between two electrons at the impurity level. This term plays an important role in the formation of a magnetic moment on the localized level as, in order to be magnetic, the impurity orbital must be singly occupied.

3) The transition between impurity-conduction states is represented by an extra term, $V_{k\ell\ell'}$, in the interaction Hamiltonian assuming hybridization between the conduction electrons and the electron situated at the impurity.

The resulting Hamiltonian, for a case of a single nondegenerate $d$ orbital, is given by
\[ H = \sum_{k,\sigma} E_k a_{k,\sigma}^* a_{k,\sigma} + \sum_{\sigma} E_d d_{\sigma}^* d_{\sigma} + Ud_{\sigma}^* d_{-\sigma}^* d_{-\sigma} - \sum_{k,\sigma} V_{dk}(d_{\sigma}^* a_{k,\sigma} + a_{k,\sigma}^* d_{-\sigma}), \]

where the \( a_{k,\sigma} \) (\( a_{k,\sigma}^* \)) are the destruction (creation) operators for the conduction electron with Bloch wavevector \( k \) and \( d_{\sigma} \) (\( d_{\sigma}^* \)) are the destruction (creation) operators for the \( d \) electron state with spin \( \sigma \).

The meanings of the r.h.s. terms of the Hamiltonian can be summarised as follows:

i) the first term represents the unperturbed energy of free electrons.

ii) the second term represents the unperturbed energy of the \( d \) state on the impurity atom.

iii) the third term accounts for the repulsion between electrons with opposite spins at the impurity site (that for electrons with parallel spin being ruled out by the Pauli exclusion principle).

iv) the fourth term is the \( s-d \) (or \( s-f \)) hybridization term.

Before discussing the results of the many-body Hamiltonian it is useful to mention the findings of the simple and well-discussed [see Cohen-Tannoudji et al (1977) p1502] problem of one particle subjected to the initial condition of occupying a discrete state, \( |\varphi_d\rangle \), which is coupled to a pseudo-continuum of states by some perturbation. This system is equivalent to the Anderson model (eq. 1.8) in the absence of Coulomb repulsion (\( U = 0 \)). As a result of the coupling the particle will stay in the \( |\varphi_d\rangle \) state for a finite time only, the transition rate being determined by the Fermi golden rule [see Cohen-Tannoudji et al (1977) p 1291]. This means that \( |\varphi_d\rangle \) is not a stationary state: it will be characterized by an effective energy \( E_d' \) and a finite lifetime. Here \( E_d' = \varepsilon_d + \Delta \varepsilon_d \), where \( \Delta \varepsilon_d \) is the shift of the unperturbed energy of the discrete state, \( \varepsilon_d \), by action of the coupling. Therefore, the probability of finding the particle in the discrete state decreases exponentially in time. The system will evolve from the initial state to a superposition of states of the continuum. The energy distribution of the final states will be in the form of a Lorentz curve of width \( \Delta \), proportional to the density of states of the continuum at \( \varepsilon_d \), centred at the energy \( E_d' \). This process is usually denominated as the creation of a resonance.

Anderson solved eq. 1.8 via a mean-field approximation. Here this consists of replacing the 2-bodies operator in the third term of eqn 1.8 with a 1-body operator, \( \sum_{\sigma} U < n_{d,\sigma} > n_{d,\sigma}^* \), where \( n_{d,\sigma} \) is the density, \( d_{\sigma}^* d_{\sigma} \), operator and \( < n_{d,\sigma} > \) represents the average density, or expectation value, of electrons with up (or down) spin.
The main result of the solution of the many body problem shows similarities to the simple one-particle case mentioned above:

The density of states of the bare conduction electrons is increased by a Lorentzian factor with a width $\Delta$ centred at $\varepsilon = \varepsilon_d + \Delta \varepsilon_d + U <n_{d-\sigma}>$. Here $\varepsilon_d$ represents the energy of the unperturbed $d$ orbital, $\Delta \varepsilon_d$, is a term analogous to that encountered in the simple one particle case and $U <n_{d-\sigma}>$ is the effect of the Coulomb repulsion from the electrons of opposite spin. $\Delta$ can be approximated by a constant equal to $\pi V^2 \rho_\varepsilon(\varepsilon_d)$, where $V$ is the appropriate average of the hybridization term $V_{dk}$ and $\rho_\varepsilon(\varepsilon_d)$ represents the density of states of the conduction electrons in the host metal at the energy of the resonance.

Depending on the competition between hybridization $V$ and Coulomb repulsion $U$ one can define two limiting cases:

1) The broadening of the localized level can be neglected compared to the Coulomb interaction, i.e. $\Delta << |\varepsilon_d|$ and $\Delta << U$. In this case, if the energy of the singly occupied level is below the Fermi level, the state of the impurity results magnetic or not depending on whether the energy required to fill the second level of the impurity, $\varepsilon_d + U$, is above or below the Fermi level.

2) The other limit is when a broad resonance is formed at the Fermi level and the Coulomb repulsion is relatively small compared to the width of this level, i.e. $|\varepsilon_d|, U << \Delta$. In this case the Coulomb energy does not significantly modify the density of states related to the localized level. The state is therefore non-magnetic but the fluctuations in the occupation numbers for different spins cause magnetic moments to be formed for a short time (phenomenon known as localized spin fluctuations).

In general, the width of the density of states of the virtual state of the impurity must be studied and the net magnetization, $m = <n_{\sigma}> - <n_{-\sigma}>$, calculated.

In his original paper Anderson discusses the order of magnitudes of the repulsion term, $U$, with a few examples. In the case of rare-earths (which is the one of our interests for its link with HF systems) he assesses $U \sim 15$ eV and the hybridization term $<V_{av}> \sim 1$ eV at most. It can, therefore, be concluded that for rare earth impurities magnetic cases are to be expected almost exclusively.

An exact solution of the Anderson Hamiltonian with a single localized orbital was found by Wiegmann (1980). The Anderson model Hamiltonian in a system with a periodic lattice of atoms containing localized f-electron states interacting with each other by Coulomb repulsion $U$ at the same site, is the basis of many attempts to describe the thermodynamic and transport properties of HF's. However, before mentioning some of these attempts, it is instructive to describe the theoretical model devised to explain the behaviour of the resistivity in systems with magnetic impurities.
The s-d model and the Kondo solution

A simple model, usually referred to as the s-d exchange model (even though, because of applications to HF systems, should be more appropriately addressed as the s-f model), was based on the supposition that a magnetic moment is formed at the impurity. While discussing the Anderson model, as mentioned earlier, this is a plausible assumption for rare-earth impurities. Moreover, the experimental findings of the magnetic susceptibility at high temperature confirm this hypothesis for HF systems. Once the moment is formed, the approximation is that its interaction with the conduction electrons (assumed populating 4s or 5s bands) could be treated separately. In the s-d model, the conduction electron spin $s$ is coupled to the local moment of the impurity with angular momentum $S$ by an effective exchange coupling $J$ leading to an Heisenberg-like spin Hamiltonian \[ H_{sd} = -JS \cdot s. \] The exchange term $J$ is positive or negative for ferromagnetic or antiferromagnetic couplings respectively and its sign and intensity could be left as a parameter to be determined by experiments. The greatest success of the s-d model was provided by Kondo (1964) who succeeded in explaining the resistivity minimum in magnetic impurities by assuming an antiferromagnetic $J$ exchange coupling. Kondo performed the calculation of the s-d model Hamiltonian within a third order perturbation theory i.e. in the second Born approximation of scattering between conduction electrons and impurity electron. It is the spin-flip of the conduction/magnetic-impurity electrons during their interaction the "engine" which keeps the conduction electrons' Fermi-Dirac energy distribution (and therefore the temperature) in the calculation of the scattering probability. In this sense, the scattering on a magnetic impurity shows a many-body character which is absent in the normal scattering by a potential. The underlying physical idea is that during the scattering the angular momentum of the electron of the impurity fluctuates (i.e. it changes its projection $S_z$ along the main quantization axis direction) and the fluctuation depends on different scattering channels with the conduction electrons of the Fermi sea, whose occupancies are determined by the Fermi distribution. The Kondo results show remarkable features:

i) for an antiferromagnetic coupling (negative $J$) the contribution to the resistivity from the s-d interaction decreases with increasing temperature; the experimental minimum in the resistivity is therefore accounted for by the theory.

ii) at low temperatures a logarithmic term in the expression of the resistivity, $\rho(T)$, dominates. Kondo calculation of $\rho(T)$, gives [Kondo, 1969]

\[
\rho(T) = \rho_0 + bT^5 + aJ^2S(S+1)[1 + 4J\rho\ln(k_BT/D)],
\]

1.9
where \( \rho \) is an average conduction electron density of states, \( S \) is the spin of the impurity, \( D \) is the half-width of the conduction band, and \( \rho_0, b \) and \( a \) are experimental constants. As the temperature approaches zero the logarithmic term diverges. This divergence indicates that at low temperatures one should calculate further terms of the perturbation expansion because the current correction is not small. The calculation of the higher correction terms was performed by Abrikosov (1965) and Nagaoka (1965). An important result of the higher order corrections is that if one defines a Kondo temperature, \( T_K \) as

\[
k_B T_K = D \exp\{-1 / [J|\rho(0)|]\},
\]

where \( \rho(0) \) is the conduction-electron density of states at the Fermi energy, the scattering amplitude diverges as \( T \) reaches the temperature \( T_K \).

A detailed analysis below \( T_K \) shows that when \( T \to 0 \) the spin part of the resistance no longer increases but tends toward some finite limit. The expression for the total resistivity (in the absence of phonon effects) given by Nagaoka is the following,

\[
\rho = A + \frac{B}{2} \left( 1 - \frac{\ln(T / T_K)}{\left[ \ln^2(T / T_K) + \pi^2 S(S + 1) \right]^{1/2}} \right),
\]

where \( A \) and \( B \) are constants which depend on the potential scattering \( V \), (often unknown and therefore determined by fitting procedures), \( T_K \) is the Kondo temperature and \( S \) is the spin of the impurity. The theory succeeded in explaining quite well the behaviour of the resistivity in magnetic impurities and in HF systems (in the region of temperatures greater than the low-temperature maximum). However, the agreement was satisfactory only by constraining the impurity spin, \( S \), to \( \sim 1/2 \), rather than using the value determined by the high temperature susceptibility. The \( T_K \) values for CeB\(_6\) (5 to 10K, Takase et al 1980) and CeCu\(_6\) (4K, Onuki et al, 1987) referenced in §5.1 and §6.1 were obtained by fitting eqn 1.10a to the experimental data.

iv) As a consequence of this "infinite" coupling between conduction electrons and local moments, at temperatures below \( T_K \) a many-body "quasi bound state" is formed by the local moment and the conduction electrons so that the impurity spin is screened by the electron spins. This state is often described as a singlet state. Abrikosov (1965) and Suhl (1966) have noticed that the appearance of the singularity indicates the formation of a resonance in the conduction electron - impurity scattering amplitude which is centred at the Fermi level. This resonance (Kondo resonance) is a collective effect, contributed by the entire Fermi sea.
iii) The RKKY interaction

The interaction between the impurities determines the (low temperature) magnetic ordering properties of HFs. If the conditions for the formation of the local magnetic moment are fulfilled (as discussed by the Anderson model) and the Kondo effect is explained by the interaction between conduction electrons and impurities (s-d model) it is necessary to describe the nature of the interaction between the magnetic impurities. These are coupled through their interaction with the conduction electrons. This mechanism, known as indirect exchange interaction, is called RKKY after Ruderman, Kittel, (1954) Kasuya (1956) and Yosida (1957) who separately derived it for different systems. It was obtained using the same s-d exchange Hamiltonian which was later adopted by Kondo to explain the resistivity minimum. As the interaction considers the impurities as isolated systems, its application to HFs, where the substitute of the impurities, the f electrons, do not seem at all isolated, might be inappropriate. It is however interesting to note that in the HF case all the compounds have f-atom separation greater than 4 Å, significantly greater than the limit \[ \approx 3.2-3.5 \text{ Å} \], beyond which the f-f overlap ceases unless f hybridization with s, p or d electrons occurs. Even in elemental rare-earth metals the 4f shells are smaller than the 3d shells in transition metals and their mutual overlapping is very small. Therefore it is probably valid to consider these electrons as "isolated".

The indirect interaction in a metal proceeds as follows. The magnetic moment of the impurity of spin \( S_1 \) scatters a conduction electron of spin \( s \) and the magnetic moment of the second impurity of spin \( S_2 \) sees the scattered electron. Following the steps of Kittel (1968), one can determine the interaction between two impurities separated by a distance \( x \) by calculating the magnetization \( M \) at position \( x \) via the relation

\[
M(x) = \int \chi(x-x') H(x') \, dx'
\]  \hspace{1cm} 1.11

where \( \chi(x-x') \) is the magnetic susceptibility of the medium (consisting of the conduction electrons) and \( H(x') \) is the magnetic field generated by the impurity, which could be assumed to be a point source at \( x'=0 \).

Because of the non local character of the magnetic susceptibility it is much simpler to express (via the convolution theorem) eq. 1.11 in its equivalent form in Fourier space:

\[
M_q = \chi_q H_q,
\]  \hspace{1cm} 1.12

which shows a linear response of the magnetization with respect to the magnetic field. One can therefore simply solve the Schrödinger equation for the free electron
gas subjected to one single Fourier component of the magnetic field due to the impurity.

The correction to the ground state energy of the free electron gas, $E_q$, due to the magnetic field is obtained in a second order perturbation and the magnetic susceptibility obtained via the usual relation

$$\chi_q = -\frac{1}{V} \frac{\partial^2 E_q}{\partial H_q^2}. \tag{1.13}$$

The magnetic susceptibility $\chi(x-x')$ is then simply obtained by Fourier transforming eq. 1.13.

If the magnetic field, $H_q$, is generated by a magnetic impurity with spin $S_i$ at the position $R=0$, interacting with the conduction electrons via an exchange term $J(\mathbf{r}) = J \times \mathbf{\delta}(\mathbf{r})$, one can replace $H_q$ with $J S_i$ in eqn 1.12. A second impurity, with spin $S_2$ at distance $r_{12}$ from the first impurity, therefore interacts with the field generated by the first impurity. The interaction is of second order in the exchange integral $J$. It can be shown that the interaction between the two spins of the impurities $S_i$ and $S_2$ is an oscillatory function of the distance between the impurities, $r_{12}$,

$$E_{\text{int}} \propto |J|^2 S_i \cdot S_2 (\sin 2k_F r_{12} - 2k_F r_{12} \cos 2k_F r_{12}) / r_{12}^4, \tag{1.14}$$

where $k_F$ is the Fermi wave vector of the free electron gas.

The theoretical tools described so far are summarised below. They all have been devised for the problem of magnetic impurities in a noble metal host but are very useful in a basic understanding of heavy-fermions systems.

1) The conditions for the existence of the local magnetic moment, as discussed in the Anderson model, are related to the energetically unfavourable situation of two f-electrons at the same impurity site (due to a strong Coulomb repulsion).

2) The interaction between the conduction electrons and the (now considered formed) local moment is discussed by Kondo, Abrikosov and Nagaoka via the s-d model and is able to explain the resistivity minima shown by HF.

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3 The assumption is reasonable if $J(\mathbf{r})$ extends over a region smaller than $1/k_F$, where $k_F$ is the Fermi wave-vector. In this case $J_q = \int dr \exp(iq \cdot r) J(r) = J$

4 The coupling among the impurities oscillates therefore between ferromagnetic and antiferromagnetic, with periodicity $\pi/k_F$. 
3) The interaction among the local magnetic moments, as described by the RKKY interaction, produces the interesting consequence that a point source (the magnetic impurity) leads to an oscillatory spatial function of the magnetization of the conduction electrons.

1.3 Heavy Fermion behaviour

It is interesting to discuss the transition between the regime of dilute magnetic impurities to stochiometric HF compounds. In figure 1.1 and figure 1.3 are shown, as typical examples, the behaviour of the resistivity and of the magnetic susceptibility, for the La$_{1-x}$Ce$_x$B$_6$ series, respectively. From the high temperature part of figure 1.3 one may infer that, as the magnetic susceptibility (per Ce atom) is nearly independent of $x$, each Kondo state at a given Ce atom behaves almost individually even for dense systems.

Fig. 1.3 The temperature dependence of the magnetic susceptibility of Ce$_x$La$_{1-x}$B$_6$. The susceptibility above 100 K is nearly independent of Ce concentration; ref N Sato (1984)
On the other hand, from figure 1.1 it can be seen that at low temperatures the dense f-electron systems depart from the classical Kondo behaviour observed in the dilute part of the series and the resistivity decreases again approaching, below some characteristic temperature $T^*$, the $T^2$ behaviour. This is because a kind of coherence between each Kondo state develops and the system changes its character to the so-called coherent Kondo state or Kondo lattice. In particular, for pure systems like CeB$_6$ the resistivity at $T=0$ should become zero with a peak at $T_K$. This low temperature behaviour of the resistivity is common to all HFs.

It is important to stress a conceptual difference between magnetic impurities and HFs with regard to the Kondo states. For magnetic impurities the scattering of all the conduction electrons contributes to the formation of the low temperature singlet state. All the conduction electrons are required to screen the moment of the impurity. If the mechanism were the same for HFs one might expect [Nozieres (1985)] that in a Kondo lattice there are not enough conduction electrons to screen all the f moments accounted for. The energy gain of the Kondo-lattice due to the singlet formation, $kT^*$, should be much smaller than $kT_K$, which is typical of an isolated impurity.

i) RKKY interaction and s-d interaction

The low temperature magnetic order of CeB$_6$, which was mentioned above, is realized in competition with the Kondo state. A key point of the HF problem lies, in fact, in the comparison between the RKKY interaction among the carriers of the magnetic moments (which we may think of as localized) and the interaction between the conduction electrons and each local moment. In the case of magnetic impurities it was shown that the interaction of the Fermi-electron-cloud with the electron at the impurity leads to the "suppression" of the magnetic moment at low ($T<T_K$) temperature. However, if the impurity concentration exceeds some limit (~ 50 ppm, where this figure can vary over a relatively large range [Daybell (1966)] the effects of the impurity-impurity interactions on the bulk properties of simple Kondo systems are no longer negligible. In this case the impurity spins take on preferred orientations and spin-flip scattering is suppressed$^5$. The problem, however, is not only dependent on the impurity (f-electron) concentration as otherwise, in the case of HFs, RKKY interaction should always overcome the Kondo singlet formation. As eqn 1.14 shows, $E_{RKKY} \propto J^2$, where $J$ is the exchange integral (conduction electrons - impurity) and, $^5$ In a regular Kondo lattice the RKKY indirect interaction can cause a coherent ordering of the spins and therefore prevent the Kondo singlet formation. However, Abrikosov (1988) notices that, in the case of magnetic impurities, since they are randomly distributed, a magnetic ordering cannot be attained by the RKKY interaction, where the magnetic coupling is an oscillatory function of the distance between the impurities. Abrikosov conjectures the formation (at low temperature) of a so-called spin glass where the impurity spins are frozen with a random orientation. In this environment, the spin-flip scattering of the conduction electrons is then no longer possible.
from the definition of $T_K$ in eqn 1.10, one can define a binding energy of the Kondo
"singlet" $E_{\text{Kondo}} \equiv k_B T_K \propto \exp\{-1/[J(|\chi(0)|)]$. It is the competition between these two
energies which, in the case of HFs, should define whether the ground state is
magnetically ordered or not (Doniach 1977). If one can define a critical value, $J_c$, of
the exchange integral at which the RKKY and the Kondo interaction have the same
strength, the following cases can then arise:

i) if the Kondo temperature is sufficiently high, the interaction between the f
electrons and the conduction electrons is able to compensate for the local f-derived
moments.

ii) If $J < J_c$, the $k_B T_{\text{RKKY}}$ exceeds $k_B T_K$ and the local moments are retained. However,
the interaction between the conduction electrons and the impurity influences the kind
of magnetic ordering which is realized. In the case of CeB$_6$, for example, a complex
antiferroquadrupolar magnetic phase followed, at a lower temperature, by
antiferromagnetism (Effantin et al, 1985) is reminiscent of the higher temperature
Kondo coupling.

**ii) Periodic Anderson Model Hamiltonian**

This section briefly describes some of the attempts to explain the magnetic and
thermodynamic properties of HFs. Many of these attempts assume that, as it was
mentioned before, for several HFs the ground state is non-magnetic. The formation of
the Kondo singlet suggests that the massive values of the specific heat could be due to
the formation of very flat and narrow bands originated by hybridization between the
localized f electrons and conduction electrons (s-f hybridization). However, the
existence of notable exceptions among HFs which display a magnetically ordered
ground state casts some doubt on the uniqueness of the s-f hybridization as the
mechanism which causes the heavy masses.

As anticipated, the Anderson Hamiltonian (which could be adopted to explain
various magnetic phenomena for impurities, including the Kondo effect) can be
generalized to the HF case. As the role of the single impurity is taken now by one (or
more) f-electrons per site, eqn 1.8 transforms into

$$H = \sum_{k, \sigma} \epsilon_k a_{k, \sigma}^* a_{k, \sigma} + \sum_{m \neq m'} V_{mn} \langle i \rangle f_m^*(i) f_m(i)$$

$$+ \frac{U}{2} \sum_{i, \sigma} n_{m}^\dagger(i) n_{m}^\dagger(i)$$

$$+ \frac{1}{\sqrt{N_0}} \sum_{im \sigma(k)} V_{mn} \langle i \rangle \left[ a_{k, \sigma}^* f_m(i) e^{-ik_R} + f_m^*(i) a_{k, \sigma} e^{ik_R} \right].$$

1.15
The index term \( i \) labels the \( N_0 \) f-sites at positions \( \mathbf{R}_i \); \( a_{i\sigma} \) and \( a_{i\sigma}^* \) are the destruction and creation operators for the conduction electrons with Bloch wavevector \( \mathbf{k} \), energy \( \varepsilon(\mathbf{k}) \) and spin \( \sigma \); \( f_m \) and \( f_m^* \) are the destruction and creation operators for the f electron states; \( m \) is the degeneracy of the f orbitals with energy \( \varepsilon_f \). In the model the f electrons, prior to the hybridization, have no hopping-site probability (the overlap integral between the f-orbitals of neighbouring sites is assumed to be zero) and therefore form a zero-width energy band. In the case of rare earths one assumes that the 4f shells are in a state of total angular momentum \( J \) determined by the LS coupling. Application of the Hund's rules to Ce, for example, gives \( J=\frac{5}{2} \). In this case the \( m \) degeneracy would be \( (2J+1) = 6 \).\(^6\) The repulsion term \( U \) and the hybridization term \( V_{m\sigma} \) have the same meaning as in eqn 1.8. In most treatments the limit of large Coulomb repulsion \( U \) of the f electrons is considered, which means that double occupancies of f orbitals are excluded.

One way to solve eqn 1.15, in the so-called called mean field approximation, assumes that the strong Coulomb repulsion between f-electrons can be taken into account simply by a renormalization of the hybridization element \( V_{m\sigma} \rightarrow rV_{m\sigma} = \tilde{V}_{m\sigma} \) (Fulde 1991). By reducing the matrix element \( V_{m\sigma} \) by a factor \( r = (1-n_f)^{1/2} \), where \( n_f \) is the average f electron density, one decreases the probability that a conduction electron hops into an f orbital if occupied. The solution of eqn 1.15 [Fulde (1991)] with the mean-field approximation for the special case of one conduction band and an f orbital degeneracy of \( m=2 \) (\( \tilde{V}_{m\sigma} = \tilde{V} \)) predicts two bands with energies

\[
E_+ = \frac{1}{2} \left\{ [\varepsilon(k) + \tilde{\varepsilon}_f] + \sqrt{(\varepsilon(k) - \tilde{\varepsilon}_f)^2 + 4\tilde{V}^2} \right\}, \tag{1.16}
\]

\[
E_- = \frac{1}{2} \left\{ [\varepsilon(k) + \tilde{\varepsilon}_f] - \sqrt{(\varepsilon(k) - \tilde{\varepsilon}_f)^2 + 4\tilde{V}^2} \right\}, \tag{1.17}
\]

where \( \mu \) is the chemical potential and the "renormalized" energy of the f level, \( \tilde{\varepsilon}_f \), is

\[
\tilde{\varepsilon}_f = \mu + \frac{\tilde{V}^2}{\varepsilon(k_f) - \mu} \equiv \mu + k_BT^*. \tag{1.18}
\]

As shown in figure 1.4, the conduction band hybridizes with the degenerate f level. The characteristic temperature \( T^* \) is related to the energy gain of the system due to the hybridization \( V \) and plays the role of a Kondo temperature for a lattice. The theory

\(^6\) Actually, in real materials the crystal electric field breaks this degeneracy. For example, in the case of CeB\(_6\) the sixfold degenerate \( J, J_z \) state is split into a duplet, \( \Gamma_7 \), and a quartet, \( \Gamma_8 \).
can be extended to $T \neq 0$, to obtain that only for temperatures $T$ less than a critical temperature $T_c$, of the order of $T^*$, a solution to the mean-field equations can be found, while for $T>T_c$ the conduction electrons decouple from the $f$ electrons. It is evident that the slope of the hybridized bands of this model could account for strongly renormalized band masses $^7$ and for an enhanced density of states at the Fermi energy. Because $V$ is small the $\tilde{\varepsilon}_f$ level lies slightly above the chemical potential $\mu$. The result of "pinning" the narrow quasi -particle band at the Fermi surface plays a key role in the mechanism which generates the heavy masses measured by thermodynamic measurements.

The following description, which is usually defined as the standard HF behaviour, is consistent with the model mentioned above [Steglich, 1994, Zwicknagl, 1993]:

i) above $T_K$, the conduction electrons are incoherently scattered by the localized $f$-electrons.

ii) upon cooling, the scattering increases and the $f$-electrons start to be weakly delocalized. The weakening of the magnetic moments causes the magnetic susceptibility to depart from its Curie-Weiss behaviour and approach that corresponding to the Pauli paramagnetism of the conduction electrons; at the same time the enhanced density of states at the Fermi level causes the increase in the linear coefficient of the specific heat.

iii) As the temperature falls further (below what is usually defined as $T_{ch}$, or coherence temperature), the coherent Kondo state is built: the $f$-electrons form delocalized Bloch states populating narrow bands which cross the Fermi level and dominate the thermodynamic and transport properties. The itinerancy of the "$f$-like" states originates from hybridization with the conduction electrons rather that from a

---

$^7$Recall that the definition of band mass, $m_b$, is linked to the band dispersion, $\varepsilon(k)$, by the relation

$$m_b = \hbar^2 \frac{\partial^2 \varepsilon(k)}{\partial k^2}$$
direct overlap between the f-states. The gigantic coefficient, A, of the T\(^2\) behavior of the resistivity\(^8\) (expressed by eqn 1.7) gives evidence that the main contribution to the scattering comes from "heavy" electron - "heavy" electron interactions.

iii) Realistic calculations

The final test of a theory which aims to describe a system appropriately consists in its comparison with the experiments. The mean field solution mentioned above seems to be able to account for the heavy masses measured by thermodynamic and dHvA experiments. It is evident from figure 1.4 that the hybridization leads to significant readjustments of the energy bands and, possibly, of the Fermi surface. A theory should therefore be able to compare its results with both the masses and the FS observed experimentally. Unfortunately, at the moment no \textit{ab initio} theory is able to supply quantitative results for realistic cases.

The problem of the correlation is nowadays generally addressed in terms of the Local Density Approximation (LDA), formulated by Hohenberg, Kohn and Sham (1964), (1965). These authors demonstrated that the ground-state (GS) properties, particularly the total energy \(E\), of a system of interacting particles can be related to the total electron density of the system. The criterion of minimising the total energy with respect to the electron density determines the GS wave-function. The equations which are solved by LDA are one-electron Schrödinger equations with an effective potential, \(V\), consisting of the ionic potential, \(V_{\text{ion}}\), plus two terms, describing the electron-electron interactions, which are functionals of the total electron density. The latter terms are the classical electron-electron Coulomb potential,

\[
\Phi(r) = e^2 \int \frac{n(r')}{|r - r'|} dr'. \tag{1.19}
\]

and a term related to the exchange-correlation energy through its functional derivative, \(dE_{\text{xc}}[n]/dn(r)\).

\[
V(r) = V_{\text{ion}} + \Phi(r) + \frac{\delta E_{\text{xc}}}{\delta n(r)}. \tag{1.20}
\]

The exchange-correlation energy, \(E_{\text{xc}}\), can therefore be viewed as the difference between the real (electron-electron) energy and the energy due to the pure electron-electron Coulomb term (for a review on the topic see Jones and Gunnarson, 1989). LDA has become the basis of most of the parameter-free calculations in extended

\(^8\) The \(T^2\) behaviour is a consequence of the validity of the one to one correspondence between the single particle excitations of the free electron gas and the excitations of the interacting electron gas. The excitations of the interacting electron gas are called quasi-particles and the state, in analogy with the Fermi gas, Fermi liquid.
systems. The approximation most widely used is the so-called local spin density approximation (LSD). Here the exchange-correlation energy, $E_{xc}^{LSD}$, is given by

$$E_{xc}^{LSD}[n_{\uparrow}, n_{\downarrow}] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}[n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})],$$

1.21

where $\varepsilon_{xc}[n_{\uparrow}, n_{\downarrow}]$ is the exchange and correlation energy per particle of a homogeneous electron gas with (total) spin-up and spin-down densities $n_{\uparrow}$ and $n_{\downarrow}$, respectively [Gunnarson and Lundqvist (1976)]. This approximation is considered valid if the electron density varies sufficiently slowly over the unit cell to be considered locally constant\(^9\). As in LDA exchange and correlations are treated as a functional of the total electron density, the enhanced Coulomb repulsion of the f-like states cannot adequately be taken into account. In fact, LDA predicts linear terms in the specific heat coefficients which are too small by one or two orders of magnitude. The high degree of localisation of the f-electrons implies (as far as the energy levels are concerned) a high degeneracy of some electronic configuration. This high degeneracy is, however, partially removed by the interaction of the electrons with an energy gain which is too small ($k_B T_F$), compared to the typical electron energies, to be properly calculated by LDA.

Moreover, the use of the total electron density in the classical Coulomb term, as expressed by eqn 1.19, results in an inconsistency in the calculations made via LDA. This is because the contribution of the Coulomb potential to the energy, $U_{\mathbf{r} \rightarrow \mathbf{r}'}^{dd}$, where

$$U_{\mathbf{r} \rightarrow \mathbf{r}'}^{dd} = \frac{e^2}{2} \sum_{i,j} \int d\mathbf{r} d\mathbf{r}' \frac{\left| \psi_i(\mathbf{r}) \psi_j(\mathbf{r}') \right|^2}{|\mathbf{r} - \mathbf{r}'|}$$

1.22

contains the unphysical interaction of each electron with itself. In the Hartree-Fock expression of the energy, this part of the electron-electron interaction vanishes by taking the difference of $U_{\mathbf{r} \rightarrow \mathbf{r}'}^{dd}$ with the diagonal term ($i=j$) of the Hartree-Fock exchange term, $U_{\mathbf{r} \rightarrow \mathbf{r}'}^{exc}$, (see, for example, Ashcroft (1976), p332):

$$U_{\mathbf{r} \rightarrow \mathbf{r}'}^{exc} = -\frac{e^2}{2} \sum_{i,j} \int d\mathbf{r} d\mathbf{r}' \frac{\psi_i^*(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}) \psi_j(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}.$$  

1.23

\(^9\) In this case, $\varepsilon_{xc}$ is not a functional of the electron density but simply a function $\varepsilon_{xc}(n(\mathbf{r}))$. The dominant term in $\varepsilon_{xc}[n]$ is proportional to $n^{1/3}$. This is consistent with the results of the Hartree-Fock equation for the homogeneous electron gas, where the total energy is modified by a term proportional to $k_F$ (and therefore to $n^{1/3}$) as a result of the Hartree-Fock exchange term (shown by eqn 1.23).
In the density functional exact formalism, this interaction would be cancelled too. However, in LSD approximation, this cancellation is imperfect. It turns out that the approximation is stronger when the localisation of the orbitals increases. The so-called self-interaction correction, SIC, (Perdew et al 1981) introduces a correction to the term expressed by eqn 1.21 of the form,

\[ E_{\text{SIC}} = E_{\text{LSD}}[n_i, n_i] - \sum_{i, \sigma} \delta_{i, \sigma} \sigma = \uparrow, \downarrow \]

where \( E_{\text{LSD}} \) is the LSD energy functional and

\[ \delta_{i, \sigma} = \frac{e^2}{2} \int dt \int dr \frac{n_{i, \sigma}(r)n_{i, \sigma}(r')}{|r-r'|} + E_{\text{xc}}^{\text{LSD}}[n_{\sigma}, 0] \]

is the SIC correction. The first term in eqn 1.25 corrects the above-mentioned inconsistency in the Coulomb potential term of the LSD equation for the orbital \( i \) with spin \( \sigma \) and density \( n_{i, \sigma}(r) \). The second term in eqn 1.25 is the LSD approximation to the exchange-correlation energy of a fully spin polarised system with density \( n_{i, \sigma}(r) \).

The main modification of the SIC with respect to LSD is, therefore, the presence of an orbital dependent potential. This feature has led some authors to investigate whether the SIC, known to increase the localisation of the one-electron spatial wave-functions, could provide a better description of the f-electrons in heavy-fermion systems. Szotek et al (1991) applied the method to the 4f states of praseodymium. They found that the 4f states split into two sub-bands, one fully occupied, 7.5 eV below the Fermi level \( E_F \), and one unoccupied, with its maximum located 1 eV above \( E_F \). Sakay et al (1993) calculated in La f-levels at about 6 eV above \( E_F \), as opposed to 2.7 eV obtained by the LSD calculation, and in better agreement with spectroscopy experiments. Investigations of the Fermi Surface of LaSb and CeSb via the SIC by the same authors are in progress.

An interesting semi-phenomenological theory (in the following abbreviated as RB, renormalised bands), due to Zwicknagel (1992) and Fulde (1994) tries to account for the correlations by introducing a small number of phenomenological parameters which are derived by fit with experimental results. The aim of the adjustment is the width of those electron bands which have high f-character. This is achieved by parameterising the f phase-shifts at the rare-earth or actinide sites (the particular band structure calculation used was developed from scattering theory). The f bands are mainly characterised by a width, \( \Gamma_f \), and the position of their centre of gravity, \( \tilde{E}_f \). A “standard” LDA calculation would provide an f-like band width of approximately 0.1
eV (T* ~1200 K), in clear disagreement with the masses measured. The goal of the RB calculation is to obtain band widths of 1 meV (T* ~ 12 K) with the centre of mass of the band $\hat{E}_f$ at the appropriate distance from the Fermi level (to participate to the Fermi volume, the band must cross the Fermi level).

Apart from this imposition, the rest of the calculation is *ab initio*; the effective potentials and hence the phase shifts of the conduction states are determined in the same way as in the case of normal metals. The actual calculation used is the Linear Muffin Tin Orbital (LMTO) [see for example Andersen (1975)] method. The procedure consists roughly of the following steps:

i) An initial standard LDA calculation where the f electrons are treated as “band” states (itinerant state) provides the electron densities. The same calculation could be performed assuming the f-electron as core states. The authors assert however that, relative to the problem of the electronic densities, the results are not sensitive to the prescription used in the calculation.

ii) The self consistent potential is calculated from the obtained densities.

iii) The f-bands are then modified by varying their width and centroid in the way described above. Owing to the condition of charge conservation the number of parameters introduced in the calculation is reduced to one, namely the width, $\Gamma_f$, of the f-band.

The theory achieved some success by calculating FS and band masses in CeRu$_2$Si$_2$ and CeAl$_3$ respectively, which were in good agreement with dHvA experimental results.

Renormalising the f-like bands implicitly contains a very important consequence: the volume enclosed by the FS should change when going from the regime T<T$_{ch}$ with coherent itinerant f states, to T>T$_K$, where the f-states can be treated as part of the core and hence do not contribute to the FS. As an indirect proof, the authors compare the experimental measurement of the Fermi volume of CeRu$_2$Si$_2$ with that of CeRu$_2$Ge$_2$ [King et al (1991)] which is an isostructural ferromagnetic compound where the f states are clearly localised: the difference in the Fermi volume between these two compounds is roughly one electron per unit cell.

The prediction of the change in the Fermi volume across T$_{ch}$ might be tested by experiments which can be performed in both the above-mentioned regimes of temperature (typically 2D-ACAR). As far as the author is aware, no temperature-experiments have confirmed this conjecture. Conversely, angle-resolved photoemission experiments performed by Arko *et al* (1990) suggest that the f-electron states in UPt$_3$ are still itinerant at 300K.

---

10 By measuring the frequency of the oscillations in the magnetisation as a function of the inverse of an external applied magnetic field, dHvA experiment can evaluate “extremal areas” of the FS in the direction perpendicular to the field.
According to the RB theory, a change in the Fermi volume should also be expected across the so-called “metamagnetic” transition which is shown by some HF. This is characterised by an abrupt jump, at a critical field $H_c$, in the magnetisation and a corresponding maximum in the differential magnetic susceptibility, $\chi'(H) = \partial M(H)/\partial H$. Even though the underlying mechanism is not fully understood, the properties of the transition bear some resemblance with those of a magnetic ordering which could be ascribed to the f-electrons. The dHvA results of Onuki et al (1994) for CeRu$_2$Si$_2$ are that, at $H>H_c$, the FS sheets related to the heavy cyclotron masses observed (below $H_c$) disappear. This would confirm that in the magnetically ordered state the f-electrons decouple from the conduction electrons. However, the dHvA results of Julian (1994) above the metamagnetic transition do not fully confirm Onuki’s findings. In the case of UPt$_3$, which shows a metamagnetic transition at 20 T, the heavy cyclotron masses measured below $H_c$ (170 m$_e$) maintain their characters above $H_c$ (100 m$_e$) and the FS results show that the f-electrons still contribute to the FS.

With regard to the FS calculation, it is worth stressing that, in some case, standard LDA, even though it cannot account for appropriate values of the band masses, obtains a FS which is in reasonable agreement with the experiments (performed mainly by dHvA) and does not differ sensitively by the FS calculated with the RB method.

A relevant example is given by UPt$_3$ (Harima 1995, Oguchi et al 1987, Wang et al 1987). It is certainly not a case that the compound is based on an actinide. It is widely accepted that the degree of delocalisation of the U f-electrons is much higher than that of the Ce f electrons. In fact, it is often said that the actinides “bridge” the gap between transition metals, where realistic calculations have been successful by treating the d-electrons as itinerant, and lanthanides, which have been the object of the discussion in this chapter.

1.4 Heavy-Fermions: non standard behaviour

Many questions regarding the electronic structure of HFs and on the mechanisms which generate the heavy masses are still unsolved. The measurements which will be reported in the next chapters are in fact concerned with two compounds (CeB$_6$, CeCu$_6$) where standard LDA not only is unable to calculate the correct band masses but also obtains a FS which is in strong disagreement with the experiments. Because of the general similarities between the LDA and RB calculated FSs, there are strong indications that also the RB method would not improve the results.
i) Magnetically ordered heavy-fermions

As mentioned before, CeB$_6$ (and CeSb) belongs to the class of materials where the local magnetic moments (LMM) order at low temperatures. As the ordering would indicate that the RKKY interaction prevents the formation of the singlet state f-electrons/conduction electrons (cf. § 1.2), the invoked hybridisation discussed in §1.3 loses credibility.

On the other hand, as mentioned before, also in magnetically ordered HFs the resistivity, well below the ordering transition ($T_N$), follows the $A T^2$ behaviour. The $A$ coefficient is enhanced similarly to the compounds where the f-electrons itinerant (Bloch states) description (for $T<T_{ch}$) is consistent with the experimental findings. This indicates that itinerant, strongly correlated electronic states coexist with the antiferromagnetic order.

Kasuya (1988) suggests that the coexistence between magnetic moments and Kondo states is due to the fact that the Kondo state acts mainly near the Fermi level (Kondo resonance), while the magnetic interaction comes from the global electronic states.

Steglich (1994) tries to reconcile magnetic ordering and Kondo states by stating that in magnetically ordered HFs the local f-derived moments are retained but considerably reduced. He notices in fact that the magnetic moment of CeB$_6$ in the ordered phase ($\mu \approx 0.7$ to 1 $\mu_B$) is much smaller than that measured by the high temperature region of the Curie-Weiss plot, 2.34 $\mu_B$\textsuperscript{11}. There are however very few simple ferromagnetic insulators (to date CrBr$_3$, EuO and EuS) where all ionic spins are (at 0 K) completely aligned in the ground state, (showing therefore a saturation moment, extrapolated at $T=0K$ from low temperature results, equal to the moment derived from the high temperature slope of the inverse magnetic susceptibility).

In the case of CeB$_6$, the low temperature moment must be calculated by taking into account that the ground state of the $J=5/2$ multiplet of the Ce atom is split by the crystal electric field (CEF) into a duplet and a quartet. It was originally assumed that the duplet $\Gamma_7$ [Harima (1994)],

$$ |\psi_+\rangle = -\left(\frac{1}{6}\right)^{1/2} |j_z = \pm 5 / 2\rangle + \left(\frac{5}{6}\right)^{1/2} |j_z = \mp 3 / 2\rangle, $$

was the ground state [Kawakami et al, (1980)]. The calculated moment of 0.71 $\mu_B$ for an isolated duplet (see Appendix 1), is in good agreement with the experimental results which could then be explained without any recourse to the “moment washout”

\textsuperscript{11} Kawakami et al (1980) measures a high field (B=15 T) saturation moment, at $T=0.6K$, of $\mu=1\mu_B$. It is worth noticing that at B=15T the cyclotron mass, as measured by dHvA, is still strongly enhanced ($m=18m_0$, Harrison et al, 1993). On the other hand, Effantin et al (1985) reports a value of $\mu \approx 0.28\mu_B$, obtained from neutron measurements, at $T=1.3$ K in zero magnetic field.
related to the Kondo singlet formation. More recent measurements of the anisotropy of the magnetisation in CeB$_6$ [Sato et al (1984)] indicate that the $\Gamma_8$ quartet is the ground state. As the calculated moment for the $\Gamma_8$ is 1.54 $\mu_B$ (Appendix 1), the conjecture that the moment is reduced by the Kondo effect would receive some support.

With regard to the ordering of the magnetic moments, it is also interesting to plot, in figure 1.5, the ratio between the high temperature magnetic moment (as obtained via the Curie-Weiss plot) and the (low temperature) saturation moment per magnetic atom as a function of the Curie temperature, for the case of CeB$_6$ (as well as, e.g. for EuO) and compare it with the general trend where all the itinerant ferromagnets are located (Rhodes and Wohlfart, 1963). CeB$_6$ is located off the general trend, which is another indication that the supposition of localised, un-hybridised f-electrons is plausible.

![Fig. 1.5 Ratio $q_c/q_s$ as function of Curie temperature. $q_c$, number of carriers deduced from Curie-Weiss law; $q_s$, number of carriers deduced from saturation magnetisation. $\theta$, Curie temperature; after Rhodes et al (1963)](image)

To complete the scene, the findings on the FS indicate that, as it will be described later in this thesis, the main FS sheets of CeB$_6$ and LaB$_6$ show strong similarities, [Matsui et al 1993] suggesting that the f-electrons might stay localised down to the
temperatures where HF phenomena arise [Kubo et al (1992), Harima (1994)] (this description will be abbreviated as f-core-state below).

The possibility that the s-f hybridisation generates energy bands with a narrow dispersion, crossing the Fermi level in the same position of the un-hybridised case (equivalent to LaB₆) has also been suggested [Harrison (1992)]. To invoke the hybridisation model [Wasserman et al (1989)] implies, however, that, as the f-electrons contribute to the Fermi volume, new FS sheets should appear (with respect to the FS of LaB₆). Such sheets have not been observed. Moreover, as the hybridisation between the zero-width f-band and the conduction band alters the energy dispersion of the bands (as shown in figure 1.4), the value of the Fermi level ($E_F$) must be readjusted. To account for the observed FS, the change in $E_F$ should be sufficiently small to allow the Fermi wave-vector $k_F$ to be in the same position as in the unhybridised case\(^{12}\). Therefore, as the only evidence supporting this hypothesis is the high value of the low temperature specific heat, it should be viewed simply as a conjecture.

It is therefore possible that in some LMM cases, such as CeB₆, the s-f model does not apply. In this case one should consider what other mechanisms can explain the thermodynamic (and transport) measurements.

A) One well-known mechanism which enhances the density of states at the Fermi energy is given by electron-phonon interaction (see, for example, Ashcroft (1976) p519). The screening effect of the electronic cloud and of the ions affects the interaction of two electrons with each other. The simplest way to take this into account is to replace the Fourier transform of the Coulomb potential that occurs in the exchange term of the Hartree-Fock equation for the free electrons by its screened form (Ashcroft (1976) p334-344),

$$\frac{4\pi e^2}{k^2} \rightarrow \frac{4\pi e^2}{k^2 \varepsilon_{d}(k)},$$  \hspace{1cm} 1.27

where the $k$ dependence in the dielectric constant, $\varepsilon_d(k)$, can be ascribed primarily to the ionic vibrations. The most important modification of the Hartree-Fock results is that, when the electron energy $\varepsilon(k)$, is close to $\varepsilon(k_F)$, (on the scale of the Debye energy) the energy dispersion is modified to

---

\(^{12}\) An interesting attempt consists in the fully relativistic spin polarised calculation, with the f-electrons treated as itinerant, suggested by Suvasini et al (1995). The results are that some bands (energy bands are split owing to the breaking of the spin degeneracy) show a similar topology with respect to the LaB₆ case, but a detailed comparison with dHvA findings shows several discrepancies. The whole FS and the calculation are still under study.
\[ \varepsilon(k) - \varepsilon(k_F) = \frac{\varepsilon^{TF}(k) - \varepsilon(k_F)}{1 + \lambda}, \]

where \( \varepsilon^{TF}(k) \) is the energy in the absence of the ionic corrections to the screening and \( \lambda \) is the enhancement factor which modifies the density of states at the Fermi energy (see figure 1.6). The value of \( \varepsilon_F \) and the shape of the FS are not affected by the ionic correction of the screening.

Although conclusive theories do not exist yet, it is accepted that in the case of magnetically ordered HFs, a mechanism analogous to the electron-phonon type enhancement in ordinary metals could be provided by electron-magnon interaction [Kasuya et al (1988)]. The evidence that in magnetically ordered HFs (typically CeB\(_6\), Harrison et al (1993)) cyclotron masses are reduced under the application of strong magnetic fields supports the idea that magnetic excitations can explain the mass enhancements of the conduction electrons [Harima (1994)].

**B)** With regard to interpreting the experimental results on CeSb Norman et al (1986) discuss the "weak coupling model" where, unlike the s-f mixing, which assumed wave-function hybridisation, the coupling is achieved through a potential interaction. This weak coupling model is actually the application of a standard rare-earth-like picture, where the 4f orbitals are viewed as site-local atomic like orbitals interacting with the conduction electrons only through electrostatic and exchange

\[ \text{Fig. 1.6 Correction to the electronic vs } k \text{ relation due to the screening by the ions. [from N W Ashcroft (1975) p 520]} \]

---

13 It should however be referenced also the theory of Wassseman et al (1989) which, by invoking the Anderson c-f hybridisation model, succeeds in explaining the mass dependence on the magnetic field in CeB\(_6\).
interactions. The model explains why in a system like CeSb the mass enhancement of the conduction electrons is only moderate ($\gamma \sim 20$ mJ/mole K$^2$).

C) Recently, Kagan et al (1992) and Kikoin et al (1995) have suggested that the origin of HF is due to uncharged Fermi excitations of spin origin which couple weakly to the conduction electrons. This would explain why the cyclotron masses observed in the dHvA experiments were always much smaller than in the thermodynamic ones (only charged carriers are seen in the dHvA effect). However, the work of Harrison et al (1993), by modelling the FS sheets of CeB$_6$ in a general case of prolate ellipsoids of revolution, obtained a density of states at the Fermi energy, $N(E_F)$, which was in good agreement with that obtained by thermodynamic measurements. Therefore, these findings do not support the theory of Kagan et al.

This short introduction was intended only to give a flavour of the variety of problems related to HF systems. As well as for several other many-body problems, an adequate understanding is far from being reached. The problem lies in a lack of universality in the HF behaviour which has favoured the proliferation of "heavy" theoretical models. A complete solution of the periodic Anderson model which, assuming an initial zero-width f-electron band, is already an oversimplification of a HF system, has not yet been achieved.

The task of the experimentalist is to explore this lack of universality. In particular, the 2D-ACAR experiments, which can be performed above and below the temperature where HF phenomena arise, can attempt to follow the formation of the "coherent states" as they have direct access to the quasi-particle wave function. The experiments which will be described in the following are only preliminary steps in this direction.
2 Positron annihilation in condensed matter

Positron annihilation technique is certainly a valuable tool for both fundamental and applied studies in solid state physics. It would take too long and would be beyond the aims of this survey to present all the applications of the Positron Annihilation Spectroscopy (PAS). It is perhaps amusing that this probe, so deeply rooted in the fundamentals of quantum electrodynamics, can be useful in such different fields, spanning from non-parity conservation to metallurgy.

Given the number of reviews which have appeared in the last 30 years or so, any introduction will always appear incomplete. Therefore, we will not discuss the fundamentals of the annihilation process but assume the positron as a given particle which is implanted into the sample, and whose final fate is to do nothing but annihilate with one electron of the material under analysis.

2.1 Positron production, implantation and thermalization

Positrons can be produced by radioactive sources (as the result of β decay) or in accelerators via pair-production reactions (a process opposite to the annihilation). The radioactive sources are most widely used in laboratories throughout the world for financial and personnel reasons. The most commonly used sources are $^{22}\text{Na}$, $^{58}\text{Co}$ or $^{64}\text{Cu}$. Positrons are emitted with a continuous spectrum of energy (conservation of energy during the emission is allowed by emission of one neutrino) with maximum energies, $E_{\text{max}}$, ranging from 0.5 to 1.5 MeV.

A problem which was studied in great detail at the beginning of the PAS era concerned the state of the positrons at the time of the annihilation. Were the time required to lose the initial (nuclear-scale) energy too long compared to the typical lifetimes of positrons in condensed matter, the use of the positron in solid state physics (where energies are of the order of the eV) would be ruled out. Lee-Whiting [1955] was the first to consider the problem of thermalization time in sodium obtaining a value of $3 \times 10^{-12}$ sec ($10^{-12}$ sec=1psec). Carbotte and Aurora [1967] re-computed the thermalization time by using many-body perturbation theory and obtaining 13 psec for sodium at room temperature. In both cases, these times are at least one order of magnitude smaller than the typical lifetimes in metals (of the order of 100-200 psec). Until now, it has therefore been accepted that for metals, which
cover the major interest of this survey, annihilation will follow thermalization.\(^1\) During the thermalization the positron penetrates inside the sample by an amount dependent on its initial kinetic energy. Implantation profiles of positrons produced by radioactive sources is another deeply investigated topic [see, for example, Brandt and Paulin, (1977)]. A fairly realistic assumption of the implantation profile \(I(x)\) for a \(\beta^+\) energy spectrum is a simple exponential,

\[
I(x) = I(0) \exp(-\alpha_+ x), \tag{2.1}
\]

where \(I(0)\) is the positron density at the impinging surface and \(\alpha_+\) is the absorption coefficient. That coefficient is reasonably well described by the following expression [Brand and Paulin (1977)],

\[
\alpha_+ = 16 \rho E_{max}^{-1.43} \left[ \text{cm}^{-1} \right], \tag{2.2}
\]

where \(\rho\) is the material density and \(E_{max}\) is the positron end point kinetic energy.

Eqn 2.1 yields also the range \(r_x\) within which \(x\%\) of the positrons undergo an annihilation. Table 2.1 includes some data for positrons emitted by \(^{22}\text{Na}\).

<table>
<thead>
<tr>
<th>Element</th>
<th>(\rho [\text{gr/cm}^3])</th>
<th>(t_{\text{therm}} [\text{ps}])</th>
<th>(\alpha_+ [\text{cm}^{-1}])</th>
<th>(r_{90%} [\text{mm}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>2.7</td>
<td>13.2</td>
<td>104</td>
<td>0.221</td>
</tr>
<tr>
<td>C</td>
<td>2.25</td>
<td>4.1</td>
<td>87</td>
<td>0.265</td>
</tr>
<tr>
<td>Mo</td>
<td>10.2</td>
<td>13.8</td>
<td>394</td>
<td>0.058</td>
</tr>
<tr>
<td>Ni</td>
<td>8.90</td>
<td>20.2</td>
<td>344</td>
<td>0.067</td>
</tr>
<tr>
<td>W</td>
<td>19.35</td>
<td>24.7</td>
<td>747</td>
<td>0.031</td>
</tr>
</tbody>
</table>

*Table 2.1 [De Vries 1987] Thermalization times \(t_{\text{therm}}\) and positron ranges \(r_{90\%}\) for positrons from \(^{22}\text{Na}\).*

From the ranges appearing in table 2.1 it is clear that the typical penetration of positrons emitted by radioactive sources legitimises their use for bulk studies. However, the fact that for heavy elements a considerable fraction of the positrons stops in the first few microns is often overlooked. Care must be therefore taken to

\(^1\) More subtle is the problem of thermalization of a positron in an insulator. Here, the only channel accessible when the positron energy goes below the electron-hole excitations threshold, is the process of lattice vibrations which may not be efficient enough to complete the thermalization prior to the annihilation [De Benedetti et al, 1950]
avoid layered structures (typically oxides) at the surface which could jeopardise the quality of the information extracted.

If the initial kinetic energy of the positron is in the nuclear energy range, the "ashes" of the process are typical of nuclear spectroscopy. In fact, the object of a PAS measurement mostly involves the detection of γ rays with energies of the order of the 511keV rest mass of the electron (positron)\(^2\). There is one advantage in the high energy of the annihilation products. The penetration of γ rays of half MeV is such that they can escape without appreciable attenuation or scattering from reasonably small samples.\(^3\) This escape probability is very different from that of other condensed matter probes like the soft x rays or the charged particles which are extremely sensitive to surface purity.

### 2.2 Annihilation Cross sections

To proceed, we now need to know more about the features of the measurable quantities. The most likely output of an annihilation process of free positrons with electrons is the emission of two γ rays. The spin averaged cross section of the process is, in the case of relative velocity of the particles, \(v\), which are small with respect to the speed of light, \(c\), (Dirac, 1930)

\[
\sigma^{(2)} = \frac{\pi r_0^2 c}{v}, \tag{2.3}
\]

where \(r_0\) is the classical electron radius, \(r_0=\frac{e^2}{m_0c^2}\), (\(e\) and \(m_0\) are the charge and mass of the electron). As all the particles in a cylinder of height \(vdt\) will cross the cross sectional area, \(\sigma^{(2)}\), within the time \(dt\), it turns out that the annihilation probability, \(P\), in the time \(dt\) is the product of the particle density \(dn/dV=ne\) and the volume of that cylinder, \(\sigma^{(2)}vd\). It is therefore independent of the relative velocity \(v\) and equal to

\[
\Gamma^{(2)} \equiv \frac{dP}{dt} = \frac{1}{dV} \frac{dn}{dt} \sigma^{(2)} \equiv \pi r_0^2 c n_e \cdot \tag{2.4}
\]

Less likely is the process where \(e^+\) and \(e^-\) annihilate via 3 γs. The ratio between the spin averaged 3γ and 2γ two cross sections is in fact [Berestetskii et al 1971],

---

\(^2\) In experiments with slow positron beams particles may be directly detected. It is the case, for example, of positron Auger spectroscopy, where the Auger electrons are measured or of the positron microscope where slow positrons are directly monitored with channeltrons or micro-channel plates.

\(^3\) The half thickness of a 0.511 MeV γ ray in lead is \(\sim 4\)mm.
\[
\frac{\sigma^{(3)}}{\sigma^{(2)}} = \frac{1}{378}.
\]

One can apply these results to the simplest possible system (as far as the annihilation process is concerned). This system is given by the bound state of one electron and one positron, called positronium (Ps). The study of Ps has greatly contributed to the testing of quantum electrodynamics theory. In this thesis, the study of Ps is also necessary because, on a much more practical level, Ps provides a useful tool to check the quality factors of a 2D-ACAR spectrometer. The energy levels of Ps differ from those of hydrogen owing to its reduced mass, \( \mu_{Ps} \) \( (\mu_{Ps}=m_0/2 \approx \mu_{H}/2) \) and to its Bohr radius \( a_{Ps} \) \( (a_{Ps}=2a_0=2 \times 0.529 \text{ Å}) \), where \( \mu_{H} \) and \( a_0 \) are the hydrogen reduced mass and the Bohr radius, respectively\(^4\). The binding energy of Ps, \( E_{Ps}=6.8 \text{ eV} \), is half that of hydrogen (13.6 eV =1 rydberg). The general selection rule (following from conservation of charge parity [Berestetskii et al 1971]) for the annihilation of Ps from a state of orbital angular momentum \( l \) and total spin \( s \) into \( n \) photons is given by

\[
(-1)^{l+s} = (-1)^n,
\]

where the state with spin \( s=0 \) is the singlet,

\[
\chi_0 = \frac{1}{\sqrt{2}} \left[ |\uparrow_{e'} \downarrow_{e'} \rangle - |\downarrow_{e'} \uparrow_{e'} \rangle \right],
\]

and that with total spin \( s=1 \) is the triplet state

\[
\chi_1 = |\uparrow_{e'} \uparrow_{e'} \rangle
\]

\[
\chi_0 = \frac{1}{\sqrt{2}} \left[ |\uparrow_{e'} \downarrow_{e'} \rangle + |\downarrow_{e'} \uparrow_{e'} \rangle \right]
\]

\[
\chi_{-1} = |\downarrow_{e'} \downarrow_{e'} \rangle.
\]

Eqns 2.7 and 2.8 refer to the spin part (often written more compactly as \( \chi_{s_z}^S \)) of the eigenstates.

\(^4\) Note that the fact that Ps has radius which is twice that the hydrogen does not imply that the volume of Ps is bigger: the centre of rotation (centre of mass) of Ps is in fact midway between the two particles while for hydrogen it almost coincides with the proton.
Let us consider here only the \( l=0 \) state, as the annihilation cross section for orbital angular momentum \( l\neq0 \) is much smaller (Berko, 1980). It follows from eqn 2.6 that the singlet state must decay into an even number of photons, and the triplet state into an odd number of photons\(^5\).

One can then use eqn 2.4 to calculate the annihilation rate \( \Gamma^{(2)} \), the inverse of which is the average lifetime, \( \tau \), for the singlet state of Ps (parapositronium). As the electron density at the positron is given by

\[
|\psi(r)|^2_{r=0} = \frac{1}{\sqrt{\pi a_P^3}} \exp \left( -\frac{r}{a_P} \right) = \frac{1}{\pi a_P^3},
\]

and eqn 2.4 corresponds to the initial state *averaged* over spins, one obtains (note that \( \Gamma^{2\gamma}_{\text{ortho}} = 0 \))

\[
\Gamma^{2\gamma}_{\text{para}} = 4\pi r_0^2 c (\pi a_P^3)^{-1} = \frac{1}{125 \, \text{psec}}.
\]

To obtain the lifetime of orthopositronium, by using the cross section for annihilation at \( 3\gamma \) and the fact that \( \Gamma^{3\gamma}_{\text{para}} = 0 \), one obtains,

\[
\Gamma^{3\gamma}_{\text{ortho}} = (\pi a_P^3)^{-1} \sigma^{(3)}_\nu \frac{4}{3} = \frac{1}{140 \, \text{nsec}}.
\]

Eqn 2.10 and 2.11 reflect the fact that the cross sections 2.4 and 2.5 come from taking the average over the spins. This means that since each eigenstate of Ps (in the absence of external perturbations) is stationary before the annihilation takes place, it will annihilate with the intrinsic cross section of the allowed (\( 2\gamma \) or \( 3\gamma \)) process which is higher of a factor 4 (for the singlet) or 4/3 (for the triplet) with respect to the spin averaged annihilation rates.

As we are dealing with states with finite lifetime, it is worth estimating the order of magnitude of the energy width \( \delta E \) of these states. From the uncertainty principle,

\[
\delta E \approx \frac{\hbar}{\tau} \approx \begin{cases} 7.7 \times 10^{-7} \times E_{Ps} \quad &\text{para} \\ 6.9 \times 10^{-10} \times E_{Ps} \quad &\text{ortho} \end{cases},
\]

---

\(^5\) This rule is general and does not refer only to the positronium atom.
where $\tau$ is the lifetime of the two states. Therefore the energy width is small compared to $E_{ps}$ and so the positronium may be regarded as being a quasi stationary state.

### 2.3 Momentum conservation

Owing to the conservation of the momentum of the annihilated particles, the outcoming $\gamma$ rays carry with them the information regarding the momentum of the electron-positron pair\(^6\). In the most likely $2\gamma$ annihilation event, that information manifests itself, in the laboratory frame, with two effects:

i) Doppler shift:

One $\gamma$ ray (with energy $E_2$) is "red shifted" and the other (with energy $E_1$) is "blue shifted" with a difference in energy which is proportional to the component of the momentum pair, $p_z$, along the direction of the photon emission axis.

$$p_z \approx \frac{E_i - E_2}{c}.$$

ii) Deviation angle.

The two $\gamma$ rays are emitted with a deviation angle from anticollineary, $\theta$, which is proportional to the projection of the momentum of the pair in the plane normal to the photon emission axis, $p_T = (p_x, p_y)$.

$$\bar{p}_T = \left\{ \begin{array}{l} p_x = \theta m_e c \\ p_y = \theta m_e c \end{array} \right.$$  \hspace{1cm} 2.13

Eqn 2.12 and 2.13 are valid in the case of small velocities ($v/c \ll 1$) of the pair\(^7\). They can be proved easily with this assumption (let us take a 2-dimensional case. The 3-D extension is straightforward).

The geometry of the process is illustrated in figure 2.1. The main photon emission axis is the $z$ axis of the reference frame. As the total deflection angle is $\theta$, each photon makes an angle of $\theta/2$ with the photon axis.

---

\(^6\) As the positron can be assumed to be thermalized at the time of the annihilation, even at room temperature the momentum of the positron is typically one order of magnitude lower than the Fermi momentum. This does not mean that the positron effect is negligible. This problem will be discussed further below.

\(^7\) This assumption is always fulfilled in case of valence and conduction electrons.
Conservation of energy implies that

\[ E_1 + E_2 = 2m_0c^2 - E_{e^+, e^-} , \]

where \( E_1 \) and \( E_2 \) are the energies of the \( \gamma \)-rays, \( 2m_0c^2 \) is the sum of the rest masses of the electron and the positron; \( E_{e^+, e^-} \) represents the sum of the (total) binding energies of the electron and (if any) of the positron at the time of the annihilation. For outer electrons, \( E_{e^-} \) (of the order of the eV) is certainly negligible with respect to the \( 2m_0c^2 \) (1022 keV) term, but for inner shells it can be of the order of several tens of keV. However, one can disregard this case here because the contribution of the close shells to the momentum distribution is of much lesser importance than that of valence and conduction electrons owing to the strong Coulomb repulsion between the positron and the positive ion composed by the nucleus and the inner electrons.

**Fig. 2.1** Parallelogram rule of the annihilation process: the \( z \) axis coincides with the main photon emission axis. To make them visible, the \( p_\pi \) and \( p_z \) momenta of the pair are not to the same scale as the momenta of the photons. The difference \( p_{1z} - p_{2z} \) also cannot be observed in this scale.

Conservation of the momentum (see figure 2.1) implies
\[ p_{e^+e^-} = p = p_1 + p_2 \]  

\[
\begin{align*}
 p_x &= p_{1x} + p_{2x} = \frac{E_1}{c} \sin \frac{\theta}{2} + \frac{E_2}{c} \sin \frac{\theta}{2} \\
 p_z &= p_{1z} - p_{2z} = \frac{E_1}{c} \cos \frac{\theta}{2} - \frac{E_2}{c} \cos \frac{\theta}{2},
\end{align*}
\]  

(2.15a, 2.15b, 2.15c)

where \( p_{e^+e^-} \) is the total momentum of the pair and \( p_j \) and \( p_z \) are the photons' momenta.

From eqn 2.14 and 2.15c one gets

\[
\begin{align*}
 E_j &= m_0 c^2 + \frac{cp_j}{2} \left( 1 + \frac{\theta^2}{8} \right) \\
 &= m_0 c^2 + \frac{cp_j}{2} \left( 1 + \frac{\theta^2}{8} \right) \\
 E_j &= m_0 c^2 - \frac{cp_j}{2} \left( 1 + \frac{\theta^2}{8} \right) \\
 &= m_0 c^2 - \frac{cp_j}{2} \left( 1 + \frac{\theta^2}{8} \right),
\end{align*}
\]  

(2.16a, 2.16b)

by neglecting terms in \( \theta^2 \), which proves eqn 2.12. Substituting eqn 2.16a and eqn 2.16b into eqn 2.15b one obtains,

\[ p_x = 2 m_0 c \sin \frac{\theta}{2} \approx m_0 c \theta . \]  

(2.17)

By monitoring in coincidence the energies of the annihilation \( \gamma \) rays and their deviation angle one could therefore obtain the full 3-D momentum of the electron-positron pair.

To test the feasibility of a direct 3D \( e^+e^- \) momentum density experiment it is worth calculating the order of magnitudes of the physical quantities to be measured.

Atomic units (a.u.) will be used throughout this survey unless explicitly mentioned.

In this system \( e=m_0=\hbar=1, c=137 \), 1 length a.u. = Bohr radius \( (a_0)\approx 0.529 \text{ Å} \) and 1 energy a.u. = 2 rydberg = 27.2 eV.

A typical order of magnitude of electronic momenta in atomic physics can be obtained by applying the Bohr quantization condition of angular momentum,

\[ p a_0 = \hbar \Rightarrow p = \frac{\hbar}{a_0} = 1 \text{ a.u. [mom]}; \]

Inserting this result in eqn 2.17 gives a deflection angle, \( \theta \), of
\[ \theta = \frac{p}{m_0c} = \frac{1}{137} \text{[rad]} = 7.3 \text{[mrad]} \]  

From eqn 2.18 one also obtains the equivalence between the most frequently used units in angular correlation (ACAR) experiments, \(1 \text{mrad} = 0.137 \text{ momentum a.u.}\).

As another example, the Fermi momentum of copper (0.72 a.u.), as obtained from the free electron model (FEM), gives a Fermi angle of 5.25 mrad.

The Doppler shift of 1 momentum a.u., corresponding to an energy of 1 rydberg (0.5 energy a.u.), is, via eqn 2.16a,

\[ \frac{cp}{2} = \frac{137 \times 1}{2} = \frac{137}{2} \text{[energy a.u.]} = 1.86 \text{keV} \quad 2.19 \]

The Doppler shift originated by an electron at the Fermi surface of copper is 1.34 keV.

It is interesting to note that an electronic kinetic energy of few eV originates a Doppler shift in the \(\gamma\) rays of the order of the keV.

The reason lies, of course, in the role played by the rest mass of the particles. This can be seen by showing how, in the relativistic expression of the total energy for one particle with kinetic energy \(E_T\) (assuming the other particle is at rest), the rest mass energy, by combining in quadrature with \(E_T\), influences the \(pc\) term of eqn 2.17:

\[ E = \sqrt{p^2c^2 + m_0^2c^4} \Rightarrow pc = \sqrt{(E_T + m_0c^2)^2 - m_0^2c^4} \quad 2.20 \]

Even if \(E_T \ll m_0c^2\), which means that the square root in eqn 2.20 can be simplified to \(\sqrt{2E_T m_0c^2}\) by neglecting the term in the second order in \(E_T\), the kinetic energy is multiplied by the enormous factor of the rest mass energy of the particle. This is what causes the high value in the Doppler shift of the zero mass \(\gamma\) ray.

It is also interesting to compare the possibilities of resolving momenta with the up-to-date energy and angle-resolved spectrometers. With the advent of the solid state detectors the resolutions, \(\delta E\), at the energy of 511 keV, are approaching 1 keV; this value can be transformed into an equivalent correlation angle \(\delta \theta\) as follows:
\[
\frac{c\delta p}{2} = \delta E \Rightarrow \\
\delta p[a.u.] = \frac{2\delta E[a.u.]}{c} = \frac{2(1000 / 27.2)}{137} = \frac{537}{mom\ a.u.} = 3.9\ mrad 
\]

2.21

The figure of 3.9 mrad is comparable with atomic electrons' momenta and almost 10 times worse than the typical resolutions which are achieved in ACAR experiments. The drawback of the different resolutions along the 3 resolved directions, together with experimental complications, rule out therefore at the present time the deployment of detection systems which can measure the 3 components of the momentum of the pair. The experiments actually performed involve therefore an integration along one (2D-ACAR) or two (1D-ACAR) directions. Despite the inferior resolution, experiments of the longitudinal component of the e+e- pair are also performed, mainly for applied studies, and will be briefly described later on.

It is finally interesting to speculate whether the non-relativistic approximation, which is used throughout in ACAR experiments, is valid when applied to the heavy elements. It is in fact well known that band structure calculations for heavy elements are nowadays performed by solving the relativistic Dirac equation rather than the ordinary Schrödinger equation. Fig. 2.2 shows the radial density for the rare earth Gadolinium. One can see that the f-electrons (which were discussed at length in

---

8 Some attempt has however been made, without conclusive results.
9 Relativistic calculations are interesting because the Dirac equation has different symmetry properties with respect to the Schrödinger equation and treats the spin-orbit coupling correctly. Owing to the strong Coulomb potential, the biggest relativistic effects are for s-states nearer to the nucleus.
chapter 1) are located much more closely to the nuclei than are outer s, p or d electrons. Still, the maximum of the radial density is roughly at 0.75 a.u. By application of the uncertainty principle, one can obtain a related momentum figure of 1.33 momentum a.u. which is not much higher than the figures quoted in the examples given above. One can conclude therefore that, as far as the measurements of the deflection angles (or Doppler shifts) are concerned, one is still within the limit of validity of a non relativistic approximation.

2.4 Momentum density

Although the fundamentals of the annihilation process will not be discussed here, it is worth pointing out a problem discussed by Ferrel (1956). A key assumption, underlying the interpretation of the experimental results, is that the transition matrix elements which lead to the emission of the photons are independent of the initial momentum of the annihilating particles. The consequence is that the direction of the main photon emission axis is isotropic. The basic idea consists in the fact that, since each interaction of an electron or positron with the radiation field can create only one photon, the annihilation process must be viewed as a two steps process:

i) one photon is created but the two particles are still present. The photon has energy $m_0c^2$ (and momentum $m_0c$). One of the two particles must therefore acquire the same (opposite) recoil momentum (intermediate state) which is much higher than the initial momentum of the particle.

ii) The recoiling particle annihilates then with its anti-counterpart and the second photon is emitted.

The process is described by a second order Hamiltonian operator and the intermediate momentum will enter into the denominator of matrix elements of the form

$$\sum_{k^e} \frac{1}{\varepsilon_k - \varepsilon_{k^e}} \langle f_k | H_{\text{int}} | k^e \rangle \langle k^e | H_{\text{int}} | i_k \rangle.$$  \hspace{1cm} 2.22

where $H_{\text{int}}$ is the interaction (annihilation) Hamiltonian operator, $\varepsilon_k$ is the energy of initial state $| i_k \rangle$ (consisting of the one positron-n electron system) and $\varepsilon_{k^e}$ that of the intermediate state (with high momentum due to the recoil). The final state, $| f_k \rangle$. 


consists of n-1 electrons and the two photons. The initial momentum can therefore be neglected in the denominator. The total scattering amplitude is obtained by summing over all the intermediate states and has no "memory" of the initial state.

One can therefore assume that by measuring the distribution of the momenta of the photons one can map the distribution of the momenta of the pair. As we measure angles (in real space) to obtain momenta, the most suitable base to describe the process is the momentum representation (our experiment actually is in momentum space). It is well known that this base consists of plane waves defined as (in a.u.)

\[ \psi_{p_0}(r) = \frac{1}{(2\pi)^{3/2}} e^{ip_0 \cdot r} \]  

To simplify, let us consider the annihilation of only one electron, in a generic ket state \( |\psi_k\rangle \), with one positron uniformly distributed in the normalisation volume. From the \( r \) representation\(^{10}\), \( \langle r | \psi_k \rangle = \psi_k(r) \), of that particular state, the transformation in momentum representation can be obtained, by using the closure and orthonormalization relations of the \( \psi \) and \( r \) base, as

\[
\langle v_{p_0} | \psi \rangle = \int d\mathbf{r} \langle v_{p_0} | \mathbf{r} \rangle \langle \mathbf{r} | \psi \rangle, \quad \text{where,}
\]

\[
\langle v_{p_0} | \mathbf{r} \rangle = \left[ v_{p_0}(\mathbf{r}) \right]^\dagger = (2\pi)^{-3/2} \exp(-ip_0 \cdot \mathbf{r}).
\]

Then, the probability density \( Pdp \) of measuring a momentum \( p \) in \( dp \) is:

\[
Pdp = \langle v_{p_0} | \psi \rangle^2 dp = dp \left| \int d\mathbf{r} \exp(-ip \cdot \mathbf{r}) \psi(\mathbf{r}) \right|^2
\]

\[
= dp \left| \text{FT}[\psi(\mathbf{r})] \right|^2.
\]

The result of our experiment (our observable) is therefore proportional to the square modulus of the Fourier transform of the electron wave function (in its \( r \) representation).

The complex case of a system made of n electrons interacting with one positron was studied in detail by Chang Lee (1957). The multi-particle problem, as normally happens in many-body problems, is soluble only with approximations. Most commonly accepted is the Independent Particle Approximation (IPM) which neglects

\(^{10}\) where the generic state \( |\psi\rangle \) is defined by its infinite projections in real space \( \psi(\mathbf{r}) \).
the possibility that the annihilation of an electron from a specific state is accompanied by the transition of another electron into this state, i.e. wave functions of other electrons are not changed as a result of the annihilation. It can therefore be shown that in the IPM approximation the probability of annihilation with the $k_{th}$ electron, $\rho_{k}^{2}\gamma(p)dp$, is

$$\rho_{k}^{2}\gamma(p)dp = \frac{\pi r_{o}^{2}c}{(2\pi)^{3}} \left| \int dx \exp(-i p \cdot x) \psi_{k}^{\pm}(x) \psi_{c}^{\pm}(x) \right|^{2} dp ,$$  

which is proportional to the square modulus of the Fourier transform of the overlap integral between the electron and positron spatial wave function.

By summing over all the occupied electron states, one obtains the total electron-positron momentum density of the system.

$$\rho_{IPM}^{2}\gamma(p) = \sum_{k} \rho_{k}^{2}\gamma(p) .$$  

The IPM expression for the total annihilation rate $\lambda$, is finally obtained by integrating eqn 2.28 over all the moments of the initial electron-positron states,

$$\lambda = \int \rho_{IPM}^{2}\gamma(p)dp .$$  

By exchanging the order of integration between $r$ and $p$, the expression for the total annihilation rate $\lambda$ transforms into

$$\lambda = \int \rho_{k}^{2}\gamma(p)dp \propto \sum_{k} \int dr |\psi_{c}^{\pm}(r)\psi_{c}^{\pm}(r)|^{2}$$

$$= \pi r_{o}^{2}c \int dr n_{c}^{\pm}(r) n_{c}^{\pm}(r) ,$$  

where $n_{c}(r)$ and $n_{c^{\pm}}(r)$ are the total electron and positron density respectively. Eqn 2.30 is normally the starting point equation for positron lifetime calculations in condensed matter$^{11}$.

$^{11}$ It should however be stressed (see later for details) that the IPM approximation leads to a momentum density shape in good agreement with the experiments but to a calculated total annihilation rate which can be wrong up to a factor of ten with respect to the measured lifetimes.
2.5 The Sommerfeld model

It is instructive to calculate the typical 1D and 2D-ACAR parameters for the simplest metallic system, the free-electron (or Sommerfeld) model (FEM) at zero temperature. It will be seen that its interest is not only pedagogical. In fact, for several metals the FEM model provides a good approximation to reality.

It is well known that the eigenstates of the FEM are plane waves\(^\text{12}\),

\[ \psi(r) = \frac{1}{\sqrt{V}} \exp(i \mathbf{k} \cdot r), \tag{2.31} \]

where \( V \) is the normalisation constant.

In order to satisfy the Born-von Karman (or periodic) boundary conditions, the wavevectors \( \mathbf{k} \) must be of the form

\[ k_x = \frac{2 \pi}{L} n_x; \quad k_y = \frac{2 \pi}{L} n_y; \quad k_z = \frac{2 \pi}{L} n_z, \tag{2.32} \]

where \( L \) represents the size of the quantization box of volume \( V=L^3 \) and \( n_i \) is integer.

As in the FEM the electrons do not interact with each other, the ground state of the \( N \) electron system is built by populating levels with increasing wavevector \( \mathbf{k} \), up to the Fermi wavevector \( k_F \), in a manner consistent with the Pauli exclusion principle\(^\text{13}\).

\(^\text{12}\) The plane waves are also the solutions of the Hartree and Hartree-Fock equations for the more realistic Jellium system (see for example Inkson, 1984). In this system the ionic positive charge is transformed into a uniform positive background which prevents the interacting electrons from exploding under the influence of their combined Coulomb repulsion. In the Hartree-Fock equation the energy eigenvalues, \( \hbar^2 k^2 / 2m \), are corrected by a \( k \)-dependent term describing the effects of the electron-electron interaction.

\(^\text{13}\) As one has to fill an enormous number of levels (of the order \( 10^{22} \)) before running out of electrons, the \( k_i \) levels are always treated as continuous variables with the additional constraint that the number of allowed points in \( k \) space is just the volume of the \( (k\text{-space}) \) region divided by the volume of \( k \)-space reserved per each \( k \) point, \( (2\pi L)^3 \). Then, the density of states, \( g(k) \), of the levels in \( k \) space is (including the electron spin degree of freedom) \[ g(k)dk = \frac{2V}{8\pi^2} dk. \]
A spherical Fermi surface, \( k_x^2 + k_y^2 + k_z^2 = k_F^2 \), separates occupied and unoccupied states. We assume that the only positron present in the sample\(^{14}\) is thermal (\( k^+ = 0 \)). Its wavefunction is therefore simply \( \psi(r) = 1/\sqrt{V} \).

The momentum density is immediately calculated via eqn 2.27 and 2.28 (the Fourier transform of a plane wave is the delta function) as,

\[
\rho^2(p) \propto \sum_{k_F} \left| \int dx \ e^{i(p-k)x} \right|^2 = \int dk \ |\hat{\psi}(p-k)|^2 = \Theta(p - k_F),
\]

where the 3D step function \( \Theta(p - k_F) \) represents the Fermi sphere. In the Sommerfeld model, therefore, the momentum density consists simply of a remapping, from \( k \) to \( p \) space, of the Fermi sphere, or occupation density.

As 2D-ACAR and 1D-ACAR measure projections of the 3D \( e^+ - e^- \) momentum density, one has to integrate 2.33 along 1 (i) or 2 (ii) resolved directions.

i) the 2D (once integrated) projection is

\[
\rho(p_x,p_y) \propto \int dp_z = 2\sqrt{p_F^2 - p_x^2 - p_y^2},
\]

The projection therefore has the form of an inverted hemisphere (figure 2.3). It may be helpful to realise that a projection is nothing but counting the number of occupied states, at a given \((p_x,p_y)\) point, along the integration direction \( p_z \). At \( p = 0 \) the intensity of the projection gives the diameter of the Fermi sphere; the intensity then decreases down to zero at the Fermi circle \( (p_x^2 + p_y^2 = p_F^2) \). It should be noted that the discontinuity at the Fermi momentum in the 3D momentum density has become a second order discontinuity (in the first derivative) in the projected momentum density.

It is clear that the combination of integration direction and topology of the Fermi surface determines the "visibility" of the FS features in the projected data. For example, integrating a cylindrical momentum distribution along the main cylinder axis gives a first order discontinuity also in the projected data. This is not the case with integration along different symmetry directions.

\(^{14}\) Typical intensities of the radioactive sources used in ACAR measurements give at most a fluency of \( 8 \times 10^7 \ e^+/\text{sec} \) onto a 20 mm\(^2\) surface. Typical annihilation rates are roughly 100 times higher.
So far, it appears that the measurement of the (electron-positron) momentum density is very useful in extracting information on the properties of the Fermi surface. Although the search of the FS does not exhaust the possible questions that an ACAR experiment could try to address\textsuperscript{15}, such a search is certainly one of its principal aims.

ii) The 1D (doubly integrated) projection can be easily obtained by a transformation into cylindrical coordinates. One obtains then,

\[
\rho(p_z) \propto \int_{|\rho| \leq p_F} dp_x dp_y = \int_0^{2\pi} d\theta \int_0^{\sqrt{\rho^2 p_F^2}} p dp = \begin{cases} \pi \big( p_F^2 - p_z^2 \big) & (p_z < p_F) \\ 0 & (p_z > p_F) \end{cases}.
\]

\[
2.35
\]

\textsuperscript{15} ACAR experiments are also often performed on semiconductors and insulators, mainly to address questions related to the symmetry of the electron wave-functions and the effective masses of the positron. The physics of positronium is also an object of ACAR studies in insulators such as quartz or organic materials.
The doubly integrated momentum density is therefore an inverted parabola with a cut at the Fermi momentum. A parabolic component (or a hemispherical 2D momentum density) is observed in the angular distributions of many metals\textsuperscript{16}. In addition, a broader component is often present in the spectra of a roughly gaussian shape (see figure 2.4). Its origin can be ascribed partly to the annihilation with more tightly bound electrons and partly to more subtle features due to the conduction electrons which can be attributed to the effect of the crystal potential. These features will be widely discussed in the next paragraph.

\textbf{2.6 Periodic systems}

The FEM approximation is often a poor approximation of a real system. The atomic potential, whose effect is completely neglected in the FEM, must be taken into

\textsuperscript{16} Alkali metals are those which the FEM best describes.
account if one wants to explain the not unimportant fact of how the material stays together. In condensed matter most of the electronic structure armoury was devised for periodic systems. Most of the experiments that have employed the ACAR technique have been performed so far on crystalline structures as well. This should not really be considered a limitation, since the ability to produce amorphous metals - i.e. non crystalline structures - is a complicated technology which has developed fairly recently. It is therefore important to predict the results of a positron annihilation experiment in a periodic system. In the following, we will take as given the basics of crystallography, like crystal structures, Bravais lattices, reciprocal lattice vectors (in the following denoted by \( G \) or \( K \)) and Bragg (and von Laue) diffraction theory.

One can define the Brillouin zone as the cell in reciprocal space confined by the smallest possible wavevectors \( k \) which fulfill the Bragg condition, \( k \cdot G = \frac{1}{2} G^2 \).

The new parameter which enters into the theory is the crystal potential. The potential has the periodicity of the underlying Bravais lattice, \( U(r + R) = U(r) \), for all Bravais lattice vectors \( R \).

In a periodic system the complete translational invariance of the eigenstates of the FEM is broken, since the Hamiltonian does not have complete translational invariance in the presence of a non constant potential. A lower symmetry invariance is however assured by the Bloch theorem, according to which the solutions of the Schrödinger equation in a periodic potential are plane waves, modulated by a function, \( u_k(r) \), having the periodicity of the crystal structure,

\[
|\psi_k^+(r)\rangle = \frac{1}{V^{1/2}} e^{ikr} u_k(r).
\]

Eqn 2.36 can be obtained by expanding the solutions, \( \psi_k(r) \), and the periodic potential, \( U(r) \), into the following sets of plane-waves

\[
\psi_k(r) = \sum_k C_k e^{ikr} ; \quad U(r) = \sum_G U_G e^{iG \cdot r} ;
\]

by inserting 2.37 into the Schrödinger equation, this becomes the well known secular equation for the energy eigenvalue \( \varepsilon \) and the coefficients \( C_k \)

\[
\left( \frac{\hbar^2 k^2}{2m} - \varepsilon \right) C_k + \sum_G U_G C_{k-G} = 0.
\]
For a fixed $k$ in the first Brillouin zone, the set of equations represented by eqn 2.38 couples all (and only) the coefficients of plane waves whose wave-vectors differ by a reciprocal lattice vector $G$. The solution is then,

$$\left| \psi_k (r) \right> = \frac{1}{V^{1/2}} \sum_G C_{k,G} e^{i(k-G)r} .$$

2.39

The matrix elements between plane waves whose wave-vectors differ by a reciprocal lattice vector are, by using the expansion of the crystal potential in 2.37,

$$\langle e^{iG_2 \cdot r} | H | e^{iG_i \cdot r} \rangle = U_{G_2-G_i} ,$$

2.40

where $H$ is the Hamiltonian operator.

To solve eqn 2.38 one truncates the expansion for the potential in eqn 2.37 and the number of coefficients $C_{k,G}$ in eqn 2.39 at some point, to obtain a set of eigenvalues $\varepsilon_k^n$ and associated $C_{k,G}^n$ ($G=-i,-i+1,...,i-1,i$) eigenvectors (here $n=2i+1$) per each $k$ point ($k$ is limited to the first BZ). The dispersion relation $\varepsilon_n^G (k)$ is therefore multivalued, the index $n$ usually being called the band index$^{17}$.

The eigenstates in eqn 2.36 are simultaneous eigenstates of the Hamiltonian operator and of the translation operator $T_R$.

$$T_R | \psi_k (r) \rangle = e^{ik \cdot R} | \psi_k (r) \rangle$$

2.41

Eqn 2.41 can be adopted to define the Bloch wave-vector, or crystal momentum, $k$. As thoroughly discussed in all textbooks, this is not the electronic momentum which we measure with a 2D-ACAR experiment (consider the positron at rest and uniformly distributed for the present). Although the energy eigenstates are stationary, the associated momentum will not be stationary but will depend on the position of the electron in the crystal cell. One can then calculate the expectation value of the momentum operator for each of the energy eigenstates. In other words, in a periodic system the momentum is not a good quantum number. The crystal momentum $k$ is, on the other hand, a good quantum number and provides the "label" for the electronic states (when reduced to the first Brillouin zone).

$^{17}$ As the convergence of the plane waves is quite slow, in modern band structure calculations the expansion is always performed on other sets of polynomials.
With these ideas in mind, it is necessary to understand how the periodic potential will affect the output of ACAR experiments. To do so, one can insert the Bloch solutions, expanded into plane waves as in eqn 2.39,

\[ |\psi_k^-(r)\rangle \propto e^{ikr} \sum_G E(k + G)e^{iGr}, \]

\[ |\psi_k^+(r)\rangle \propto \sum_{G'} P_{G'} e^{iG'r}, \]

into the expression for the momentum density given by eqns 2.27 and 2.28. No temperature effect is considered here \((T=0)\). The electron expansion coefficients, \(E(k + G)\), are function of the position, \(k\), of the state in the energy band. The positron expansion coefficients, \(P_{G'}\), are simply constants as only one positron at a time is present in the system. The particle populates the bottom of the positron conduction band \((k^+=0)\).

The resulting momentum density is

\[
\rho_{k^+}^{e-} (p) \propto \sum_n \theta(E_F - \varepsilon_{k,n}) \sum_k \delta(p - k - K) \left| \sum_G E^n (k + G) P_{k-G} \right|^2 = \\
= \sum_n \theta(E_F - \varepsilon_{k,n}) \sum_k \delta(p - k - K) \left| C^n (k + K) \right|^2 ,
\]

which, by assuming the positron to be uniformly distributed in the crystal cell, is simplified to

\[
\rho_{k^+}^{e-} (p) \propto \sum_n \theta(E_F - \varepsilon_{k,n}) \sum_G \delta(p - k - G) \left| E^n (k + G) \right|^2 .
\]

The step function \(\theta(E_F - \varepsilon_{k,n})\) restricts the summation to occupied electron states, with energies \(\varepsilon_{k,n}\) from bands \(n\). Three important characteristics should be noted:

i) Unlike the momentum density of the FEM, where each eigenstate consisted of a simple plane wave with wave-vector \(k\), contributing to the momentum density, \(\rho(p)\), with a delta function at the momentum \(p=k\), now each eigenstate, labelled by the Bloch wavevector \(k\), (see eqns 2.44 and 2.45) will contribute to \(\rho(p)\) with several delta-functions, or images, at the momenta \(p=k+G\). The images at \(G \neq 0\) are called
"high momentum components" (HMC) and are a sign of the strong oscillations which the periodic part of the Bloch function exhibits near the lattice points.\(^{18}\) ii) The electronic expansion coefficients in eqn 2.42 induce a \(\mathbf{k}\) dependence in the momentum distribution. That dependence clearly becomes stronger for states whose wave-vectors \(\mathbf{k}\) are close to the Brillouin Zone (BZ) boundaries, where one has Bragg diffraction and the FEM approximation fails completely. The functional dependence of the expansion coefficients acts as a modulation function of the occupancy step function (and of its HMCs).\(^{19}\)

If the only occupied states of the system are those which are far away from the BZ boundary, the FEM is a better approximation. Intuitively, one can actually imagine that the eigenstates with small wave-vector \(\mathbf{k}\) are more delocalised (according to uncertainty principle) and therefore less sensitive to the strongly localised crystal potential. This is why in the case of alkali metals, where only 1 S electron emerges from the underlying close rare-gas shell, the results of 1D-ACAR experiments are the Sommerfeld inverted parabolas described in § 2.5. For example, the electrons in sodium form the closest approximation of a free-electron gas of any metal and its Fermi surface is very nearly spherical. The simplicity of alkali metals also make them suitable systems for checking the prediction of many body theory.\(^{20}\)

For more tightly bound electrons, like the \(d\) electrons in transition metals, energy bands are narrower and markedly differ from the simple FEM parabolic bands. For those electrons the expansion into plane waves needs more terms and the strongest expansion coefficient is not that of lowest order. The most significant part of the \(d\)-like sheet of the Fermi surface may be therefore found at higher Brillouin zones.

iii) Eqn 2.44 shows how the presence of the positron affects the momentum distribution. The convolution character of the \(C^a(k+G)\) coefficients can be seen more clearly by directly expanding the products of the electron and positron coefficients for the \(K\)th HMC,

\[
\left| C^a(k + K) \right|^2 = \left( \sum_{G^e} E^e(k + G^u) P_{K-G^e} \right) \left( \sum_{G^p} E^p(k + G^p) P_{K-G^p} \right).
\]

\(18\) Since the momentum operator is defined as \(\hbar \frac{\partial}{\partial \psi}\), strong oscillations in the periodic part of the Bloch function imply high momenta. (This of course reflects the fact that the electron, in the proximity of the lattice points, is accelerated by the crystal potential.)

\(19\) As the momentum density must clearly go to zero for increasing momenta, it follows that it is non-periodic (unlike the Bloch wave vector density).

\(20\) The most recent and comprehensive study on alkali metals [Manuel (1993)] has, however, found that electron-positron correlation effects do not distort the HMCs in any significant way.
One can see that the contribution will consist of direct square products (diagonal, \(G''=G'\)) and cross products. The leading diagonal term is \(|P_0|^2 |E^n(k+K)|^2\) and is the only one present in the purely electronic momentum density. The other \(|P_{k-G}|^2 E^n(k+G)|^2\) products provide weaker images of the electron momentum density located at the nearby reciprocal lattice vectors. However, all these terms, together with the square terms from the other \(|C^n(k+K_i)|^2\) coefficients, would contribute toward restoring the appropriate normalisation condition of a purely electronic momentum density (and therefore the electron occupancy function) if they were all summed after a translation of the appropriate reciprocal lattice vectors \(K_i\).

However, this does not happen because of the presence of the cross terms in the products of eqn 2.46. These terms are predominantly negative in order to account for an overall electron-positron overlap integral which is only a fraction of the normalisation volume (West, 1993).

It is instructive to show the form of the momentum distribution in the case of the simplest example of a periodic system. In the lowest order of the so-called nearly free electron model, one truncates the expansion of the electronic terms in eqn 2.42 to the first two coefficients and maintains the FEM position of a completely delocalized positron. Equations 2.42 and 2.43 reduce to

\[
\begin{align*}
\left| \psi_{e^-} \right| & \propto e^{ikr} \left[ c(k) + c(k-G)e^{-iGr} \right] \\
\left| \psi_{e^+} \right| & = \text{const}
\end{align*}
\]

and can be inserted into the basic secular equation 2.38. By assuming a simple cosinusoidal (real) potential \((U_G=U_{-G}=U)\), the resulting eigenvalue equation is then (in a.u.)

\[
\begin{bmatrix}
\frac{(k-G)^2}{2} - \varepsilon & U \\
U & \frac{k^2}{2} - \varepsilon
\end{bmatrix}
\begin{bmatrix}
C_{k-G} \\
C_k
\end{bmatrix} = 0.
\]

The solution of the algebraic equation is of second order in \(k^2\) and leads to two eigenvalues and eigenvectors, one for the upper band and one for the lower band. By expressing the coefficients as a function of the distance from the BZ, one obtains, after some algebraic manipulation [Berko and Plaskett, 1958].
\[ |C_{k}^{\text{low}}|^2 = \frac{1}{2} \left( 1 - \frac{x}{(1 + x^2)^{1/2}} \right); \quad |C_{k}^{\text{up}}|^2 = \frac{1}{2} \left( 1 + \frac{x}{(1 + x^2)^{1/2}} \right) \]
\[ |C_{k-G}^{\text{low}}|^2 = \frac{1}{2} \left( 1 + \frac{x}{(1 + x^2)^{1/2}} \right); \quad |C_{k-G}^{\text{up}}|^2 = \frac{1}{2} \left( 1 - \frac{x}{(1 + x^2)^{1/2}} \right) \]

where \( x = \frac{(\mp G - k) \cdot G}{U} \). The total momentum density is therefore (dropping the vector notation),

\[ \rho(p) \propto |C_{k}^{\text{low}}(k)|^2 \delta(p - k) + |C_{k-G}^{\text{low}}(k)|^2 \delta(p - k + G) + |C_{k}^{\text{up}}(k)|^2 \delta(p - k) + |C_{k-G}^{\text{up}}(k)|^2 \delta(p - k + G). \]

This expression is a good approximation for states with wave vectors \( k \) in proximity of the zone boundary \((k=G\) and similarly for \( k=-G\), with \( G \) swapped to \(-G\)).

It is useful to identify the separate contributions of the two bands to the momentum density. An energy gap \((2U)\) of \(3.4\text{eV} \) and a BZ size of \(1.4\text{a.u.} \) are considered in this example.\(^{21}\) The lower band is fully occupied. Its contribution to the momentum distribution, shown in Fig 2.5, is then a continuous function.\(^{22}\) The upper band is occupied only for 8% of the BZ and shown in Fig 2.6.

Eigenstates whose wave-vectors are close to the BZ boundary are more likely to be Bragg scattered, from \( p=k \) to \( p=k-G \) and from \( p=-k \) to \( p=-k+G \), respectively. This causes a smooth decrease in the momentum distribution of the lower band at the BZ boundary. By summing the two contributions, one obtains the total momentum distribution, shown in Fig 2.7.

As one can see in figure 2.7, two FS breaks (at \( k_F \) and \(-k_F \)) and their two HMC, (at \( k_F-G \) and \(-k_F+G \)) appear. However, if the number of conduction electrons per atom increases and \( k_F \) (in the upper band) moves well inside the BZ, the breaks at \( \pm k_F \) will not be visible any more because the momentum density from the lower band has not yet started to decrease (and the contribution from the upper band is small). The only visible breaks will be those at \( p=k_F-G \) and at \( p=-k_F+G \).

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\(^{21}\) These figures are not related to a particular material.

\(^{22}\) It is clear that an insulator should therefore show no sharp breaks in its momentum distribution.
It is through these mechanisms that the momentum densities of the simple trivalent metals like Al resemble so closely their Fermi surfaces in an extended zone scheme. Figure 2.8 shows, as an example, the 2D-ACAR momentum density for Al. It is
evident that the FEM, by assuming three conduction electrons per atom ($k_F = 0.925$ a.u. $\theta_F = 6.75$ mrad), is in very good agreement with the experimental data.

2.7 The recovery of the Fermi surface

The search for the discontinuities in the momentum distribution which define the Fermi surface is limited by the following factors:

i) The experimental resolution

ii) The effect of the temperature

iii) The functional $k$-dependence of the expansion coefficients $|C(k + G)|^2$ (see eqn 2.44) in the momentum distribution.

iv) The contribution from the full bands.

v) The effect of a non-constant positron wavefunction.

vi) The effect of the hybridisation between energy bands

Leaving the discussion of the point i) to the description of our experimental set-up, the importance of the temperature as a factor in the smearing of the FS breaks is discussed in the following.
ii) The thermal effects due to the positron and the electron motions should both be considered. At a temperature \( T \) the momentum distribution of the electrons labelled by the Bloch wavevector \( \mathbf{k} (k \equiv p \text{ in the free electron model}) \) over the available states is governed by the Fermi-Dirac distribution,

\[
f_e(p) = \frac{1}{4(h \pi)^3} \exp \left( \frac{p^2 / 2m^*_e - \mu}{k_B T} \right) + 1,
\]

where \( \mu \) is the chemical potential, \( m^*_e \) is the effective mass of the electrons, and \( k_B \) is the Boltzmann constant. It is well known that the blurring of the Fermi surface by the action of the temperature is of the order of \( k_B T \). The effect of this smearing on the momentum (and angular) distribution can be evaluated with the usual transformations (see §2.2) and gives, for example, for Cu (\( E_F = 7 \text{eV} \)) at room temperature \( (k_B T = \delta E \approx 0.025 \text{ eV}) \),

\[
\frac{\delta p}{p_F} = \frac{\sqrt{2m(E + \delta E)} - \sqrt{2m(E - \delta E)}}{p_F} = 3.6 \times 10^{-3}
\]

\[
\Rightarrow \delta \theta \approx 0.018 \text{ mrad} = 2.46 \times 10^{-3} \text{ a.u.},
\]

which is negligible if compared to the typical angular resolutions of the state of the art ACAR spectrometers (0.3-0.7 mrad).

More significant is the temperature effect of the positron on the precision of the experiments. As there is only one positron at a time in the system, its momentum distribution is described by the Maxwell-Boltzmann distribution,

\[
f_+(p) = \left( \frac{2 \pi m^*_+ k_B T}{2m^*_e k_B T} \right)^{3/2} \exp \left( -\frac{p^2}{2m^*_+ k_B T} \right),
\]

where \( m^*_+ \) is the effective mass of the positron. By assuming an effective mass of the positron of \( m^*_+ = m_0 \), the full width at half maximum, FWHM, of the Maxwell-Boltzmann distribution at room temperature is given by

\[\text{For temperatures } T \ll T_F \mu = E_F, \text{ where } E_F \text{ is the Fermi energy, } (T_F \equiv E_F / k_B).\]
\[ FWHM_p = 2.354 \sqrt{m^*_e k_B T} \Rightarrow \]
\[ FWHM_\theta = FWHM_p / 137 = 0.53 \text{ mrad} = 0.072 \text{ a.u.} \]

which corresponds to \(~10\%\) of the Fermi momentum in the case of Cu (see §2.3). This means that whereas the thermal smearing due to the electrons is negligible, that due to the positron motion can be observed \(^{24}\). (The FS blurring due to the positron thermal motion is negligible with respect to the typical 2D-ACAR angular resolutions when the experiments are performed at reasonably low, \(T= 20-50 \text{ K}, \) temperature.)

\(^{iii)}\) It was shown in the previous paragraph (§ 2.6) how, in the nearly free electron model, one could obtain the functional dependence of the HMC of the Fermi surface (via the coefficients of expansion \(|C(k + G)|^2\)) on the Bloch wave-vector \(k\). However, (as mentioned in §2.6) when the electronic bands have a more d- (or f-) like character, the HMC of the Fermi surface will appear in many zones (owing to the stronger effect of the crystal potential), and the nearly free electron model approximation will no longer hold unless many expansion coefficients are used.

When the Fermi discontinuities are distributed over many BZs, it may be quite complicated to unravel them. In addition (point iv), the contribution from the many full bands populated by other "outer" electrons (and therefore with momenta comparable with those of the conduction electrons) is superimposed on the part full bands and introduces a smoothly varying background, whose statistical precision can overshadow the FS discontinuities.

The folding procedure proposed by Lock Crisp and West (1973) (LCW), and used extensively in the 2D-ACAR analysis, tries to overcome the problems mentioned at the points iii) and iv). That procedure consists of folding the momentum distribution back onto the first BZ by translation over the appropriate reciprocal lattice vectors. In other words, for each momentum \(p\), one derives the particular reciprocal lattice vector \(G(p)\) which, once subtracted from that momentum, obtains a reduced momentum \(p' = p - G(p)\) inside the first BZ; one then adds all the contributions of the momentum density corresponding to the same reduced wave-vectors \(k\). If the momentum distribution can be approximated to a purely electronic one (eqn 2.45), the folding can be written as,

\(^{24}\) The resulting momentum distribution at finite temperatures is then given by the convolution of eqn 2.51 with eqn 2.52 which, by neglecting the electron smearing, is easily performed. Several studies on simple metals with well-known experimental resolution spectrometers have deduced the values of the effective masses of the positron (within a range of \(\sim 1-1.8 m_e\)) and supplied tests for many theoretical calculations. For a list of references on the topic see, for example, [West (1974), Mijnarends (1979,1983)].
The last step in eqn 2.54 is consistent with the normalisation requirements of the expansion coefficients $E_n$ of the electron eigenstates ($\sum_{G} |E_n(k-G)|^2 = 1$.) As the result of the folding is a periodic function, one can consider just its reduced form to the first BZ, $\rho_{LCW}(k) = \rho_{LCW}(p)$. As the folding simply results in the Fermi occupancy function$^{25}$, every time a band crosses the Fermi level, $E_F$, the distribution $\rho_{LCW}(k)$ will exhibit a jump of 2 units (if the electronic bands are energy-degenerate with regard to the spin) at that particular $k = k_F$. It follows then that the contribution to $\rho_{LCW}(k)$ from the full bands is simply a constant.

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$25$ Or a projection of it, when one measures 1- or 2-dimensional projections of the momentum density.
Fig 2.9 shows a symbolic example of a 2D-momentum density originated by a spherical Fermi volume occupying half of the BZ (assumed to be simple cubic). The Fermi radius, \( k_F = G (3 / 8 \pi)^{1/3} \), corresponds to 49.2% of the BZ size, \( G \). The result of the 2D-LCW folding is shown in figure 2.10. The folding of the momentum density due to the part full band produces the FEM inverted hemisphere and the contribution from the full bands consists of the superimposed constant.

v) Positron effects - The LCW folding procedure will yield exactly the electron occupation number (function of the reduced Bloch wave vector \( \mathbf{k} \)) only if the positron can be assumed to be uniformly distributed over the unit cell. § 2.6 deals with the way in which the presence of the cross terms in the expansion coefficients of eqn 2.46 prevents the \( |C_n(\mathbf{k} + \mathbf{K})|^2 \) coefficients from restoring the purely electronic occupancy function.

Another way to show the positron-effect is by noting [Shiotani (1984), Kaiser at al (1986)] that the sum over \( \mathbf{G}s \) in eqn 2.54 can be reduced to its real-space representation to obtain,

\[
\rho_{LCW}(\mathbf{k}) = \text{const} \sum_n \Theta(E_F - \epsilon_{k,n}) \times \int dr \left| \psi_{\phi_n}(r) \right|^2 \left| \psi_{\phi_k}(r) \right|^2 ,
\]

2.55
i.e. the folded distribution $\rho_{LCW}(k)$ at each $k$ point is proportional to the IPM annihilation rate of the positron with the $\psi_k^\alpha$ electron. Eqn 2.2 shows that the occupancy function at the Bloch wave-vector $k$ is modulated by the overlap integral of the $k$ electron and positron density. Clearly, any jump at the Fermi wavevector $k_F$ is reduced by this modulation factor but the position of the break is maintained at $k_F$.

For some crystal structures, the positron wave-function can be sensibly non-homogeneous. A relevant example of a class of materials where the knowledge of the positron density plays a vital role is given by the high T$_c$ superconductor compounds, where relatively open regions of a large unit cell can attract the positron at the expense of other more close packed regions. In this case a comparison between the experimental LCW and the $k$-space density calculated via eqn 2.2 is essential in extracting FS information [West, (1992), Haghighi et al (1991), Sterne et al (1992), Singh et al (1990), Bansil at al (1991)].

However, even when the constant positron-wave function approximation is no longer valid, eqn 2.2 provides a good test for a comparison between experiments and theory, as the folded density may still be expected to enhance FS features. Moreover, the result of eqn 2.2 is much easier to calculate than the total electron-positron momentum density described by eqn 2.44.

Clearly, the possibility of observing the FS breaks is sensitive to a large and weakly $k$-dependent overlap integral$^{26}$. Owing to the repulsion from the positive nucleus, the total annihilation rate is dominated by annihilation with "outer" (valence) electrons. This celebrated effect makes ACAR a valuable tool for FS studies. Even when the valence electrons comprise only a small fraction of the total number of electrons in the system, they still account for more than 75% of the annihilation rate (Sterne and Kaiser, 1990)$^{27}$.

vi) Hybridisation effects - In general, the $k$-dependence of the overlap integral is not negligible when the character of the electron eigenstates changes from $s$-$p$ to being $d$-like along the energy bands, being the positron wave function essentially an $s$-state. As the electron wave functions are more spread out for nearly-free electrons ($s$-$p$ like) than for $d$ electrons, the amount of $s$-$d$ hybridisation determines the intensity of the overlap integral and, consequently, of the folded LCW intensity [Rabou et al, (1984)].

Mijnarends (1993) has pointed out that even under the assumption of a positron wave-function which is exactly uniformly distributed in the crystal cell, hybridisation

$^{26}$ As an example, the amplitude of the LCW discontinuities caused by the d bands in most transition metals does not exceed the size of 0.5 [Rabou et al (1984), Rozing et al (1991)]

$^{27}$ This figure (75%) is the lowest limit which results from calculations of the total annihilation rate including the $e^+ - e^-$ correlation. Other methods (see the same reference reported) obtain that (90-95)% of the total annihilation rate in solids comes from annihilations with the valence electrons.
can cause effects which can be confused with FS signatures after the LCW folding and, therefore, limit the recovery of the true FS.

Let us imagine two energy bands (say one s-p like and one d-like) which in the absence of a perturbation would cross each other at some \( k_0 \) point. Owing to the effect of the crystal potential (or of the spin-orbit interaction) the degeneracy at \( k_0 \) may be lifted. In this case the two bands repel each other and a hybridization gap opens (see figure 2.11). To see how the position of the Fermi level, \( E_F \), with respect to the hybridization gap affects the LCW folded momentum distribution we consider two orthonormal unhybridised electron wave-functions \( \psi_s \) and \( \psi_d \). For the sake of simplicity we will assume that \( \psi_s \) is free-electron like and that \( \psi_d \) has a very limited plane wave expansion (in a one dimensional BZ of size \( G \)),

\[
\psi_{s,k}(r) \propto \exp(ikr)
\]

\[
\psi_{d,k}(r) \propto e^{ikr} \left[ D_0(k) + D_1(k)e^{iGr} + D_{-1}(k)e^{-iGr} \right].
\]

When the hybridisation is switched on, the new functions become linear combinations of \( \psi_s \) and \( \psi_d \).

\[
\phi_{1,k} = a(k) \psi_{s,k} + b(k) \psi_{d,k}
\]

\[
\phi_{2,k} = b^*(k) \psi_{s,k} - a^*(k) \psi_{d,k},
\]

where at each \( k \) point the relation \( |a(k)|^2 + |b(k)|^2 = 1 \) ensures the orthonormality of \( \phi_{1,k} \) and \( \phi_{2,k} \).

If one assumes a constant positron wave function, the momentum density can be calculated by inserting eqn 2.57 into eqn 2.45. One can then apply the LCW procedure by folding the distribution back into the first BZ. This results in the following expressions for the two hybridised bands

\[
\rho_{1,LCW}(k) = |a(k)|^2 + |b(k)|^2 \left[ |D_0(k)|^2 + |D_1(k)|^2 + |D_{-1}(k)|^2 \right] + a^*(k)b(k) D_0^*(k) + b^*(k)a(k) D_0(k)
\]

\[
\rho_{2,LCW}(k) = |b(k)|^2 + |a(k)|^2 \left[ |D_0(k)|^2 + |D_1(k)|^2 + |D_{-1}(k)|^2 \right] - a^*(k)b(k) D_0^*(k) - b^*(k)a(k) D_0(k).
\]
From eqn 2.58 it is clear that, given the normalisation requirements of the expansion coefficients of $\psi_{d,k}$, $D_i(k)$, and of the hybridisation coefficients, $a$ and $b$, if both the bands are fully occupied, they combine to give a constant.

If, however, the Fermi energy lies in the hybridisation gap, the upper band $\rho_{2,LCW}(k)$ is unoccupied and the compensation between the coefficients will not act any more. The folded density will therefore have a $k$ dependence which could be confused with a Fermi surface effect (especially after the convolution of the actual Fermi breaks with the experimental resolution).

### 2.8 Selection rules

R Harthoorn and P E Mijnarends (1978) explored in detail the visibility of the FS breaks present in the momentum density. Here follows a brief summary of their results. An integral of the form

$$A^n(p, k) = \int dr \exp(-ip \cdot r) \psi_{k,n}(r) \psi_{e,n}(r), \tag{2.59}$$

which is present in eqn 2.44, gives non vanishing results only if the integrand contains a term which has the full point symmetry of the crystal. As a consequence, along certain lines or symmetry planes there are selection rules which force $A^n(p, k)$ to vanish. This fact can be very important in the case of the 3D-reconstructed momentum density. To illustrate the idea it is necessary to define the group of $k$, $G_0(k)$. This group consists of all rotations and reflections (in reciprocal space) that transform $k$ into itself or into a vector $k' = k + G$, where $G$ is a reciprocal lattice vector. The latter property (with $G \neq 0$) can be achieved by a reflection operation if both $k$ and $k'$ lie on the Brillouin zone boundary. An eigenfunction $\psi_{k,n}(r)$ is said to be totally

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28 As no band crosses the Fermi level, no Fermi Surface exists either in this case
symmetric if it is invariant under all the transformations, \( R \), which belong to \( G(k) \) (Hamermesh, 1962).

A simple one-dimensional example may help to clarify the problem. In this case the BZ is simply the interval \( \left[ -\frac{\pi}{a}, \frac{\pi}{a} \right] \), where \( a \) is the size of the 1D-cell in real space. A high symmetry point of the 1D BZ is at \( k=0 \), i.e. the \( \Gamma \) point.

In one dimension \( G(k)_{k=0} \) has two elements: the identity transformation (E) and the inversion transformation (I). The eigenstate (of band \( n \)) at the \( \Gamma \) point may be a totally symmetric function, i.e. an even function or non-totally symmetric function, such as an odd function. The consequence of the symmetry of the wave function on the momentum density can be seen by calculating the expansion coefficients of the Bloch wave-function. From the definition of the Bloch function (eqn 2.39)

\[
|\psi_k(x)\rangle \propto \sum_G C_{kG} e^{i(k-G) \cdot x},
\]

one obtains

\[
C_{k-G} = \frac{1}{a} \int_{-a/2}^{a/2} dx \ e^{-i(k-G) x} \psi_A(x)
\]

The coefficient \( \left| (C_{k-G})^{G=0}_{k=0} \right|^2 \) contributes to the momentum density at \( p=0 \), i.e. where the momentum equals the high symmetry point in the first BZ. Clearly, if the wave function is odd, the integral of eqn 2.60 will vanish. Moreover, in this case all the coefficients \( (C_{k-G})^{G=2n}_{k=0} \), corresponding to the HMC at even reciprocal lattice vectors will vanish owing to the anti-symmetry of the wave-function.

More generally, the full group theory analysis shows that if \( p \) lies inside the first Brillouin zone \( (p=k) \) along high symmetry points, lines or planes, only bands belonging to the totally symmetric representations (i.e. \( \Gamma_1, \Delta_1, \Lambda_1 \) etc, where the labelling refers here to a simple cubic BZ) will yield a non zero \( A^n \) integral. The same is true if \( p \) is parallel to \( k \) in higher zones. At a non high symmetry point, there is only one representation, the totally symmetric one\(^{29}\), and so the integral in 2.59 is non-zero. The momentum distribution, \( \rho(p) \), can thus show nodal points or lines or planes hiding Fermi surface breaks present at nodal positions. This effect can be very important in the case of a full 3d-momentum density. Harthoorn and Mijnarends

\(^{29}\) At a non high symmetry point, the only element which belongs to \( G^0(k) \) is the identity (E) operation. Therefore the eigenstate \( \psi_{k,n}(r) \) at the general point \( k \) is invariant for all the symmetry operations of \( G^0(k) \).
(1978) have computed tables which list the observability of the momentum density \( \rho(p) \) for simple cubic (SIC), FCC and BCC lattices.

In the case of projections of \( \rho(p) \), the integration involves mostly non-high symmetry points (where the distribution does not vanish). Consequently, the effect of those selection rules brings simply a correction to the momentum density.

These findings were adopted in a simulation of the momentum density of LaB\(_6\) (see §5.4 for details). Only one band contributes to its Fermi surface\(^{30}\) [Hasegawa et al (1977)] which consists of a set of nearly symmetrical electron ellipsoids centred at the X points and connected by thick necks along the \( \Sigma \) axes\(^{31}\). The conduction band has a totally symmetric character between the \( \Gamma \) and M (\( \Sigma 1 \)) and X - M (\( Z1 \)) points and a non totally symmetric character between the \( \Gamma - X (\Delta 2) \) and X - R (\( S4 \)) points (here the symmetry labels denote rotational operations about the La atom). The application of the selection rules mentioned has the consequence that the 3D momentum distribution of the conduction band, \( \rho'(p) \), has nodes along the X-R and \( \Gamma - X \) directions when \( p \) is in the first BZ. In higher zones, at momenta \( p \) parallel to the Bloch wave-vectors \( k \) of eigenstates with a non-totally symmetric character, \( \rho'(p) \) will exhibit nodes too. For momenta \( p \) just outside nodal planes or off nodal lines the vicinity of the node will generally make the momentum density \( \rho'(p) \) in these points rather small. The integration of the distribution along the projection direction, (say, \( <001> \)), will therefore result in a distribution of lower intensity for those \( (k_x,k_y) \) points which results by integration lines containing nodal points. The above-mentioned modification led to a 2-D simulation in better agreement with the experimental results.

2.9 Electron-Electron and Electron-Positron correlations

We have so far adopted the IPM approximation to predict the properties of our observable, and neglected completely the effects of electron-electron and electron-positron correlation. As correlations are believed to cause the unusual low-temperature phenomena shown by heavy-fermion systems, it is important to discuss the electron-positron many-body studies. It was clear since the beginning of the use of positrons as probes in condensed matter that correlation effects affect the angular correlation and the positron lifetime experiments in a very different manner:

i) The main features of electron-positron angular correlation experiments are in good agreement with the results of the IPM calculated momentum density.

ii) However, the result of the IPM calculation of the total annihilation rate \( \lambda_0 \),

\(^{30}\) It will be seen later that another minor sheet of the FS, contributing less than 0.01% to the Fermi volume, is present in LaB\(_6\).

\(^{31}\) The BZ is simple cubic and the labels refer to its high symmetry points.
\[
\lambda_0 = \int \rho_k^2 (p) d^3 p \propto \sum_k \int d_r |\psi_{e_k}^* (r)|^2 |\psi_e (r)|^2 \\
= \pi n_0^2 c \int d_r n_e (r) n_e (r)
\]

is invariably much less than the rate observed in positron-lifetime experiments. The effect is frequently expressed in terms of a many-body enhancement factor \( \varepsilon(n_0) = \lambda / \lambda_0 \), where \( n_0 \) is the uniform electron density. This failure is due to the neglect of the Coulomb forces. The total rate \( \lambda \) for a many body system of electrons and a positron is, in fact, proportional to the electron density at the positron, averaged over all positron positions. However, the IPM, by ignoring all the Coulomb forces, assumes that the electronic density at the positron is the average density in the system. This clearly causes an underestimate of the rates. Actually the positron perturbs the many-electron system by attracting a cloud of electrons which screens its positive charge. The pile-up of the electronic wave function at the positron increases the annihilation probability.

Early attempts to present a theory of correlation were due to Kahana (1963) and Carbotte (1966) and were largely confined to the so-called Jellium system consisting of a homogeneous electron gas plus a compensating positive background. They derived (for \( p < p_F \)) an enhancement factor \( \varepsilon(p,r_s) \), which multiplies the IPM momentum density \( \Gamma_{IPM}(p) \) and is a function of the parameter \( r_s = (3/4 \pi n_0)^{1/3} \),

\[
\Gamma(p) = \varepsilon(p,r_s) \Gamma_{IPM}(p); \quad p \leq p_F.
\]

The result of the calculation is that, as one approaches the Fermi momentum, the annihilation rate increases. Surprisingly, by extending the calculation for \( p > p_F \), one finds that \( \Gamma(p) \) drops almost to zero as the result of a cancellation of terms. For \( p < p_F \) the \( p \) dependence of the enhancement \( \varepsilon(p,r_s) \) can be parameterised as

\[
\varepsilon(p,r_s) = a(r_s) + b(r_s) \gamma^2 + c(r_s) \gamma^4, \quad \gamma = p/p_F.
\]

Fig 2.12 shows the celebrated effect of the e^-e^+ correlation in the momentum density as compared to the well-known result of the electron-electron correlation.

\[32\] The vector notation is dropped in the discussion.
In the latter case, because of the Pauli exclusion principle, the scattering probability of the electrons at the Fermi surface increases, because unoccupied states are more easily accessible (as a result of the scattering); the occupancy of those states at higher momentum then becomes non-zero. The increase in momentum must of course happen at the expense of states just below the Fermi level whose occupancy decreases accordingly.

The study of the electron-positron correlation showed that the annihilation probability with electrons at the Fermi surface increases.

Fig. 2.12 The effect of the correlation on the momentum density in Jellium, after Carbotte et al (1965). The curve shown is calculated by Berko (1983) for an electron density equivalent to that of the conduction band of Al ($r_F/\alpha_0=2.07$).

This is because those electrons have free phase space available to change their momentum as a result of the attractive $e^+-e^-$ Coulomb interaction. However, for $p>p_F$ the $e^+-e^-$ interactions cancel the tails resulting from the $e^--e^-$ correlation to a great extent. 1-D angular correlation experiments on alkali metals, where the FS is almost spherical, have confirmed these results. The increase in the momentum density at the Fermi momentum after the double integration of 1D-ACAR experiments results in the distinct bulge of the FEM inverted parabola shown in figure 2.13. However, the results for the free electron gas cannot be applied in a straightforward manner to materials with a more complex structure involving $d$ or $f$ bands. A discussion of $e^+-e^-$ and $e^--e^-$ correlation which takes into account the interaction of the particle with the lattice is extremely complicated. So far, attempts to evaluate the correlation have not
been very successful. To date, Mijnarens and Singru (1979) have proposed to modify eqn 2.62 with an empirical prescription to enhance the d electrons in a more appropriate way (see also Jarlborg et al, 1987) and Sorman et al (1992) have implemented an approximate method to describe both the electron and positron propagators, or Green's function, on the basis of Bloch function.

In most of the real electron-positron momentum density calculations the problem of correlation is normally addressed in terms of the Local Density Approximation which, as discussed in §1.4, is unable to take appropriately into account the enhanced Coulomb repulsion of the f-like states, typical of heavy-fermion systems.

The expression for the momentum density is, in general, modified by including in eqn 2.28 the enhancement factor term so to give [see for example Rozing et al (1991)],

$$\rho_{\psi}^{2\gamma}(p) = \sum_{n,k} \frac{\pi A_n^2 e}{(2\pi)^3} \left| \int dx \exp(-ip \cdot x) \psi_{\gamma}^{n,k}(x) \psi_{\gamma}(x) \sqrt{\gamma(x)} \right|^2. \quad 2.63$$

*Fig. 2.13 1D-ACAR along several crystal orientations for sodium. A broad Gaussian background, assumed to be due to core annihilation, has been subtracted from the distribution. The broken line is the FEM inverted parabola; the solid line is the distribution expected when the Kahana enhancement is taken into account. After Donaghy and Stewart (1967).*
Here \( y(\kappa) \) is the enhancement factor to account for the many body correlations not included in the LDA used to calculate \( \psi_{e^-}^{\kappa} \) and \( \psi_{e^+}^{\kappa} \).

Moreover, recent results of high resolution Compton profile experiments have highlighted the inadequacies of LDA in reproducing quantitatively the true electron momentum density even in simple systems (Shiotani, 1995). The Compton profile technique measures the 1D-electron momentum distribution sampling each occupied state with equal weight (for a review of the topic see, for example, Williams (1977), Cooper, 1985). The result of the experiment therefore resembles that of a 1D-ACAR with a rigorously constant positron-wave function. Although LDA-based theory could explain qualitatively the overall shape and fine structures of the observed profiles, a systematic discrepancy, observed also in early Compton experiments, was confirmed for the materials so far analysed with the high resolution setups (Li, V, Cu\(^{33}\), Shiotani, 1995). The theoretical profiles are always higher than the experimental ones at low-momenta and vice-versa at high momenta. Moreover, the fine structures observed in the experiments, such as those generated by the FS discontinuities, are not as clearly pronounced as would be predicted by the LDA-based theory. Discrepancies between theory and experiment were also observed in early 1D-ACAR experiments (Shiotani et al 1975). However, in that case the calculated spectra were lower than the experimental profiles at low momenta and higher at high momenta (after that the spectra were normalised to the same number of counts). Attempts to improve LDA with the self-interaction correction, SIC, mentioned in §1.4 (Perdew et al 1981), are in progress (Shiotani 1995 and references therein).

Nevertheless, the early conclusion that the e\(^-\)-e\(^+\) many body enhancement factor does not shift the discontinuities in the e\(^-\)-e\(^+\) momentum density from those corresponding to the FS of the system [Majumdar, (1965)] is still accepted. So, at present, there is consensus that one can obtain information on the FS topology despite lacking a complete understanding of the many-body phenomena.

At conclusion of this chapter, one might pose some questions and speculations regarding the predicted result of the annihilation of a positron in a strongly correlated electron system. As the main source of information on those systems is the de Haas van Alphen technique, it is worth mentioning the two most important results which dHvA produces. They are [see, for example, Springford (1991)]:

i) extremal areas of the Fermi surface in the direction perpendicular to an applied external magnetic field, \( B \), obtained by measuring the frequency, \( F \), of the oscillations in the magnetisation as a function of the inverse of \( B \).

\(^{33}\) The discrepancy observed for Cu was a well known earlier finding (see, for example, Cooper 1985).
ii) cyclotron masses$^{34}$, $m^*$, of the conduction electrons obtained by measuring the
damping of the oscillations of the magnetisation as a function of the temperature
[Lifshitz and Kosevich 1955].

From the FS extremal areas and the measured cyclotron mass $m^*$, the dHvA
technique can evaluate, adopting the semiclassical model, the quasi-particle velocities,
$v_k^*$, characteristic of particular orbits on the Fermi surface. If the extremal areas of the
FS are taken to be approximately circular with radius $k_r$ one obtains,

$$v_k^* = \frac{\hbar k_r}{m^*}, \text{ where } \pi k_r^2 = \frac{2 \pi e F}{\hbar c}.$$

For example, one can evaluate eqn. 2.64 for one of the several frequencies and
associated cyclotron masses [$F=2 \times 10^7$ Gauss, $m^*/m_e=80$] measured for CeCu$_6$ by
Chapman et al (1990) to obtain a velocity of $3.6 \times 10^5$ cm/s which is more than two
orders of magnitude smaller than the typical Fermi velocities in normal metals. It can
also be shown [Reinders et al (1987)] that the Fermi velocities in this range are
consistent with the values derived from the large electronic specific heat coefficient
measured in the heavy-fermion regime. The heavy-electrons behave, therefore, as if
they were slow electrons.

If these are the figures derived from magnetic experiments what should be expected
from positron annihilation experiments? Two interesting questions are i) how the
decrease in the discontinuity at the Fermi momentum due to the remarkable $e^-e^-$
correlation present in HF systems could be compensated by the effect of $e^+e^-$
correlation; ii) how the finite temperature effects might affect the enhancement
factors which consider the correlations.

As, up to now, there are no theoretical predictions one should look first at the
experiments which have been performed. The positron annihilation literature is
certainly not rich in this area. To date, only two experiments have been performed
above and below the HF critical temperatures and not on systems which display a
dramatic increase in the $C/T$ coefficient. Materials examined were CeSb by Itoh et al
(1993) and URu$_2$Si$_2$ by Rozing et al (1991). In both cases no differences, within the
limit of the experimental resolution, have been observed. Whether these findings are
due to the inability of the positron to monitor the heavy-quasi particles interesting
features$^{35}$ or to the fact that the dHvA description of heavy and slow quasi particles is

---

$^{34}$ defined as the inverse of the average velocity component $v_\perp$ along the cyclotron orbit, $n_{\perp} = \frac{\hbar}{2\pi} \int_{v_k^*}^\infty \frac{dk}{v_\perp}$.

$^{35}$ Naively, if the momentum $p$, causing the deflection angle, $\theta$, of the annihilation $\gamma$ rays can be
described as $p = m^* v_k^*$, (where the effective mass $m^*$ is high and the semiclassic velocity $v_k^*$ is small),
$p$ would still be within the range of the normal momenta measured in solids.
too much affected by the application of the semiclassical model, is unknown. It would clearly be useful if theorists took a closer interest into this intriguing problem.
3 Experimental set-ups for positron spectroscopy

3.1 Experimental techniques for bulk studies

The three conventional techniques which use positrons to probe the bulk properties of solids are angular correlation (ACAR), Doppler broadening and positron lifetime spectroscopy. Before describing in detail the 2D-ACAR system which was set up to perform the measurements reported in this survey, it is worth briefly mentioning the other two experimental techniques and their main field of application.

3.1.1 Lifetime

As described in chapter 2, the positron lifetime experiment is a useful tool in testing predictions of electron-positron many-body calculations.

Another application of lifetime experiments, which might appear to be diametrically opposite, concerns the study of defects in imperfect solids. This field has probably received the most attention from the positron community in terms of number of experiments performed. Positron lifetime is ideal for studies of any kind of open-space defect (like vacancies, multi vacancies, void and dislocations)\(^1\). Owing to the positive charge of the positron, any defect characterised by a lack of a positive ion is attractive to the positrons and is a possible positron trap.

An order of magnitude of the sensitivity of the positron to defects can be obtained by estimating the diffusion length, \(L\), (Nieminen,1993),

\[
L = \left(6D_+ \tau\right)^{1/2} \approx (1000 - 2000) \text{Å},
\]

where \(\tau\) is the positron lifetime and \(D\) is the diffusion coefficient defined by the Einstein relation,

\[
D_+ = \frac{k_B T}{m^*} \frac{1}{\langle \tilde{n}(E) \rangle}.
\]

Here \(m^*\) is the effective mass of the positron and \(\langle \tilde{n}(E) \rangle\) is the phonon scattering rate at the energy \(E\) averaged over the phonon Bose-Einstein distribution.

Typically \(D_+ = 0.1-2\) cm\(^2\) s\(^{-1}\) at room temperature. An order of magnitude of the volume sampled by the positron during its diffusion is obtained by multiplying the diffusion length \(L\) by the square of the positron thermal wavelength \(\lambda\),

\(^1\)Or studies of any change in the electron density, as during a volume expansion.
A typical volume sampled by the positron at room temperature is therefore within the order of $10^6 \text{Å}^3$. Under the assumption that a positron is trapped when its distance from the defect is within the thermal length, the sensitivity of the positron to defects can be estimated to one part per million (1ppm).

As the electronic density and particularly the core electron density will be reduced around an open-space defect, the annihilation rate will decrease.

The basic requirement for measuring the positron lifetime is a signal characterising the time of injection of the positron into the sample, the death signal being provided by the detection of the annihilation $\gamma$ ray.

A convenient natural clock is provided by the $\beta$ decay of $^{22}\text{Na}$ into $^{22}\text{Ne}$. This decay is followed by the emission of a 1275 keV $\gamma$ ray with a characteristic lifetime of a few psec [Lederer et al (1978)]. The difference in energy between the start (1275 keV) and the stop (511 keV) signals can be easily detected with slow or fast energy.

\[ \lambda = \frac{h}{p} = \frac{h}{\sqrt{3m*}kT} \approx 50\sqrt{300 / T(K)} \text{Å}. \]

---

2 The mechanism of trapping has been investigated thoroughly by several authors (Hodges 1970, Brand 1974, Dupasquier et al 1993, Puska and Nieminen 1994) and will not be discussed here.

3 The positron is emitted every 0.9 decays, the remainder of the process proceeding via electron capture.
discriminators. The positron source is usually deposited between two thin metal or plastic foils (∼1 mg cm⁻²) and then sandwiched by two identical specimens (at least 0.1-0.2 mm thick). A block scheme of the experiment is shown in figure 3.1.

As the features of the γ ray detectors used in a lifetime experiment are the same as those of the detectors used in our experimental ACAR set-up, they will be described in some detail.

They consist of a scintillator optically coupled to a photomultiplier tube (PMT). The purpose of the scintillator is to convert the γ radiation into visible or ultra-violet (UV) light. The process is in two steps: at first the energy of the radiation is transferred to an electron via photoelectric effect or Compton scattering. The electron then excites optical (or UV) levels of a large number (10³-10⁴) of atoms, which decay with the emission of light. Most scintillators used in up-to-date spectrometers are the plastic and the recent fast BaF₂ type. Owing to their low density, plastic scintillators exhibit a low efficiency and a poor energy resolution but good timing resolution. BaF₂ scintillators have much higher efficiency and even better timing resolution but can show the inconvenience of a possible pile-up of start and stop pulses in the same (start) scintillator.

When the optical (or UV) photons reach the photocathode of the PMT, photoelectrons are emitted and amplified along a chain of dynodes via secondary emission. If the timing resolution of the detection system were infinitely good, one should be able to observe at the final stage of the PMT (anode) a series of spikes of equal height (each due to a single photon) and proportional in number to the energy of the detected radiation. Owing to the resolution of the scintillator and the PMT the result consists of a cumulative pulse whose height is proportional to the energy of the γ ray. The proportionality constant is dependent on the light yield of the scintillator and on the number of photoelectrons per incoming photon which are produced at the photocathode (quantum efficiency) [Moszynski et al (1979), Knoll (1979)].

The (digital) strobes adopted for the timing must be provided by a device that triggers when the analogue anode pulse is within the energy window selected to discriminate between the start (1275 keV) or stop (511 keV) γ rays. Several attempts were made in the past to implement triggering devices independent of the height of the pulses. The time required for nuclear pulses to break the triggering threshold is, in fact, function of their amplitude. As shown in figure 3.3 γ rays of different energies

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4 As the cross section for the photoelectric effect is practically zero the only effective detection channel is Compton scattering.

5 Due to high efficiency of the BaF₂ scintillator, there are chances that one start and the correlated stop γ rays interact in succession with the crystal via Compton scattering. If the two Compton electrons generate an overall pulse with amplitude within the selected energy window, this pulse will be accepted as a valid start event but will carry anomalous timing information.
are triggered at different times (time walk problem) and this effect significantly degrades the timing resolution of the spectrometer. To override this walk problem the technique of the constant fraction timing splits the input pulse into two parts (see figure 3.2).

One part is delayed and inverted and the other is attenuated. With this method the zero crossing time is ideally independent of the height of the pulse.

Modern constant fraction discriminators (CFD) have a dual purpose of supplying a triggering signal (timing) for pulses whose height is within the windows required (energy discrimination). The art of supplying "recipes" for a good timing resolution in lifetime spectrometers has involved several groups in the last decades and will not be described here (see for example De Vries 1987).

The "fast NIM" pulses generated by the CFDs are sent to the time to amplitude converter (TPHC) which provides an analogue pulse whose intensity is proportional to the time interval between the start and stop digital pulses. The TPHC analogue output is finally converted to digital output (by an ADC) and stored according to height by a multichannel analyser (MCA) which collects the distribution of the measured time intervals. If positrons annihilate from different states in the sample the result is a sum of exponential spectra (convoluted with the experimental resolution) which can be analysed by fitting procedures [Kirkegaard and Eldrup (1981)]. Anyone who has tried to analyse positron lifetime spectra will be aware of the difficulty of extracting reliable results when several exponential (to be fitted) are present in the spectra. In Bologna we performed our studies on precipitation phenomena on Aluminium alloys (Abis et al 1989-92) by routinely performing the lifetime...
experiments on the same sample with two spectrometers and monitoring the scatter in the results. The two set-ups utilise plastic and BaF$_2$ scintillators respectively$^6$.

### 3.1.2 Doppler broadening

As mentioned in chapter 2, the energy analysis of the annihilation $\gamma$ rays enables one to obtain information on the component of the momentum of the electron-positron pair along the direction of the photon emission axis. In principle, one could perform a very accurate energy analysis with a spectrometer adopting the method of crystal diffraction. However, this technique is not used, as, owing to the low efficiency of such spectrometers, a very intense (and expensive) positron source is needed.

In practice, Doppler spectrometry is performed with intrinsic Ge detectors connected via a preamplifier to a spectroscopy amplifier and then to the ADC. The energy resolution attained by such a system is in the range 1.0-1.4 keV at the 511 keV energy$^7$. As pointed out in § 2.3, this resolution is comparable to the signals originated from annihilations of electrons in conduction bands. For this reason, the use of the Doppler broadening (DB) technique has often been devoted to complement lifetime experiments in defect studies$^8$. The fact that the DB experiment does not require any coincidence system as opposed to the lifetime (start-stop $\gamma$-rays delayed coincidence) and ACAR (annihilation $\gamma$-rays coincidence) experiments allows a rapid accumulation of data with very small sources (20 minutes to acquire a spectrum of $\sim 10^6$ counts with 3.7$\times 10^5$ Bq of $^{22}$Na source). Owing to the inferior resolution, good stability of the system is very important to monitor the small variations of the measurable parameters involved in the study of bulk defects. In Bologna we improved the quality of the data by performing the experiments in a purpose-built thermostated box. Moreover, we reduced the background due to the Compton shoulder of the 1275 keV $\gamma$ ray emitted by the $^{22}$Na source by setting a 511-511 keV $\gamma$-rays timing coincidence between the Ge detector and a 3"$\times$3" NaI crystal scintillators. At the expense of a very modest loss of data caused by the coincidence system (75% of efficiency with respect to the un-gated count-rate) we reduced the background by a factor of 12 at the right and 7 at the left of the photopeak of the

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$^6$ In the case of BaF$_2$ spectrometers we have adopted the well known 90° geometry of the detectors to reduce the probability of a start signal affected by the pile-up of a 1275 keV and 511 keV $\gamma$ rays (see previous footnote) when the (anticollinear) stop is a proper 511 keV $\gamma$ ray.

$^7$ A semiconductor radiation detector is essentially a diode (p-n junction) working in reverse bias. The width of the depletion region represents the active volume of the detector.

$^8$ An "open space" defect, like a vacancy or a void, affects the electron-positron momentum distribution, $\rho(p)$, principally with two reinforcing effects: i) the absence of the crystal ionic centre (nucleus plus core electrons) eliminates the contribution to $\rho(p)$ from the fast electrons of the closed shells. ii) the lack of the ionic periodic crystal potential in open space defects eliminates the HMC of the momentum distribution of the weakly bound electrons. The resulting momentum distribution is therefore strongly enhanced at low momenta.
annihilation $\gamma$ ray. Spectra were finally digitally stabilised to correct for gain instabilities. The quality of the data (Abis et al 1989-92) was greatly improved by these adjustments.

3.2 Angular Correlation set-up

3.2.1 1D-ACAR

Almost 40 years passed since Berko and Plaskett (1958) reported their angular correlation studies in oriented single crystals of Al and Cu. Their paper was a combination of careful theoretical predictions and cautious experiments. The 1D-ACAR technique was adopted to measure the anisotropies of the (2D integrated) momentum distribution along different crystal directions. Since then, because of the 1D-ACAR double integration which obscures much of the details of the 3D momentum distribution, 1D-ACAR FS studies on complex metals relied mostly on measuring differences between projections along high symmetry axes. A real understanding of the nature of these anisotropies often required a great deal of theoretical analyses. This is why the 1D-ACAR experiment was considered, according to the well known fermiologist Cracknell (1973) "....as one of the indirect methods of Fermiology...".

A block scheme of the experiment is shown in figure 3.4. The detectors usually consist of long, cylindrical shaped NaI(Tl) scintillators (coupled to PMT), behind collimating slits which define the resolution of the apparatus. The integration directions consist of the direction parallel to the main axis of the spectrometer, $p_z$, and the direction parallel to the slits, $p_y$. The angle subtended by the slit is selected to be much bigger than the angular distribution in that direction (usually $\approx 100$ mrad). One detector is fixed and the other mounted on a rotating arm stepped automatically for measuring the coincidence count rate as a function of the angle $\theta$.

![Fig. 3.4 Geometry of the 1D-ACAR experiment. The detectors, D, are behind collimating slits. The slit long axis ($p_y$) is normal to the plane of the figure.](image)

When measuring oriented single crystals the crystal is positioned with the direction (say <100>) to be measured parallel to the x direction of the spectrometer. As usual,
the small angle approximation allows one to identify the momentum \( p_T \), which originates the deflection \( \theta \), with its projection on the x direction, \( p_x \), as

\[
p_x = p_T \cos \frac{\theta}{2} = 2m_0c\sin \frac{\theta}{2} \cos \frac{\theta}{2} = m_0c\sin \theta \approx m_0c \theta
\]

The ancillary equipment is similar to that of a 2D-ACAR set-up and will be described when discussing the Bristol apparatus.

1D-ACAR spectra have to be corrected due to the non-infinite length of the slit aperture [(Mijnarends (1969)]. The finite size causes a slight distortion in the spectra and underestimates the broad components at the expense of narrow components of the momentum distribution. This happens because as \( \theta_x \) increases, the range of the momentum distribution in the direction parallel to the slit (y), \( \Theta_y(\theta_x) \), decreases\(^9\). Therefore, as the slit has finite sizes, the ratio between the range \( \Theta_y(\theta_x) \) and the angle covered by the slit, \( \Omega_{\text{slit}} \), is function of the angle \( \theta_x \). The long slit approximation of the integration domain to infinity is then stronger at \( p_x = \theta_x m_0c = 0 \), where \( \Theta_y \) is at a maximum (for an isotropic distribution).

### 3.2.2 2D-ACAR

The 2D-ACAR experiment, by reducing the number of integrations to one, gained a much greater sensitivity to the functional dependence of the momentum density and the FS topology and received more attention from the scientific community. The geometry of a generic 2D-ACAR set-up is shown in figure 3.5

\(^9\)for a spherical distribution with a cut-off at \( p_{c.o.} \), the range of the distribution parallel to the direction of the slit \( \Theta_y(\theta_x) \) decreases according to \( \Theta_y(\theta_x) \approx \left( \theta_x^2 \left( \theta_x m_0c \right)^2 \right)^{1/2} \).
The angle is obtained by summing the corresponding spatial coordinates on the CAM1 and CAM2 detectors and dividing by the distance $L$. The momenta $p_x$ and $p_y$ are obtained, within the usual small angle approximation, as

$$
\begin{align*}
    p_x &= (j + l) \frac{m_0 c}{L} \\
    p_y &= (m + i) \frac{m_0 c}{L}
\end{align*}
$$

where $j$ and $l$ are the $x$ coordinates of the first and second detector, respectively, and $m$ and $i$ are the corresponding $y$ coordinates.

### 3.2.3 Discrete Detectors

The first to implement a 2D machine for real measurements (and not just for demonstration studies) was Berko (1977) at Brandeis University (Boston). His spectrometer consisted of two multiple detector arrays. Each detector comprised 32 3.8 cm diameter by 5 cm long NaI(Tl) scintillators coupled to PMT. Lead shielding was used to reduce inter-detector Compton scattering and to limit the aperture of each scintillator to 15 mm diameter. The advantage of a discrete detector is that the collimating apertures provide a clear-cut definition of the angular resolution. The main disadvantage of the Brandeis spectrometer consisted of the discrete field of view: stepping motors had to be used to translate one detector (the other remaining fixed) in order to span the whole angular distribution. However, until recently, the spectrometer was still being used and, owing to its good design and quality of construction, providing data of quality not inferior to the more modern position sensitive detectors which were then being used in the field. Among other discrete detectors spectrometers it is worth remembering the 256 BGO ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$) crystal scintillators-photomultipliers-amplifiers system set up at Tsukuba by Tanigawa et al (1985,1993).

### 3.2.4 Proportional Chambers

There is little doubt that the high density proportional chambers (HDPC) in use in Geneva [Bisson et al (1982)] are the best performing 2D-ACAR system. As the counting efficiency of proportional counters at the energies of the annihilation $\gamma$ rays is very small, Geneva HDPC were designed with a lead-glass $\gamma$ to electron converter proposed by Jeavons (1978). The HDPH at Geneva attain the best spatial resolution of the position sensitive detectors (PSD) currently used in 2D-ACAR studies (1-1.5 mm) and an efficiency of the same degree of PSD which adopt scintillators. The drawbacks are a lack of energy resolution and a timing resolution (in the coincidence for $\gamma$ ray selection) of 100-300 nsec compared to the 60 nsec of the Bristol set-up. The
complexity of this system and its non-availability on the market have prevented many potential "annihilators" from using it, as yet.

### 3.3 Anger Cameras detectors

Gamma-ray (Anger) cameras were introduced in 2D-ACAR experiments by West (1980) at University of East Anglia. These devices have been used in the field of medical imaging [Anger (1958)] and upgraded during the course of almost 40 years to reach excellent stability, good resolution and reliable imaging.

The detectors which performed the experiments described in this survey were purchased by ENEA from General Electric in 1991. Paolo Bartolomei and the author carried out the initial testing of the Anger cameras. The design, realisation and initial testing of the 2D-ACAR set-up (timing coincidence, construction of the angular signal, storage and representation of the data) is the result of the collaboration of the author with Sandro Taiocchi. Additional suggestions came from Piero Sferlazzo, Allen Mills and Kelvin Lynn from Brookhaven National Laboratory (BNL) during visits to the BNL 2D-ACAR set-up. Credit is also due to Stephan Berko, Richard Lee (from Brandeis University) and Richard Howell (from Livermore Laboratory).

The detectors (see figure 3.6) consist essentially of a large crystal scintillator optically coupled to an assembly of PMT. As a $\gamma$ ray of given energy will yield a constant number of photons in the scintillator (neglecting border effects), each PMT will sample a fraction of photons depending on the proximity of the tube in question to the point of interaction of that $\gamma$ ray with the crystal.

In principle, three PMTs would be sufficient, in a planar geometry, to determine the baricenter of the interaction. In practice a much higher number of PMTs is used to improve the spatial resolution. The Bologna Anger Cameras Starport 400 AC 12.5 consist of a 42 cm diameter, 1.25 cm thick thallium-activated sodium iodide, NaI(Tl), crystal scintillator, optically coupled to a close-packed honeycomb array of 61 PMTs.

#### 3.3.1 Resistor network

Each anode is connected through a resistor to a common four-line bus (see table 3.1).

<table>
<thead>
<tr>
<th>Tube n°</th>
<th>$R_{x+}$</th>
<th>$R_{x-}$</th>
<th>$R_{y+}$</th>
<th>$R_{y-}$</th>
<th>$R_{\text{parallel}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>$R_1$</td>
<td>$R_2$</td>
<td>$R_3$</td>
<td>$R_4$</td>
<td>$R$</td>
</tr>
<tr>
<td>i+1</td>
<td>$R_5$</td>
<td>$R_6$</td>
<td>$R_7$</td>
<td>$R_8$</td>
<td>$R$</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>$R$</td>
</tr>
</tbody>
</table>

*Tab 3.1 Flow chart of the resistor network.*
The resistors are organised to give a linear correlation between the current through the resistor and the position. The total energy is obtained by summing in parallel the signals of four lines $x^+, x^-, y^+, y^-$. As the parallel resistance of the four lines is the same for each PMT, the energy output is independent of the position of the detection. The energy signal enables the event to be stored and displayed in the form of a 2D $(x,y)$ histogram. This enable signal is generated when the energy of the event is within an energy window selected by the user. That window usually corresponds to the photopeak of the $\gamma$ ray selected (in our case the 511 keV annihilation $\gamma$ ray).

Because the light output from the crystal is proportional to the $\gamma$ ray energy, the output pulses $x^+, x^-, y^+, y^-$ increase for different $\gamma$ ray energies, causing a shift of the displayed image. Obviously the position of the event must not shift with the $\gamma$ ray energy. The final positional signals $x$ and $y$ are therefore obtained by taking the differences $x^+ - x^-$ and $y^+ - y^-$ via two differential amplifiers. With this technique one can also control parameters such as size and offset of the image.

As can be seen in figure 3.7, the resistance $R$ controls the size of the image and the difference $R_{2+} - R_2$ controls an offset in the output $x$ co-ordinate$^{10}$.

---

$^{10}$ If $R$ is reduced to 0 the size is reduced to 0 as $x^+$ and $x^-$ are shorted. If $R_{2+}$ is increased by $\Delta$, the $x^+$ pulse will increase with respect to ground by an amount $\Delta x$; $x^-$ is correspondingly reduced by $\Delta x$ and the difference $x^+ - x^-$ is changed by the constant offset $2\Delta x$. 
Several corrections are built into the detectors to reduce non-uniformity which, in the case of medical imaging, may assume dramatic importance. Two important devices are built in the detector head:

### 3.3.2 Hardware corrections

1) **PMT Autotune**

Each PMT is furnished with an Automatic Control Gain that compensates for PMT gain changes.

A drift in the gain of a PMT (as shown in figure 3.8) is a typical cause of non-uniformity in the single camera response as it alters the response of that PMT in the energy window selected to build the image. In the Starport 400 AC the gain stabilisation is accomplished with a reference LED (light emitting diode) built into each PMT which is turned on for 1 to 5 µsec every 1 millisecond. The response from the PMT on the constant LED flashes are sampled and compared to a reference gain setting (gain potentiometer). If the PMT response does not correspond to the gain setting, the voltage between two dynodes in the PMT is automatically adjusted (Autotune) until the gain reaches the preset value. Note that this preset value is independent (within the possible limits) of the PMT high voltage (HV) as the (negative) HV is common to all the phototubes. Each LED is connected in series with a temperature-dependent device in order to yield a temperature-independent LED light output.

2) **Correction due to the finite size of the PMT**

Pulses generated by γ rays which hit the centre of the PMTs have higher intensity than those coming from γs which hit the boundaries in between the tubes. A dynamic linearity circuit compensates for this problem.

### 3.3.3 Software corrections

After the four spatial lines $x^+$, $x^-$, $y^+$, $y^−$ are sent from the detector head to the computer console they are processed by several boards whose purpose is very briefly outlined below. The stream of data along the boards is controlled by the traditional hand-shake: data are announced by a DATA READY going low. Data taken are announced by a DATA ACCEPTED (RD) going high, which, in turn, resets the DATA READY.

1) **ADC : Analogue control board**

Its main function consists in performing a filtering of signal levels and pile up events.

2) **DAD : Analogue A/D board**

The analogue signals are converted to digital by this board. The four $x^+$ $x^-$ $y^+$ $y^−$ lines are first converted into bipolar signals, $x$ and $y$, by two op-amps operating as differential amplifiers, and then passed to the 12 bit A/D converter. The energy signal
is obtained by adding in parallel the four $x^+ x^- y^+ y^-$ lines and passing them to the A/D converter.

3) CORR The correction board

In this board the digital pulses are corrected via look-up tables whose purpose is to reduce artefacts due to non-uniformity in the efficiency of the detector and to distortion in the spatial linearity.

i) Spatial linearity correction: The corrections to the distortion of the image is realised by setting an acquisition with a uniform grid (phantom) parallel to the x direction of the detector. The spectrum obtained is analysed and compared to the ideal grid. The procedure is then repeated by rotating the grid by $90^\circ$ to correct the distortions in the y direction. Corrections for each (x, y) pixel are then calculated and stored in the form of look-up tables which are applied to subsequent acquisitions.

ii) Energy correction: The correction to local variations in the efficiency is obtained by acquiring a dual image: one image is generated by the events at position (x,y) whose energies lie in the lower energy window selected ($E^-$ in figure 3.8) and the other one for all the events with energy in the upper energy window set ($E^+$ in figure 3.8). For pixels (x,y) generated by well-tuned PMT the two images would have same intensity. If however, in some part of the detector the gain of the PMTs is such that the energy baricenter of the $\gamma$ ray in question is in the lower (or upper) position with respect to the overall energy signal generated by the totality of the PMTs, the lower (upper) image will be enhanced. The look-up tables are generated by producing corrections per each (x, y) pixel which enhance or de-enhance its intensity. As the algorithm is approximate, the corrections are generated by iterating till the deviations between the dual images are reduced to acceptable levels. The positional variations in the efficiency depend on the energy and the corrections must therefore be generated for each $\gamma$ ray used for the imaging.

4) DT The discrimination and termination board

This board selects $\gamma$ rays utilised to build the image according to the energy window set. Moreover, the DT board stops the acquisition after a preset time or total integral count is attained.

Fig. 3.8 Upper: Before the correction; Lower: after the software compensation.
5) FO The framing and offset board

This board performs ancillary reorganisation of the data which is not required in the 2D-ACAR set-up.

In operation, for optical performances (mainly to reduce border effects), the effective area of detection is reduced electronically to a fraction of the total active area of the detector. For example, for a binning of 256×256 channels the Image Circle Radius (ICR) is kept to 120 channels.

3.4 2D-ACAR electronics

The digital positional signals utilised to build the angular signals are retrieved from the Starport DT board (Lee 1990). The pulses consist of 10 bits for x and y direction respectively in a 1024×1024 channels matrix. The DATA READY from the DT board causes the storage of the digital (x,y) signals in external interface boxes at a close distance (30 cm) from the Starport console. After the data are stored in the interfaces there is no interaction between the Starport and the external processing unit. In one of the interface boxes (B=2) the x coordinate is reversed. The inversion is due to the mirror geometry of the detectors which are positioned face to face. As it is shown in figure 3.5, with reference to the axes of one detector (say detector 1) the other is rotated of 180° about the y axis. To measure the angle we therefore sum \((x_1 + \bar{x}_2, y_1 + y_2)\).
Due to the data processing of the several boards, the time delay between the analogue energy pulse output of the first (ADC) board and the DATA READY (1 µsec wide) of the DT board is 9.5 µsec. The time jitter of the DATA READY with respect to the ADC analogue signal is ∼ 0.2 µsec for an energy window comprising only the photopeak (∼20% width). The jitter increases up to ∼ 2 µsec for a ∼40% wide window. To improve the performances the timing coincidence is performed on the analogue ADC energy signals.

Those signals are retrieved through a 4.7 KΩ resistor, in order not to disturb the stream of data in the Starport, and sent via the interface boxes to an external standard NIM amplifier-single channel analyser (SCA). The time jitter of the digital SCA output with respect to the analogue energy input is considerably smaller than that of the DATA READY: from 10 nsec for a 20% wide energy window up to 30-40 nsec for a ∼40% wide window. The SCA digital signals are then delayed via a chain of 6 monostables and each set in broad coincidence (1 µsec width) with the DT board DATA READY. This preliminary coincidence guarantees that the SCA signal is correlated to the (x,y) event of that DATA READY and not to other (x,y) events analysed by the Starport during the 9.5 µsec delay between the two pulses (see figure 3.9). The outputs of the two coincidences SCA - DATA READY (from camera 1 and camera 2) then feed the last (adjustable) coincidence which, in the positive case,
enables the storage cycle of the sums \((x_1+x_2, y_1+y_2)\)\(^{11}\). With this set-up the resolving time of the coincidence is \(\sim 2.4 \mu\text{sec}\).

The resolving time is reduced to 60 nsec with an optional narrow coincidence acting on the NIM SCA digital pulses. The consensus of the narrow coincidence gates the output of the second monostable used to delay the SCA pulses (point 2M in figure 3.9) and also has effect in single acquisition. In this way one can store \((x_i,y_i)\) pulses from one detector, say \(i\), gated by the detection of \(\gamma\) rays in the other detector. The SCA pulses accepted from the narrow coincidence then follow the stream of data described above.

To centre the timing coincidence more accurately Sandro Taiocchi designed an auto-centring coincidence device. Its basic idea is that the output count rate of the coincidence is constantly optimised by an up/down scaler connected to a digital-to-analogue converter (DAC) which adjusts the time length of a monostable inserted in the circuit. With this device one can keep a very narrow resolving time, thus reducing the amount of chance (accidental) coincidences, without worrying about loss of true coincidences due to time drifts in the coincidence system.

In more detail, the 2 SCA feed two monostables of \(\sim 0.6 \mu\text{sec}\), one of which has a time duration controlled by the DAC. If the monostable of fixed duration ends first the adjustable monostable will be shortened by one step (256 steps correspond to \(\pm 200\) nsec) and vice versa. The narrow coincidence operates at the the end of the two monostables and is made so that the termination of the first monostable opens a gate of 50 nsec during which the second monostable can enable the main coincidence circuit (point 2M in figure 3.9).

The sums \((x_1+x_2,y_1+y_2)\) are binned in a matrix whose finest mesh is \(2048 \times 2048\) channels. The data can then be compressed and biased as required.

### 3.5 Functional checks

Several functional checks were performed to test the quality factors of the single detectors and of the coincidence system.

The overall quality factors of the two detectors, as measured by GE company, are listed in table 3.2. The parameters listed in tab 3.2 are obtained by measuring the response of the detectors to a grid of known spacing. In particular, the definition of intrinsic differential and absolute linearity are as follows:

---

\(^{11}\) The storage is according the "add one" criterion, which means that the intensity at the \((x_1+x_2, y_1+y_2)\) address is substituted by the intensity incremented by one, after the new event.
Differential linearity - is the standard deviation of the deviation of the position of the peaks corresponding to the pixels not shadowed by the grid with respect to the ideal grid pattern.

Absolute linearity - is expressed as the maximum amount of spatial displacement of the observed peaks from the ideal pattern.

<table>
<thead>
<tr>
<th>Performance</th>
<th>Camera 1</th>
<th>Camera 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic Spatial resolution (FWHM) at 140 keV</td>
<td>3.7 mm</td>
<td>3.9 mm</td>
</tr>
<tr>
<td>Intrinsic Energy resolution (FWHM) at 140 keV</td>
<td>11.1%</td>
<td>11.0%</td>
</tr>
<tr>
<td>Intrinsic Differential Linearity</td>
<td>0.1 mm</td>
<td>0.1 mm</td>
</tr>
<tr>
<td>Intrinsic Absolute Linearity</td>
<td>0.6 mm</td>
<td>0.6 mm</td>
</tr>
</tbody>
</table>

*Tab 3.2 Nema Standard performance of the Starport 400 AC 12.5 GE*

1) Evaluation of the local spatial resolution at 511 keV

As the spatial resolution may show an energy dependence, it was important to verify the results of tab 3.2 (at energy of 140 keV) at the energy of the 511 keV γ rays. This was achieved by placing in front of one detector a 3.7 $10^5$ Bq $^{22}$Na test source behind a 5 cm thick lead brick with a 2.6 mm diameter through-hole. To eliminate the contribution from the 1275 keV γ ray (and background radiation) only event outputs which were in timing coincidence with 511 keV pulses detected in the second detector contributed to the image (see figure 3.10). The measurement was repeated for different positions of the lead brick. This method was applied to measure the spatial resolution of both detectors. The peak in the region corresponding to the hole could be fitted by two well resolved Gaussians; the broader one (20% intensity) was ascribed to γ rays not properly collimated by the lead hole. The narrow Gaussian gave for both detectors a FWHM of less than 3 mm after the subtraction in quadrature of the 2.6 mm hole. This confirmed the well-known result that at higher energy the spatial resolution improves as the number of photons produced per each detection event is higher and the statistical fluctuations decrease. However, due to the complexity of the system (designed to work at average energies from 100 to 300 keV) the improvement in the resolution was lower than what expected on the basis of pure energy considerations. Local variations in the fitted FWHM of the peaks were within the statistical errors.
2) Absolute efficiency at 511 keV

The efficiency of the single detectors was evaluated by positioning a positron source of known intensity at 88 cm from the centre of the detectors. $^{68}$Ge emits 0.9 positrons per decay and has a half life of 287 days. The activity of the source was

$$S = S_0 \cdot 2^{-666/287} = 0.74 \times 10^6 \text{ Bq},$$

where 666 is the age of the source (in days) at the day of the measurement. If $d$ is the distance source-detector and $r$ the radius of the detector (nominal 20 cm), the solid angle fraction subtended is

$$\frac{\Omega}{4\pi} = \frac{2\pi}{4\pi} \left(1 - \frac{d}{\sqrt{d^2 + r^2}}\right) = 0.0123.$$

The count rate measured can be expressed as

$$C_{\text{rate}} = \frac{\Omega}{4\pi} \times \epsilon_{0.511} \times S \times Y,$$

where $\epsilon_{0.511}$ is the absolute efficiency at the photopeak and $Y=2 \times 0.9$ is the yield of annihilation $\gamma$ rays per disintegration. From eqn 3.7, the efficiencies obtained were $\epsilon_{0.511} = 12.8\%$, $\epsilon_{0.511} = 12.4\%$ for camera 1 and camera 2 respectively and within the normal expectation values for NaI(Tl) crystals of this thickness.

The estimate of the efficiency was confirmed by measuring the count rate in coincidence, $C_{\text{coinc}}$. The positron source was positioned on the axis joining the centres of the detectors as shown in figure 3.5 at the same distance from the detectors. At small distances (say 80 cm) the typical angular deviations from anticollinearity of the annihilation $\gamma$ rays (say 10 millirad) are comparable with the angular resolution. Therefore, the $\gamma$ rays can be approximated as anticollinear. The coincidence count rate is then, from eqn 3.7,

$$C_{\text{coinc}} = \epsilon_1 \epsilon_2 \frac{\Omega}{4\pi} S Y.$$

Therefore $\frac{C_{\text{coinc}}}{C_1} = \epsilon_2$, where $C_1$ is the count rate of the detector whose efficiency is not being measured.
However, as the angular distribution introduces a small deviation from the anticollinearity, it is possible for some $\gamma$ ray pair to hit detector 1 and to miss detector 2. A more precise estimate of the efficiency in coincidence is therefore obtained by restricting electronically the radius of the detector whose efficiency is measured. With this method every time a $\gamma$ ray hits the detector with the smaller radius selected, the other (correlated) $\gamma$ ray will definitely hit the opposite detector (see figure 3.11). Therefore, in this case

\[ C_{\text{coinc}} = \varepsilon_1 \varepsilon_2 \frac{\Omega(r_1)}{4\pi} SY, \]  

and

\[ C_2 = \varepsilon_2 \frac{\Omega(r_2)}{4\pi} SY, \]

where $\Omega(r_i)$ is expressed by eqn 3.6. The ratio $r_2/r_1$ was set at 1.5.

Therefore, one obtains

\[ \frac{C_{\text{coinc}}}{C_2} = \frac{\varepsilon_1 \varepsilon_2 \Omega(r_1)}{\varepsilon_2 \Omega(r_2)}. \]  

3.9

The efficiencies measured with the coincidence method do not suffer from uncertainties in the estimate of the source activity. The absolute efficiencies at the photopeak measured amount to 12.5% and 12.6% for camera 1 and camera 2 respectively, in good agreement with those measured in single mode.

3) Spatial calibration

As mentioned above, a uniform single-camera response is more important for medical imaging than in the 2D-ACAR experiment. In the latter case in fact, the angles obtained ($\theta_x, \theta_y$) are contributed by the several pairs $(j,i)$ from the 2 detectors ($x_1^j + x_2^j, y_1^j + y_2^j$) which add up to give the same sums (see eqn 3.5). This means that local variations in one detector due to regional crystal or PMT deficiencies will be averaged by summing them with those (uncorrelated) from the other detector.

There is however one single detector parameter which is very important in yielding a good angular resolution: if the detectors are positioned at the same distance from the sample, the spatial calibration (mm/channel) must be identical. Conversely, a
single angle, $\theta$, will originate a distribution of responses in the spectrometer. This can be seen easily for $\theta=0$ in a one dimensional position sensitive detector pair.

Let us assume that the calibrations are $C_1$ and $C_2$ mm/chann. Depending on the direction of the photon axis, the response of the spectrometer (in number of channels) will vary from $2L/C_1$ to $2L/C_2$, where $2L$ is the size of the linear detector. (see figure 3.12)

The maximum spread in the response is for $\theta=0$, when all the $N$ detectors' channels contribute to that angle i.e. $(0,N-1), (1,N-2),\ldots,(N-1,0)$. The response of the spectrometer to an angular distribution $f(\theta) = \delta(\theta)$ is therefore the rectangular distribution (cylindrical for 2D circular detectors) shown in figure 3.13.

The functional test LINCOR attains the same standard spatial calibration for all the Starport detectors. Two point sources are positioned on selected calibration marks on the detector and the size and offset (described in figure 3.7) are adjusted till the spots corresponding to the two sources fulfil the requirements of the test.

The spatial calibration was then measured by positioning the GE phantom designed for the Spatial Linearity Correction along the x and subsequently along the y directions of the detector. One way to obtain an average spatial calibration is to fit the positions of the peaks corresponding to the pixels not shadowed by the phantom grids (having a spacing of 6.5 mm). The average distance in channels between neighbour peaks can then yield an average calibration.

Moreover, the author designed a faster and more accurate method (since adopted at Brandeis University and Brookhaven National Laboratory) which consists of applying a Cosine-Fourier-Transform (CFT) to the data and finding the maximum in the frequency domain. By knowing the grid spacing one can then obtain the overall spatial calibration.

As one knows the approximate periodicity, the program finds the frequency corresponding to the maximum via successive approximations. A rough estimate of
the maximising frequency is first obtained and then computed more precisely with finer and finer mesh (in the frequency region of interest) varying simultaneously the phase which attains the maximum of the CFT. By changing the spatial integration domain and checking the differences in the periodicity obtained one can assess the uncertainty due to the discrete sampling. Tab 3.3 shows the results of the CFT method for a binning corresponding to a matrix of $256 \times 256$ channels.

<table>
<thead>
<tr>
<th>Detector</th>
<th>direction</th>
<th>calibration mm/channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>camera 1</td>
<td>x</td>
<td>1.600±0.001</td>
</tr>
<tr>
<td>camera 1</td>
<td>y</td>
<td>1.598±0.001</td>
</tr>
<tr>
<td>camera 2</td>
<td>x</td>
<td>1.598±0.001</td>
</tr>
<tr>
<td>camera 2</td>
<td>y</td>
<td>1.599±0.001</td>
</tr>
</tbody>
</table>

*Tab 3.3 Spatial calibration of the two detectors at the energy of 140 keV, corresponding to the energy of the radioisotope $^{99}$Tc*

The four calibrations were therefore found to be identical, within the estimated error. The calibrations shown in Tab 3.3 were determined at the energy of 140 keV, corresponding to the energy of the radioisotope ($^{99}$Tc) most commonly used for medical imaging. As the half thickness of the $\gamma$ ray in lead at 140 keV (0.35 mm; Wapstra 1959) is less than 10 times smaller than that at 511 keV, the GE phantom could not be used with the 511 keV source in use in the 2D-ACAR experiment. The calibration at 511 keV could be evaluated with another method (which will be described later) only along the x direction and was found to be close to that shown in Tab 3.3.

4) Measurement of the resolving time

To measure the resolving time, two sources shielded from each other are positioned in front of the detectors. The rate of the accidental coincidences, $C_{\text{chance}}$, depends on the resolving time, $2\tau$, through the well known relation (Knoll, 1979)

$$2\tau = \frac{C_{\text{chance}}}{C_1 C_2},$$ 3.10

where $C_1$ and $C_2$ are the detectors' single count rates. The resolving time $2\tau$ measured was 57 nsec, in agreement with what was expected from the design of the coincidence circuit.

---

12 The spread in the frequency corresponding to the period of the grid, obtained with this method is $\approx 1/10$ of the Nyquist frequency of the discrete sampling.

13 As the 511 keV $\gamma$ ray was very close to the cut-off of the detector in the high energy region, some deviation from an energy independent calibration could be expected.
It is interesting to look at the angular distribution of the accidental coincidences. It is shown in figure 3.14. The shape of the distribution is generated by the different number of effective detector pairs that contribute to the angular distribution (uniform for random coincidences) at a particular angle. The distribution, called Momentum Sampling Function (MSF), or tent function, (West, 1981) is a function of the planar geometry of the detectors, of their finite angular opening, and of variations in the local efficiencies.

![Fig. 3.14 The 2D angular distribution obtained by positioning two uncorrelated $^{22}$Na sources in front of the detectors.](image)

To obtain an expression of the MSF we give the same absolute orientation to the $D_1$ and $D_2$ detectors, as specified in figure 3.15.

Clearly, for a deflection angle $\theta_x$ an event at $x_1 + L \theta_x/2$ in detector 1 will be correlated with an event at $(-x_1 + L \theta_x/2)$ in detector 2 having a detection probability $\varepsilon_2(-x_1 + L \theta_x/2)$. An angular distribution $\rho(\theta_x, \theta_y)$ will cause a response in the spectrometer, $M(\theta_x, \theta_y)$, obtained by integrating over the detection area of one detector (say 1), the detection coordinate on the other detector being uniquely determined by the angular distribution in question.

$$M(\theta_x, \theta_y) = \int dx_1 \int dy_1 \left( \varepsilon_1(x_1 + L \theta_x/2, y_1 + L \theta_y/2) - \varepsilon_2(-x_1 + L \theta_x/2, -y_1 + L \theta_y/2) \rho(\theta_x, \theta_y) \right)$$

3.11
When the angular signal comes from two uncorrelated sources, as in figure 3.14, \( \rho(\theta_x, \theta_y) = \text{const.} \). The response of the spectrometer therefore reduces to the convolution of the single detectors images. For perfectly uniform circular cameras of radius \( r_c \) (\( \varepsilon_i \) constant), the MSF\((r)\) is simply the area overlap of the cameras' circles when the centres differ by \( r \).

In this case, by simple geometrical relations one obtains

\[
\text{MSF}(r) = \frac{1}{\pi r_c^2} \left( 2 r_c^2 \cos^{-1}\left( \frac{r}{2 r_c} \right) - r \sqrt{r_c^2 - \frac{r^2}{4}} \right).
\]

The shape of the ideal tent function obtained from circular detectors is shown in figure 3.16. Though the acquisition of a spectrum (such as that shown in figure 3.14) obtained via uncorrelated sources would provide a direct determination of the MSF, the method is in-practical and never performed for two reasons:

i) the low count rate of chance coincidences would require long acquisition times (many days).

ii) as the regional variations in the single detectors are combined with the self-absorption of the \( \gamma \) rays in the sample under study, the acquisition of a realistic tent function must reproduce the exact geometry of the experiment under interest, which would be impossible to realise with the two sources method.
In practice the MSF is obtained by taking the convolution of the single cameras' responses stored during the 2D-ACAR the acquisition.

3.6 Limits of the current 2D-ACAR set-ups

As described in §2.3, typical angular distributions in solid state physics are of the order of a few millirad. The resolution of the Anger Cameras is of the order of a few (3-5) mm. Ideally, the 2D-ACAR spatial resolution for a point source would be given by the convolution of the angular resolution functions of the single detectors (defined as the ratio between the spatial resolution and the distance sample-detector). Under the assumption of Gaussian resolution functions with FWHMs $\delta\theta_1$ and $\delta\theta_2$ the convolution reduces to a Gaussian whose FWHM is the sum in quadrature of $\delta\theta_1$ and $\delta\theta_2$. In practice this ideal is seldom achieved in PSD, where the measurement of a single angle is contributed by several detectors pairs. A realistic value of the resolution will be between $(\delta\theta_1^2 + \delta\theta_2^2)^{1/2}$ and $\delta\theta_1 + \delta\theta_2$.

In Bristol we set the detectors 12 mt. away from the source in order to have an approximate value of the angular resolution (due to a point source) of 0.5 millirad. At this distance the linear sizes of the detectors subtended an angle of 33 millirad, or 1.9°. In the current setting of the 2D-ACAR experiment, the small angle subtended by the detectors is a very important requirement which deserves some attention. The
requirement is due to the fact that we store only the relative angles between the photons and we lose all the information related to the direction of the photon emission axis. That axis spans the solid angle which is subtended by the detector. For linear detectors subtending an angle $\omega$ the photon emission axes can deviate from the major spectrometer axis by a maximum of $\omega/2 - \theta/2$, where $\theta$ is the deflection angle. Two effects have to be considered:

a) A given momentum $p$ will cause different responses in the detector depending on its projection onto the particular photon axis. The spread in the responses acts as an additional resolution to be combined with the intrinsic resolution of the system.

b) The photon axis spread introduces an uncertainty in the projection direction. When the momentum distribution of the material is not isotropic (as it most often happens for measurements on single crystals) this uncertainty must be taken into account.

a) For the sake of clarity, the discussion is limited to one dimensional detectors. Let us consider the response of the detectors to a momentum $p$, making an angle $\alpha$ with the main axis of the spectrometer. The response of the detector will depend on the direction of the photon emission axes spanning between $ph^+$ and $ph^-$. The deviation angle $\theta$ is in fact proportional to the projection of $p$ normal to $ph^\pm$. Let us assume that $\beta$ is the maximum angle the photon axes can make with the main axis of the spectrometer to permit the detection of the $\gamma$ pair ($\beta \approx \omega/2 - \theta_{0.5}/2$, where $\theta_{0.5}$ is an estimate of the FWHM of the angular distribution).

Two photon axes ($ph^+$ and $ph^-$) are depicted in figure 3.17. Within the usual small deflection angles approximation, the response of the detectors to the $\gamma$ rays pairs $\gamma^+$ and $\gamma^-$ (only one $\gamma$ ray for each pair is shown in figure 3.17) is

$$\frac{\theta^+}{2} \approx \frac{p \sin(\alpha + \beta)}{2m_0c},$$

and

$$\frac{\theta^-}{2} \approx \frac{p \sin(\alpha - \beta)}{2m_0c}.$$  \hspace{1cm} (3.14)

The spread in the response of the spectrometer is then

$$\Delta \theta = \max \left( \frac{p}{m_0c} \cos \alpha \sin \beta, \frac{p}{m_0c} \sin \beta \right).$$  \hspace{1cm} (3.15)
which is most noticeable for small values of $\alpha$. By assuming a typical deflection angle ($p/m_{0}c$) of $\theta_{0.5}$, one obtains an upper limit in the uncertainty $\Delta \theta$ as,

$$\Delta \theta \approx \theta_{0.5} 2 \beta \approx \theta_{0.5} 2 \left( \frac{\omega - \theta_{0.5}}{2} \right).$$  \hspace{1cm} 3.16

The requirement that $\Delta \theta$ is smaller than the angular resolution $\delta \theta$ yields therefore a constraint on the angular size, $\omega$, of the detector. The criterion,

$$\Delta \theta < \delta \theta \Rightarrow \frac{\omega}{2} < \frac{1}{2} \theta_{0.5} + \frac{\delta \theta}{2 \theta_{0.5}},$$  \hspace{1cm} 3.17

e nsures no more than a modest degradation of the effective momentum resolution. By inserting $\delta \theta \approx 0.5$ mrad and $\theta_{0.5} \approx 10$ mrad in eqn 3.17 one obtains 30 mrad as an upper limit of the detector semi-angle which is almost twice the semi-angle selected by the Bristol spectrometer in operation.

If the momentum distribution were completely anisotropic [say $\rho(p) = \delta(p - p_{0})$] one would be able to correct for the spread by calculating the photon axis per each detection pair and, from geometric relations, reconstruct the angle $\theta$ which generated the detector responses.

b) However, this correction is not possible for a distribution of momenta. To realise this let us look at figure 3.18 which shows three momenta $p_{1}$, $p_{2}$ and $p_{3}$ having the same projection on the photon axis $e_{1}$. Obviously the responses of $p_{1}$, $p_{2}$ and $p_{3}$ in case of a projection onto the main axis of the spectrometer $e_{0}$ (which represents the
ideal integration direction) are different and there is no way to correct for this in the present generation of 2D machines.

A possible solution to this uncertainty consists of the simultaneous storage of several projection direction matrices. It would include the following steps:

1) Set a detector pair subtending large solid angles with respect to the sample point.
2) For each detection pair calculate the photon axis (from the two detection points) which determines the projection direction of that particular momentum.
3) Store the information related to that projection separately (grouping the photon axes into a reasonable mesh).

At the end of the acquisition one would obtain several separate projections within the solid angle subtended by the spectrometer and would be able to reconstruct the 3D-momentum density according to reconstruction techniques.

The possibility of this experiment is, at the moment, remote. It would require a detector with extremely good angular resolution, to be positioned at a reasonable distance from the sample-source assembly in order to subtend a solid angle consistent with the crystal symmetry of the sample. At a close distance the effect of a non point-like source would require a totally different radioactive sources design. Moreover, at a close detector-sample distance the divergence of the $\gamma$ rays also could not be neglected. This means that for a photon axis making an angle $\beta$ with the main axis of the spectrometer the deviation $\Delta = |\vec{x}_1| - |\vec{x}_2|$, where $\vec{x}_1$ and $\vec{x}_2$ are the detector co-ordinates of the $\gamma$ detections, is related to the transverse momentum, $p_\perp$, by the relation

$$p_\perp \simeq m_0 c \frac{\Delta}{L} \cos^2 \beta,$$

where L, is as usual, the detector-sample distance.

With regard to the current 2D-ACAR set-up it is clear that the uncertainty in the projection direction prevents any attempt to align the single crystal within less of (say) 1° with respect to the axis of the spectrometer (the integration axis).
3.7 The Bristol set-up

The centrally placed source assembly system was built prior to the arrival of the author in Bristol and will be very briefly described. Its realisation was due to A Alam, S Usmar, J Clayton, N Wilkinson and H Fretwell. Details are described in Fretwell (1993).

The whole system is mounted, for alignment and calibration purposes, on a movable bed allowing precise horizontal displacements perpendicular to the major axis (detector-sample-detector), z, of the machine. The sample chamber is a 120 mm long by 100 mm diameter horizontal (normal to z) stainless steel cylinder closed at each end by the pole pieces of a commercial electromagnet used to focus the positrons from the source onto the sample (maximum intensity ~1 tesla). Smaller diameter arms, placed in the vertical direction, provide for evacuation, the entry of the cryostat cold finger (from below) and the introduction of samples (from above) via a vacuum gate valve. The positron source ($7.4 \times 10^8$ Bq, equivalent to 20 mCi of $^{22}$Na, supplied by Amersham), is inserted into the system via a bar through a hole drilled in one of the pole pieces.(see figure 3.19)

![Block scheme of the top view of the sample (s) source (sr) geometry. The source is positioned in place through one of the pole pieces (p) of the electromagnet. The detectors (D1,D2) are shielded from the source via lead blocks and the yoke of the electromagnet (not shown here).](image)

The bar, whose end is machined with the same material of the pole pieces, stays in place during the measurements and allows some adjustment of the position of the source with respect to the sample. The sample mount mates, after the insertion, with the cold finger of the cryostat and locates the sample, facing the source, in the centre of the $\approx 4$ cm pole gap. The cryostat cold finger end (originally a female copper cone) and the male end of the sample mount were re-machined in order to provide an absolute orientation to the sample mount (aligned with the main axis, z, of the spectrometer) after the insertion. After the modification we could assess that the
misalignment between the reference direction of the female cone (fixed to the cryostat) and the z axis of the spectrometer was less than 0.5°. The sample mount incorporates a holder, compatible with the departmental x-ray diffraction machine, having two rotational degrees of freedom which allow one to orientate the single crystal according to the selected directions. Machined lead collimators envelop the chamber, shielding the detectors from the radiation emitted directly by the positron source.

The CTI cryostat operates with a two stage closed cycle and uses helium gas as a working fluid. An aluminium shroud is mounted at the first stage of the cryostat to reduce radiant heat loads at the second stage. The working base temperature of the system is ≈20K.

On the arrival of the detectors in Bristol they were positioned in the existing 2D-ACAR laboratory. As differences in the sample-to-camera distance for the two detectors degrade the resolution in exactly the same manner as the differences in the average spatial gain do (as described previously), particular care was spent in trying to set detector sample distances and orientations of the main detectors' axes to equal values. The alignment involved conventional mechanical and optical techniques.

### 3.8 Measurement of the angular resolution

At completion of the set-up of the whole detector-source-sample-cryostat-vacuum assembly the first experiment which was performed consisted of the measurement of the overall angular resolution of the system. In general, if $F(v)$ is the distribution of the physical observable $v$, the result of a measurement of the observable, $M(v)$, is the convolution of $F(v)$ with the experimental resolution of the system, $R(v)$.

$$M(v) = F \otimes R \equiv \int dv' F(v - v') R(v') .$$  \hspace{1cm} 3.19

Clearly, the response of the system to a distribution $F(v)=\delta(p-p_0)$ is exactly the resolution function (times the MSF). Nature provides us with systems where a fraction of the overall momentum distribution can be approximated (within the limits of the current experimental resolutions) to a delta function. Those systems are the insulators where there is a non-negligible probability of forming positronium ($Ps$) atom. The formation of Ps was studied during several decades (see for example Ore 1949, Mogensen 1974) and will not be discussed here. The insulator which we chose for our first experiment was crystalline quartz ($SiO_2$). Several ACAR measurements (Brandt et al 1969, Greenberg et al 1970, Berko at al 1977) on quartz helped in understanding the experimental findings: Superimposed onto a broad (FWHM~10
mrad) and featureless distribution (which was ascribed to annihilation of positrons with the electrons of the full bands of quartz), was observed a much narrower distribution (FWHM<1mrad) at \( p = \theta \) and satellite peaks appearing at the projections of the reciprocal lattice vectors onto the measured momentum direction. The explanation of that result is now established: the narrow distribution is the momentum distribution of parapositronium, described by the Maxwell-Boltzmann distribution,

\[
f_{Ps}(p) = \left(2\pi m^*_Ps k_B T\right)^{-3/2} \exp\left(-\frac{p^2}{2m^*_Ps k_B T}\right),
\]

where \( m^*_Ps \) is the effective mass of the positronium. The satellite peaks are the celebrated High Momentum Components of the parapositronium peak thoroughly discussed in chapter 2. The observation of the HMC of parapositronium in quartz is a clear-cut proof of the Bloch theorem and provides very strong evidence of the dualism particle-wave.

An evaluation of the width of the distribution (the integration of a Gaussian along one direction is still a Gaussian) requires the knowledge of the effective mass of Ps in quartz. This measurement was performed by Ikari et al (1979, I) with a high resolution 1D-ACAR setup (0.38 mrad FWHM). The value of \( m^*_Ps \) obtained at low temperature was \((1.67\pm0.15)\times2m_e\). In a second paper Ikari (1979, II) established a weak temperature dependence of \( m^*_Ps \) which was empirically described by the following expression,

\[
m^*_Ps = \left(2m_e\right)\frac{a}{1-bT},
\]

where \( a=1.62\pm0.15 \) and \( b=(2.0\pm0.7)\times10^{-4} \) K\(^{-1}\).

From eqn 3.21,

\[
m^*_Ps(T)_{T=30} = (3.3 \pm 0.3)m_e \quad \text{and} \quad m^*_Ps(T)_{T=300} = (3.4 \pm 0.3)m_e.
\]

The temperature dependence of the effective mass can therefore be neglected in our evaluation of the resolution.

The full width at half maximum, FWHM, of the Maxwell-Boltzmann distribution is then given by

\[
\text{FWHM}_p = 2.354\sqrt{m^*_Ps k_B T} \Rightarrow \text{FWHM}_\theta = \text{FWHM}_p / m_e c = 0.98(T(K)/300)^{1/2} \, \text{mrad}.
\]

At the base temperature of our system (T\(\sim\)20-25 K), the FWHM\(\theta\) of the thermal distribution of parapositronium is \(\sim 0.27 \) mrad.
If one assumes that the experimental resolution function can be approximated by a Gaussian the deconvolution of the experimental distribution from the thermal distribution of the Ps is simply a Gaussian whose FWHM is the difference in quadrature between the FWHM observed and the FWHM expressed by eqn 3.22. The momentum distribution of quartz, after the MSF correction, is shown in figure 3.20.

Before estimating the resolution we had to confirm the spatial calibration which had been attained by each detector (see § 3.5). This was measured (for the x direction) by translating the source-sample chamber along the movable bed by equal steps of known length (an equal number of turns of a micrometric screw). It is worth noting that a movement of 1 mm of the sample causes a shift of 2 mm in the $(x_1+x_2)$ spectrum as the baricenter of the $\gamma$ rays emitter changes of 1 mm for both detectors. The positions of the narrow peaks of parapositronium were fitted by a straight line whose slope attained the calibration\textsuperscript{14}. The obtained calibration of 1.617 mm/chann (very

\textsuperscript{14} The processing units is linked to a Personal Computer 80386 via a Fast ComTech acquisition system. Its board has 1 MBytes memory which can store up to $512 \times 512$ matrices with 4 bytes per bin.
close to that measured for the single detectors at 140keV) at the conversion range and sample-detector distance selected corresponded to 0.1348 mrad/chann. The consequent total field of view was 68 mrad in a matrix of 512 $\times$ 512 channels.

However, because the Momentum Sampling Function (see figure 3.16) goes to zero at a matrix radius of 240 channels (32 mrad), and to limit the uncertainty in the photon emission axis direction, the acquisition was limited to a central sub matrix comprising 256 $\times$ 256 channels. The corner of that matrix, placed at 24.4 mrad from the centre of the distribution, has a statistical weight (expressed by the value of the MSF) of 14% with respect to the centre ($p=0$) of the MSF matrix. In further acquisitions (mainly in materials with large BZ) we increased the acquisition matrix up to a matrix of 288 $\times$ 288 channels. The corner of that matrix is located 27 mrad from its centre (the MSF is 6.9% of its value at the centre). Great care had to be taken in the data analysis due to strong enhancement of the noise (in the outer region of the matrix) during the MSF correction (see next chapter for details).

The overall angular calibration (x and y directions) was tested by measuring the positions of the Umklapp peaks of the parapositronium in quartz. The hexagonal crystal was positioned with its $c$ axis parallel to the main axis, $z$, of the spectrometer, which is the average integration axis.

The direct and the reciprocal lattice vectors are defined as

$$R = \begin{pmatrix} a & 0 & 0 \\ -a/2 & \sqrt{3}/2 & 0 \\ 0 & 0 & c \end{pmatrix} ; \quad G = 2\pi \begin{pmatrix} 1/a & 1/a\sqrt{3} & 0 \\ 0 & 2/a\sqrt{3} & 0 \\ 0 & 0 & 1/c \end{pmatrix}$$.  

*Fig. 3.21 The central part of the momentum distribution of parapositronium. The first series of Umklapps draw an almost perfect hexagonal pattern.*
where $a$ and $c$ are 4.91 Å and 5.4 Å, respectively. In the $p_x$, $p_y$ plane, $|G| = 5.706$ mrad. Figure 3.21 shows the position of the Umklapp peaks in the central $128 \times 128$ channels matrix after the subtraction of the broad distribution contributed by the valence electrons (approximated to a Gaussian). Apart from the difference in the resolution between the $x$ and $y$ direction which will be discussed later, the position of the peaks is extremely consistent with an hexagonal pattern. The $x$ and the $y$ positions of the satellite peaks agreed to within 0.1% and 0.7% with those of the theoretical pattern, respectively. Because of such small differences an equal calibration for both directions was assumed.

Figure 3.21 shows a remarkable difference in resolution between the $x$ and $y$ direction. The reason is due to the very different extent of the source in the two resolved directions. Along the axis source-sample, $x$, the source size is determined only by the penetration of the positrons (0.1-0.2 mm) and therefore is negligible with respect to the spatial resolution of the detectors. However, along the normal direction, $y$, the source size is determined by the convolution of the spatial resolution with the source spot onto the sample. By fitting the central peak with a Gaussian (the temperature was 25 K) a FWHM of $4.7 \pm 0.2$ channels and $8.0 \pm 0.2$ channels for the $x$ and $y$ directions, respectively, was obtained. For the $x$ direction, the subtraction in quadrature of the thermal width of the positronium gives the so-called optical resolution (i.e. the ideal resolution for a point source):

$$\delta \theta_x = \sqrt{(4.7 \times 0.1348)^2 - 0.27^2} = 0.57 \pm 0.02 \text{ mrad, } (0.078 \text{ a.u}).$$

The resolution due to the source spot in the $y$ direction can be obtained by subtracting from the $y$ resolution the total $x$ resolution (optical convoluted with thermal),

$$\delta_{yS} = \sqrt{8^2 - 4.7^2} = 6.47 (\text{chann}) \times \frac{1.617}{2} = 5.2 \text{ mm},$$

by assuming that $\delta_{yS}$ can be approximated by a Gaussian. (The division by two is due to the fact that the source size gives a double contribution to the resolution because we sum the $y_1+y_2$ co-ordinates.)

The last figure comprises the combined effects of the source spot and of the divergence of the beam due to the a non negligible cyclotron radius, $r_c$\textsuperscript{15}. One can calculate $r_c$ for the maximum energy of the $\beta^+$ energy spectrum of the positrons, $E_T^{\text{max}} = 0.54$ MeV for $^{22}\text{Na}$.

As kinetic energy and rest mass energy combine linearly to give the total energy, one obtains

\textsuperscript{15} Due to the Lorentz force, free positrons travelling in a magnetic field, $\mathbf{B}$, describe a spiral trajectory. The radius of the spiral is the cyclotron radius and the axis of the spiral is parallel to the direction of $\mathbf{B}$.}
\[ E_T^{\text{max}} + E_0 = (1 + \alpha)m_0c^2 = m_0c^2 \gamma = \frac{m_e c^2}{\sqrt{1 - v^2 / c^2}}; \]

therefore, \( \gamma = 1 + \alpha \) and \( \frac{v}{c} = \frac{\sqrt{\alpha^2 + 2 \alpha}}{1 + \alpha} \),

where \( \alpha = 1.056 = (0.54/0.511) \).

The cyclotron radius, \( r_c \) is related to the cyclotron frequency \( \omega, eB/\gamma mc \), via the relation (Jackson, 1975)

\[ r_c = \frac{v}{\omega} = \frac{\sqrt{\alpha^2 + 2 \alpha}}{1 + \alpha} \frac{\gamma mc}{eB} = \frac{3.06 \times 10^3}{B(G)} \text{(cm)}. \]

Therefore, a magnetic field of 1 T (10^4 G) will force the fastest positrons into a cyclotron radius of 3 mm, which is certainly not negligible with respect to the source size\(^{16} \). Since the cut-off of the spectrum is at \( E_{\text{max}} = 0.54 \text{ MeV} \), very few positrons will show this high divergence. An upper limit for the average cyclotron radius can be obtained by approximating the \( \beta^+ \) energy spectrum to a step function \( \rho(E) = \theta(E - E_{\text{max}}) \). One can then obtain,

\[ \langle r_c \rangle = \frac{m_e c^2}{eB} \int_0^{\pi^2} d\theta \sin^2 \theta \int_0^\alpha dx \sqrt{x^2 + 2x} \]

\[ = \frac{\pi m_e c^2}{4 eB} 1.11 = \frac{1.5 \times 10^3}{B(G)} \text{(cm)}. \]

In eqn 3.26, the angular average gives the average velocity component normal to the direction of the magnetic field \( B \).

The average cyclotron diameter is therefore \( \frac{3 \times 10^3}{B(G)} \text{(cm)} \). Though this figure is approximated, it seems that a clear benefit to the resolution in the \( y \) direction should be attained by increasing the size of the B field to 2 T.

The size of the quartz sample (a disk of diameter \( D \approx 1.2 \text{ cm} \)) were such that the sizes of the positron spot at the sample were determined combining size of the

\(^{16} \) The figure of eqn 3.25 refers, obviously, to particles with initial velocity, \( v \), normal to the direction of the magnetic field \( B \).
physical source and effectiveness of the magnetic focusing. When the sizes of the sample are smaller than the source spot they determine the resolution along the y direction (obviously the count rate decreases proportionally to the sample surface).

3.9 Count rates attained

A final test of the system consisted in the comparison between the ideal count rate and the one actually observed\(^\text{17}\).

The count rate in single-mode acquisition, selecting energy windows containing (only) the photopeak, was \(\sim 3000\) cps, for the sample quartz. The ideal rate, given by eqn 3.7, is, neglecting the self-absorption of the \(\gamma\) rays in the sample,

\[
C_{\text{rate}} = \frac{2\pi}{4\pi} \left(1 - \frac{d}{\sqrt{d^2 + r^2}}\right) \times \varepsilon_{0.511} \times S \times Y \times Ab_{\text{air}},
\]

where the coefficient \(Ab_{\text{air}}\) is the photons' fraction due to the attenuation from 12mt of air, \(Ab_{\text{air}} \sim 0.9\), and the other symbols were defined before.

Substituting in eqn 3.7 the values \(Y = 2 \times 0.9\), \(\varepsilon_{0.511} = 0.125\), \(S = 3.7 \times 20 \times 10^7\) Bq, \(d = 12\) mt and \(r = 120 \times 1.617 \times 10^{-3}\) mt, gives a \(C_{\text{rate}}\) of \(\sim 9 \times 10^3\) cps. The ratio between actual count rate and ideal count rate gives a positron yield of 35\%, which is typical of the state-of-the-art 2D-ACAR spectrometers\(^\text{18}\).

In a 2D-ACAR experiment the ratio between the coincidence count rate (\(\sim 210\) cps) and the single mode count rate (\(\sim 3000\) cps) depends on several factors like the single detectors efficiencies, the self-absorption of the \(\gamma\) rays in the sample, the attenuation of the photons in air and the range of the angular distribution under measurement\(^\text{19}\).

By neglecting the self-absorption in the sample, one can estimate an ideal coincidence rate as,

\[
C_1 \varepsilon_{0.511} Ab_{\text{air}} = 3000 \times 0.125 \times 0.9 = 338\text{(cps)},
\]

17 In operation the single detector and coincidence counting rates were constantly monitored in order to detect possible instabilities of the electronics, of the sample position and of the source sealing. This was very helpful in order to reject some spectra during the data analysis.

18 Ideally one should achieve a yield of 50\%, if all the positrons emitted in the forward (source-sample) direction reached the sample. In practice this is never realised even though one tries to increase the yield by depositing the \(^{22}\text{Na}\) source onto a so-called reflector which can re-emit a fraction of the positrons in back-scattering.

19 As in the case of quartz the volume of the momentum distribution ascribed to the narrow parapositronium peak (with \(\rho(p) \approx \delta(p)\)) corresponded only to a few percent of the total volume, the overall momentum distribution had a width comparable with that of a typical free electrons-positrons momentum distributions in solids.
where the symbols have the same meaning as in eqn 3.7. Expression 3.27 represents the ideal coincidence rate which would be attained by an angular distribution $\rho(p) = \delta(p)$, i.e. with a correlation angle of 180° between all the $\gamma$ ray pairs.

The real coincidences yield, $C_{\text{coinc}} = 210$ cps, is ≈62% of the maximum coincidence rate and represents a good compromise between a reasonable count rate and an angular opening of the spectrometer which does not affect the performances of the spectrometer (see West, 1981 and § 3.6).
4 Data analysis

The data analysis of a 2D-ACAR experiment is a step-by-step procedure involving several computer programs which have been implemented at Bristol and Arlington. The procedures followed in the collection and routine analysis of the data are described below.

4.1 Sample centring and Momentum Sampling Function correction

After having x-rayed the single crystal in order to select the desired projection direction, the sample holder is inserted into the system. A common problem of a 2D–ACAR measurement is related to the asymmetry of the set-up along the direction, $x$, of the source-sample axis. As the positron source is positioned at one side of the sample and the penetration range of the positrons is quite small (~0.1 mm), most of the annihilations will happen in a region of the sample where the $\gamma$ rays pairs (which reach the detectors) may be subjected to very different attenuations.

Figure 4.1 shows two $\gamma$ ray pairs which make two angles of different sign with respect to the $x$ axis. As the pair $\gamma_1^+ - \gamma_1^-$, with positive deflection angle $\theta_{x1}$, makes a shorter path within the sample, $S$, it will undergo less of an attenuation than the pair $\gamma_2^+ - \gamma_2^-$ with negative deflection angle, $\theta_{x2}$. The intensity in the angular distribution $N(\theta_{x1})$ will therefore be enhanced in comparison with $N(\theta_{x2})$. This effect causes an asymmetry in the recorded distribution along the $\theta_x$ direction (the asymmetry is absent in the normal direction of the detector plane, $\theta_y$). The asymmetry also affects the calculation of the centroid of the distribution, ideally underlying the $(p_x,p_y)=0$ point. One way to reduce the problem is to cut the single crystal so that the surface facing the positron source deviates by a small angle$^1$ from the parallelism with the $z$, sample-detectors, direction (as for the sample in dotted lines, $S'$, in figure 4.1). By doing this, all the $\gamma$ reaching the detectors will be attenuated almost independently of the positive or negative direction of $\theta_x$. Obviously, this is only

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$^1$ Of the order of the angle subtended by the detectors (1° or 2°)
possible if the crystal has been prepared explicitly for a 2D-ACAR experiment. Moreover, the asymmetry can also be reduced via the correction with the Momentum Sampling Function. As mentioned in §3.5, this is defined as the convolution of the single camera responses,

\[ MSF(r) = \int dx \, CAM_1(x) \, CAM_2(r-x) = FT^{-1}(FT[CAM_1(x)] \times FT[CAM_2(x)]) , \]

where \( CAM_1 \) and \( CAM_2 \) are the single cameras' images\(^2\). As the asymmetry discussed will also be present in the structure of the single camera responses, the shape of the MSF will reflect the self-absorption of the \( \gamma \) rays in the sample. (An example of a skewed experimental MSF is shown in figure 4.2)

The correction,

\[ \rho(p_x,p_y) = \frac{N(p_x,p_y)}{MSF(p_x,p_y)} , \]

will therefore restore the proper symmetry, beyond the appropriate statistical weight of each \((p_x,p_y)\) pixel.

It must be stressed that the MSF simply accounts for the total number of configurations, each with given efficiency due to the sample absorption, which contribute to a given sum \((X=x_1+x_2,Y=y_1+y_2)\). This number will always be at a maximum at the centre of the 2D-ACAR matrix (at \(X=N/2\), \(Y=N/2\), where \(N/2\) is the size of the single cameras matrices and \(N\) the size of the 2D-ACAR matrix). Clearly, a \( \gamma \) ray emitter which is located off-centre with respect to the straight line joining the centres of the detectors, will show an asymmetric 2D-ACAR response with

\(^2\) Two programs for the MSF calculation were implemented by the author: the first operates the convolution in real space. A new version of the code proceeds in Fourier space, utilising the Fast Fourier Transform algorithm (eqn 4.2), to speed up the procedure. In this manner the computing time is reduced of a factor of ~ 50-100.
an ideal \( p=0 \) point off-centre (because of sample absorption). After the MSF correction the spectrum will be more symmetric but still off-centre.

The procedure which we thought was most appropriate to begin any new measurement was therefore the following:

1) The base temperature (25-30 K) was selected.

2) Low statistic (\( 10^7 \) counts in \( \approx 1.5 \) hours acquisition time) single-camera spectra were acquired and a MSF generated. The MSF was then calculated and a low statistic 2D-ACAR spectrum acquired. That spectrum was corrected with the MSF and the centroid of the matrix calculated. The x position was then adjusted, by translating the whole source-sample assembly along its track, in order to have the centre of the corrected spectrum at the ideal centre of the matrix. The statistical error \( \Delta y_c \) of the centroid, \( y_c \), of a histogram of uncorrelated measurements (\( y_i, \ldots \)) stored in a vector of \( N \) elements is given by the following expression,

\[
\left( \frac{\Delta y_c}{y_c} \right)^2 = \frac{N}{\left( \sum_{i=0}^{N-1} y_i \right)^2} \sum_{i=0}^{N-1} y_i^2
\]

A few million counts, (3 to 4 hours' acquisition time) were sufficient to ensure that the error of the centroid was less than 1/10 of a channel (equivalent to 0.08 mm) and below the precision attainable by the adjustment.

At the selected position, the single cameras' responses were acquired again to generate a second MSF for the final correction.

In this way the series of digital operations required to locate the ideal \( p=0 \) point at the centre of the acquisition matrix was significantly reduced. In fact, any shift of the spectra of a fractional number of channels introduces correlation between first neighbours bins and is equivalent to a \( 2 \times 2 \) channel matrix smoothing (if the shift is operated using a bilinear interpolation). Obviously, the search of the FS discontinuities in the spectra can be jeopardised by interpolations which could be avoided.

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3 Owing to the convolution character of the MSF, one can construct an MSF of high statistical precision by using single cameras spectra with the overall statistics mentioned in the text (corresponding to approximately 200 counts per pixel).

4 As the y position of the sample-source assembly was not adjustable, the heights of the detectors were selected, once and for all, in order to locate the position of the narrow parapositronium peak (measured in quartz) at the centre of the \( (\theta_x, \theta_y) \) matrix.
In the previous discussion it was assumed that the centre \((p=0)\) of the distribution was adequately represented by the calculation of the centroid. The validity of this assumption requires the symmetry of the distribution (after the MSF correction). Various groups have tried different methods of finding the centre of the spectrum.

At Arlington (West 1994), and Livermore (Howell 1994) the procedure adopted (in the following addressed as reflection-subtraction analysis) consists in subtracting from the data a matrix where the channels of each direction are swapped, i.e. a reflection with respect to the main axes of the matrix \((x=(N-1)/2, y=(N-1)/2)\) is applied. Figure 4.3 shows the result of applying this to a simulated 1D spectrum: when the point of reflection is the centre of the vector, the two peaks in the difference, \(p^+, p^-\) indicate that the reflection point is not the high symmetry point of the spectrum. By varying the reflection point until the two peaks disappear one can then obtain the centre \((p=0)\) of the distribution. However, the procedure works well only if the distribution is symmetric. If it is not, the difference distribution still shows two peaks owing to the different shapes of the leading and trailing edges of the distribution.

When the distribution is symmetric, the centre of the distribution (calculated as described above) does not differ appreciably from the first moment of the spectrum. It is therefore very important to make the initial MSF correction so as to restore the appropriate symmetry before calculating of the centre of the distribution. The differences between the centroid and the centre calculated via the reflection-subtraction method were always limited to a small fraction (0.1-0.2) of channel\(^5\).

### 4.2 Symmetrization of the 2D-ACAR spectra

A controversial issue of the 2D-ACAR data analysis is the application of the folding operations (symmetrization) to which the data can be subjected (Smedskjaer, 1990).

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\(^5\) The author attempted few fitting procedures to calculate the centre of a distribution which is not symmetric (Gaussian functions convoluted with exponentials of different slope, or Gaussians of different intensities on the two sides), but none very satisfactory.
In Bristol we always preceded the folding by a careful inspection of the anisotropy present in the data. The test involves the analysis of the radial anisotropy of the data, which is realised by taking the difference, $RA(p_x,p_y)$, between the centred and MSF corrected data, $N(p_x,p_y)$, and its angular average,

$$RA(p_x,p_y) = N(p_x,p_y) - N(\sqrt{p_x^2 + p_y^2}).$$  \hspace{1cm} 4.4$$

A rapid way of obtaining the angular average is to transform the data into polar coordinates and then to average over the angular variable. Two similar codes were implemented by the author and M. Brand at Arlington (the Arlington's routine is usually used because of its higher speed).

The radial anisotropy spectra (RA) were examined for evidence that, within the limitations of the prevailing statistics and the anisotropy in the angular resolution discussed in § 3.8 ($\delta \theta_y > \delta \theta_x$), they reflected the appropriate projected crystal point symmetry. If that symmetry was satisfactory we folded the data with respect to the $p_x=0$ and $p_y=0$ axes of the matrix, to improve their statistics. Occasionally, if the highlighted anisotropy had a symmetry deviating from the matrix symmetry axes, a small rotation (between 1° and 2°) was applied to the data prior to the folding (bearing in mind that a rotation introduces a correlation and a smoothing in the data). Figures 4.4 and 4.5 show an example of the consequence of the symmetrization of the spectra to the momentum density of LaB$_6$ integrated along the <100> direction. It is clear that most of the features are common to the two figures. However, as the dynamic of such an anisotropy is always quite small with respect to the intensity of the distribution, the increase of the statistics by a factor of 4 after the double folding brings a noticeable advantage. For example, in figure 4.4 the maximum dynamic of the anisotropy (i.e. the difference between the maximum and the minimum of the anisotropy) is 5.3% of the maximum of the matrix corresponding to ~10 times the statistical error of the maximum. After the folding the dynamic of the anisotropy is reduced to 3.5% (as due to the average of 4 non equivalent pixels) but increased to 13 times the statistical error of the maximum.

4.3 Data handling procedures

A significant problem of the 2D-ACAR experiments lies in the small sizes of the effects that one wants to detect. As the positron annihilates with all the outer electrons, regardless of their position in the energy band (labelled by the Bloch wave-vector $k$) or of the kind of band hosting them (valence or conduction), most of the counts present in the data are related to electron eigenstates which are not relevant to FS
detection. Very often their contributions to the spectra consist of a featureless and nearly isotropic background (which can be modulated by the effect of the positron wave-function), superimposed on signals which can be ascribed to FS effects.

The aim of the large extent of data handling in the 2D-ACAR analysis is to eliminate the uninteresting contributions or to reduce them to a constant. This is the essential philosophy of the analysis of the RA of the data, described in § 4.2, or in the LCW.

The symmetry of the momentum density of the full bands may reflect the symmetry of the BZ of the crystal.

---

**Fig. 4.4** Radial anisotropy of the momentum density of LaB$_6$ integrated along the <001> direction. The spectrum is unsymmetrized. The grid represents the BZ in a repeated zone scheme. In the grey scale image, black corresponds to low intensity and white to high intensity.

**Fig. 4.5** The same as figure 4.4 for the spectrum which is now symmetrized along the $p_x$ and $p_y$ directions of the spectrometer.
procedure, described in §2.7. Certainly, a direct elimination of the "unwanted" signals, such as in the dHvA experiment, where only the electrons at the FS contribute to the oscillations of the magnetisation observed, would be a breakthrough in the power of the 2D-ACAR experiments. One might (naively) think of subtracting the momentum densities of two acquisitions, with electric DC field in two opposite directions. It is well known that the action of a DC field is to displace the whole Fermi volume by an amount proportional to the electric field, $E$, and the collision time $\tau$. The operation of taking the difference between the two spectra would eliminate the momenta of all the electrons residing inside the Fermi volume. The momenta of the electrons residing in the vicinity of the Fermi surface would be displaced by a small amount, depending on the direction of the electric field and will not be cancelled by the difference. However, a simple calculation shows that the displacement in velocity by means of a feasible electric field would be of the order of $10^{-10}$ of the size of the Fermi velocity, nine orders of magnitude smaller than our angular resolution (!).

### 4.3.1 Radial anisotropy

Given the apparent impossibility of directly eliminating unwanted signals, one must revert to the data handling algorithms currently available. The main hypothesis of the RA algorithm is that the contribution to the momentum distribution generated by the full valence bands is essentially isotropic. In other words, the RA highlights the FS topology whenever the anisotropy of the total momentum distribution is mainly caused by the interruption of the momentum density of the conduction band at the $k_F+G$ points. These interruptions occur along directions which have the BZ, rather than the radial symmetry.

The procedure was first adopted by Berko, (1983) for copper. The topology of the FS of noble metals is very simple and consists of a distorted sphere, contributed by the 4 or 5 s electron, with protrusions along the <111> directions, the celebrated noble metal necks, reaching the borders of the BZ (where the FS disappears). However, the momentum density is affected by the 5 full bands (ascribed mainly to the d electrons) which lie near the conduction band. The result of a 2D-ACAR experiment is a relatively featureless distribution. The search for the necks via the radial anisotropy is rendered effective by the almost isotropic shape of the d component of the momentum distribution. To test the reliability of the spectrometer we performed a measurement of copper, whose radial anisotropy is shown in figure 4.6. The Cu single crystal was positioned with the <111> axis along the integration axis, $p_z$, of the spectrometer.

---

7 From undergraduate textbooks, $\langle v \rangle = J / e n, \approx 10^{-2}$ cm/sec, where $\langle v \rangle$ is the average drift velocity caused by an electric field generating a current density $J$ (take, for example, $J \approx 20$ A/mm$^2$), $e$ and $n$ are electron charge and density ($n \approx 10^{22}$ cm$^{-3}$).
and with the \(< \overline{1} 10 >\) and \(< \overline{1} \overline{1} 2 >\) axes parallel to the \(p_x\) and \(p_y\) axes of spectrometer, respectively. The crystal structure of noble metals is FCC. By projecting the reciprocal lattice vectors ("recips") \(V_1 = \frac{2\pi}{a} (-1,1,1)\) and \(V_2 = \frac{2\pi}{a} (1,1,-1)\) (two "recips" are sufficient for a planar geometry) on the base chosen for the measurement, one obtains

\[
\begin{pmatrix}
V_1_{,x \tau 10} & V_1_{,x \tau 22} \\
V_2_{,x \tau 10} & V_2_{,x \tau 22}
\end{pmatrix} = \frac{2\pi}{a} \begin{pmatrix} \sqrt{2} & \sqrt{2/3} \\ 0 & -\sqrt{8/3} \end{pmatrix} = \begin{pmatrix} 9.5 & 5.48 \\ 0 & 10.98 \end{pmatrix} (mrad),
\]

where \(a = 3.61\) Å is the crystal lattice constant of copper.

The very evident maxima which lie in an hexagonal pattern\(^8\) (and the high momentum components of these maxima) characterise the high intensity of the distribution at the position of the necks projected onto the measurement plane. This is because the electron eigenstates (labelled by the Bloch wavevector \(k\) in the first BZ) along the \(<111>\) equivalent directions are occupied up to the BZ boundary.

Owing to the elimination of any pattern with radial symmetry, the signature of the spherical Fermi surface in the first BZ is washed out. The high momentum components of a spherical (or cylindrical) FS, could nevertheless be visible, in general, in the Umklapps (HMC) of the first BZ\(^9\). An advantage of the RA in comparison with the LCW procedure (described in §2.7) is that the prior knowledge of the "recips" to be inserted into the LCW summation is not needed. On the other hand, the procedure introduces long range correlation among all those \((p_x,p_y)\) pixels which are at the same distance from the centre of the matrix. It is evident that two momentum distributions which only differ by a radially isotropic contribution will possess the same radial anisotropy (this result will be used in the discussion of CeB\(_6\)).

---

\(^8\) There are 8 equivalent \(<111>\) directions, two of which are along the integration direction.

\(^9\) In this case the FS images do not possess radial symmetry.
A recent example of the usefulness of analysing the radial anisotropy was offered by the observation of one of the main sheets of the FS in the high T_c superconductor YBaCuO by the Arlington group (Haghighi et al,1991).

4.3.2 LCW analysis

The LCW analysis is certainly a very useful tool which was applied successfully to several materials. It has performed best in the analysis of elemental and alloys systems based on transition metals (see for example Kaiser et al, 1987). As mentioned in §2.6, as a consequence of the higher localisation of the d orbitals, the d-band part of the momentum distribution is distributed over many replicas of the first BZ (in a repeated zone scheme). The LCW folding procedure is therefore particularly effective in recovering the k space occupancy. An important parameter characterising the LCW folded data is their dynamic, \( D_y \), defined as \( D_y = (\text{Max} - \text{Min})/\text{Max} \), where \( \text{Max} \) and \( \text{Min} \) are the maximum and minimum of the LCW data, respectively\(^\text{10}\). For transition metals, \( D_y \) is between 0.15 and 0.20 (for 2D projections). This figure decreases to a few percent for complex systems, where the contributions from a very large number of full bands are superimposed on those from the conduction electrons. When \( D_y \) approaches 1% the information extracted by the LCW procedure is unreliable as the small positron wave function effects which most often modulate the occupancy may substantially affect the result. This occurs, for example, in the case of semiconductors like Si or Ge (Alam, 1994), which have no Fermi surface and whose \( D_y \) should therefore be zero.

The LCW computer program which was mostly used in the data analysis was written at Arlington (TX) by J Kaiser. The author received it from M Brand (Arlington), tested and modified it for the inclusion of error calculations of the folded data. In the course of the analysis the results were often compared with a similar code implemented by A Alam. The essential points of the method were described in §2.7. Arlington's program contains a useful routine which calculates the projection of the "recips" of the assigned crystal structure in the plane normal to the integration direction. After the "recips" are calculated, a sub-matrix \( \rho(p) \), containing an integer number of projected "recips", is selected. As the value of the "recips" \( G_i \) is hardly ever commensurate with the mesh of the apparatus, a bilinear interpolation is required to fold \( \rho(p + G_i) \), while performing the sums of the type

\[
LCW(p) = \sum_{i} \rho(p + G_i),
\]

\(^\text{10}\) As discussed in §2.7, for a constant positron wave function, the ratio \( D_y \) indicates the fraction of conduction electrons (with respect to the total number of electrons) sampled by the positrons.
as described in §2.7. This interpolation introduces a first neighbours correlation in the LCW folded data.

It is easy to lose track of the statistical errors during the analysis because of repeated data handling. It is therefore very important to have a clear idea of the error bars, when reporting the dynamic of the LCW data. The operations to which the data are subjected from the acquisition until the LCW summation are summarised below.

i) MSF correction - The MSF correction introduces an enhancement of the statistical noise at the borders of the acquisition matrix. As the raw data $N(p_x, p_y)$ are characterised by a Poisson distribution (see for example Bevington, 1965), their standard deviation is $\delta N(p_x, p_y) = \sqrt{N(p_x, p_y)}$. The raw data are then corrected via eqn 4.2, $\rho(p_x, p_y) = N(p_x, p_y) / MSF(p_x, p_y)$.

Neglecting the error on the high statistics $MSF(p_x, p_y)$, the standard deviation of the corrected data $\rho(p_x, p_y)$ is given by

$$\delta \rho(p_x, p_y) = \frac{\sqrt{N(p_x, p_y)}}{MSF(p_x, p_y)} = \frac{\rho(p_x, p_y)}{\sqrt{MSF(p_x, p_y)}}.$$  \hspace{1cm} (4.7)

In our set-up, the statistical error of the corrected data at the corners of the matrix is $\approx 7$ times higher than the square root of the counts. However, the recorded distribution has such low intensity in that range of momenta (at $\approx 3.3$ a.u. from the centre of the matrix) that the results of the data analysis (for example of the LCW routine) are not seriously compromised by the high statistical error of that region.

ii) Centring - Folding - By eliminating the shift of a fraction of channels during the centring of the data one can avoid the linear interpolations which introduce correlation between nearest neighbour pixels of the matrix. This means that the subsequent folding implies the summation of uncorrelated events.

iii) LCW - In the LCW summation given by eqn 4.6 one can therefore reconstruct the final errors with the following steps:

1) for each pixel $(p_x, p_y)$ the real statistical error is reconstructed by means of eqn 4.7 through the knowledge of the MSF$^{11}$.

2) the error on the pixel sum (in eqn 4.6) is built with the usual error propagation expressions [e.g. see Bevington (1965)]. This includes the error propagation in the bilinear interpolation routine which accounts for the fact that, in general, the projected

$^{11}$ As an accurate knowledge of the MSF is not important in the calculation of the error bars, the real MSF is here replaced by its mathematical expression (for detectors with uniform efficiency), which is given by eqn 3.12.
"recips" are not an integer number of channels. One can then obtain a matrix (of the same size as the LCW one) which contains true statistical errors. The LCW data will be however affected by significant correlations within a $2 \times 2$ matrix size.

4.4 Recent developments of the data analysis

The advent of position sensitive detectors (PSD) and of large acquisition matrices (from $256^2$ to $512^2$ bins) gave a great impulse to the 2D-ACAR field in the search of new forms of data analysis. The two algorithms described above (radial anisotropy and LCW) suffer from different drawbacks: in the case of the radial anisotropy the main problem lies in the fact that it is usually very difficult to make predictions of its output. The correlation between pixels which are equidistant from the centre ($p=0$) of the matrix can, in fact, generate unexpected structures. The LCW algorithm, despite its more quantitative features, suffers from the effects of a non-uniform positron density (in real space) which can modulate the electron occupancy (in $k$ space) thus significantly obscuring the FS discontinuities (see §2.7). For complex systems (see for example the discussion of LaSrCuO in Sterne et al, 1993) the calculation of the positron wave function became essential to separate the FS signals from other effects.

The experimentalist is therefore left with two choices:

1) Obtain a calculation of the electron-positron momentum density of the system and compare strictly the experimental results with the theory. One compares the experimental "raw" data with the theory or, most often, the RA and the LCW of experimental data with the theoretical data subjected to the same treatment. In this case the 2D-ACAR experiment can be regarded as an indirect method of extracting FS information.

2) Often, only the (electronic) band structure calculation and the consequent derivation of the FS topology is available. In this case, one can try to implement algorithms which eliminate from the experimental (or LCW folded) data the effects of the non uniform positron density.

The positron wave function affects the LCW folded data according to the expression quoted in §2.7,

$$\rho_{LCW}(k) = \text{const} \sum_{n} \Theta(E_F - \varepsilon_{k,n}) \times \int_{\Omega} \left| \psi_{e_{n}}(r) \right|^2 \left| \psi_{k}^{e}(r) \right|^2. \quad 4.8$$

The step function $\Theta(E_F - \varepsilon_{k,n})$ restricts the summation to occupied electron states, with energies $\varepsilon_{k,n}$ from bands $n$. $\psi_{e_{n}}$ and $\psi_{k}^{e}$ are the positron and electron wavefunctions from band $n$ as discussed in §2.7. West (1992) approaches the problem by
expanding in Fourier series the modulation function expressed by the integral of eqn 4.8 (the wave vectors of the series-expansion are given by the Bravais vectors of the crystal \( R_j \)):

\[
\rho_{LCW}(k) = \text{const} \sum_n \theta(E_F - \varepsilon_{k,n}) \times \sum_{R_j} a^n_j \cos(k \cdot R_j),
\]

where the \( a^n_j \) are unknown expansion coefficients. The expansion is limited to cosines because of the square modules present in the integral in eqn 4.8. The procedure is effective if the expansion can be truncated after a few terms. In this case the true occupancy \( \theta(E_F - \varepsilon_{k,n}) \) can be recovered by an expression of the form,

\[
\sum_n \theta(E_F - \varepsilon_{k,n}) = \frac{\rho_{LCW}(k)}{\sum_{R_j} a^n_j \cos(k \cdot R_j)},
\]

where \( \rho_{LCW}(k) \) is the matrix of the experimental LCW folded data and the \( a^n_j \) are adjustable parameters which can be determined by a fitting procedure. The method met with some success in the high \( T_c \) YBaCuO, where the positron is mainly residing along the CuO chains (Singh et al, 1990). As the system can be approximated as one-dimensional the expansion would then be limited to,

\[
\int dr \left| \psi_{\varepsilon_j}(r) \right|^2 \left| \psi_{\varepsilon_n}(r) \right|^2 \cong (1 + a_1 \cos k_x R_x + a_2 \cos 2k_y R_y + \ldots).
\]

However, the method suffers from the fact that, especially for projected data, the cosine expansion can simulate (and therefore hide) the appropriate functional dependence of the occupancy.

More recently, the Arlington group (O'Brien et al, 1994) and the Bristol group have implemented image enhancement methods which show some similarity. Their ultimate goal is the recognition of sharp features when they are superimposed on a smoothly varying background. The basic idea, typical of pattern recognition techniques, is to take differences between the data and some functional of the data, in an attempt to single out the local anisotropy of the momentum \( p \), or crystal momentum, \( k \), distributions.

The Bristol method (later abbreviated as max-ent) is described in Dugdale et al, (1993), Dugdale (1993). It can be considered a two-step procedure: the first part of the method is a deconvolution routine which can also be used as a stand-alone image enhancement method. The code is designed to deconvolute the spectra from the smearing of the resolution function, \( R \), using the method of the 'Maximum entropy'
(see also Hoffmann et al, (1993), for the application of Maximum entropy to 2D-ACAR data).

In analogy with the statistical thermodynamics definition, the entropy of the data is defined as

\[ S = -\sum_{i}^{N} p_i \ln(p_i), \tag{4.12} \]

where \( p_i \) are the pixel matrix intensities.

In the Bristol code the spectra are iteratively corrected in order to minimize the chi-squared, defined as

\[ \chi^2 = \frac{1}{N} \left( \frac{D_{i,j} - F_{i,j} \otimes R_{i,j}}{\sigma_{i,j}^2} \right)^2, \tag{4.13} \]

with the additional constraint to maximize the entropy. In eqn 4.13 \( D_{i,j} \) are the experimental data and \( F_{i,j} \) are the trial functions (generated as described in Dugdale, 1993 and Gull 1985) convoluted with the resolution function \( R_{i,j} \). The code utilises empirical parameters in order to compromise between maximizing the entropy and being consistent with the data. The entropy constraint is particularly effective in reducing artefacts dependent on the noise which are often present in deconvolution techniques. However, care must be exercised in the search for the Fermi breaks because, obviously, the entropy of discontinuities such as those generated when the conduction band is interrupted at \( k_F \) (in a 3D-momentum distribution, a step function) is lower than that of the smooth function generated by the smearing of the breaks by the action of the experimental resolution. The result of the algorithm will therefore be to yield deconvoluted data closer to the ideal discontinuity within the limits of the entropy constraints.

In the two-step Arlington procedure (abbreviated as band-pass), the first step is to smooth the spectrum (equivalent to an increase of the entropy). The smoothing, obtained by convoluting the data with an equally weighted square array is realised with an extremely fast routine of the graphic-math package PVWAVE (or IDEAL) with a computing time which is weakly dependent on the size of the smoothing array and, in general, shorter than a few seconds also for 512 x 512 channels data matrices.

In the Arlington method the choice of the size of the smoothing array gives somewhat more flexibility in the search for the hidden FS topology which one is trying to reveal.

The second step of both methods is to take the difference between the raw data (actually corrected and folded) and the manipulated data (deconvoluted via maximum
entropy or smoothed). Figure 4.7 shows a schematic example of the band-pass method.

![Diagram showing smooth and subtract technique](image)

Fig. 4.7 A one dimensional schematic example of the smooth and subtract technique. The smoothed spectrum has been shifted downward to improve the visibility of the method. By taking the difference between the raw and smoothed spectra, the sharp features of the distribution will be enhanced at the expense of the smoothly varying features.

Both procedures can be defined as high pass filters, in that they eliminate the frequencies lower than those contained in the resolution function (max-ent) or in the smoothing array (band-pass). In the case of the band-pass method, the process of taking the difference of the spectra strongly enhances the noise. A third step is then a low pass filter which involves a light smoothing of the high passed data (the smoothing array chosen has size which are smaller than the FWHM of the experimental resolution). The band pass procedure is then simply

\[ M_{bp} = W_l \otimes (M - W_{n,m} \otimes M), \]  \hspace{1cm} (4.14)
where $M$ are the raw data, $W_{n,m}$ represents the smoothing array\textsuperscript{12}, $W_l$ is the square low-pass final smoothing and $M_{bp}$ are the enhanced data. Owing to the entropy constraint, the final smoothing is not required in the max-ent method. In the case of the band-pass procedure the author implemented a simple approximate and fast method (described in Appendix 2) of calculating the statistical errors of the filtered data which are used to produce the final errors of the LCW $k$-space density. The subsequent LCW summation then attains realistic error bars in the $k$-space density at $(k_x,k_y)$ points. The LCW intensities of neighbouring points exhibit, however, strong correlations within the range of the low pass $W_l$ smoothing array\textsuperscript{13}.

The usefulness of band-pass and max-ent depends on the fact that, whereas the modulations induced in the momentum distribution (and in the LCW folded data) by a non-constant positron wave-function are slowly varying, the FS discontinuities are high frequency signals. The possible contributions to the momentum density from annihilation of positrons trapped in defects and therefore sampling electrons whose momenta do not reflect the perfect crystal electron momentum distribution (see §3.1) should also generate low frequency signals superimposed on the FS breaks.

As band-pass and max-ent are particularly effective in highlighting the local anisotropy of the spectrum, the intensity of the distribution at sharp-edge points will be enhanced. The idea of taking the difference between the spectrum and some functional of the spectrum itself resembles the one applied in the radial anisotropy. One advantage of the new techniques is the much reduced extent of the correlations introduced between the data. As in the radial anisotropy matrices the correlation has a (radial) symmetry which is totally different from that of the BZ, the application of the LCW folding to those matrices may lead to unpredictable results. Owing to the band-pass (or max-ent) short range correlations (which have a symmetry which can be made consistent with that of the BZ) the LCW procedure becomes much more meaningful.

As an example, one can apply the band-pass to the 2D-LCW of a FEM sphere shown in figure 2.10 (neglecting noise and positron wave function effects). Figure 4.8 shows that the Fermi circle is the most prominent feature. However, the band-passed data will exhibit a decrease at the centre of the distribution where the 2D occupancy has the maximum and is, therefore, flat. One must therefore be wary of the possible artefacts which the procedure can introduce, especially in the 2D-ACAR LCW, where the integrated occupancy is function of the $(k_x,k_y)$ point. Again, a model FS is

\textsuperscript{12} In the Arlington recipe the sizes of the smoothing array are consistent with those of the experimental resolution. Often, one may prefer to choose the array sizes as a function of the physical quantities of the system being measured, being primarily the sizes of the BZ and of the FS topology one is after.

\textsuperscript{13} This introduces an inconsistency in the display of pixels carrying errors anomalously large with respect to the spread of the data correlated on a scale of $N$, where $N$ is the size of the smoothing array.
essential in the test of the reliability of the techniques described above. Looking at the difference between figure 4.8 and the original occupancy shown in figure 2.10 one might wonder what can be gained by such procedure. Its advantages can be understood if one superimposes a slowly varying background of much higher intensity on the FS signals. This is shown in the examples reported in O'Brien, (1994) and Dugdale (1993) and in the analysis of CeB$_6$, LaCu$_6$ and CeCu$_6$ data which will be reported in the next chapters.

![Fig. 4.8 The band-pass algorithm applied to the 2D projection of the FEM Fermi sphere (i.e. the inverted hemisphere shown in figure. 2.10). The rapid variation at $k_F$ shows how the technique highlights the rapid variations of the k-space occupancy. Note, however, the artefact at the centre of the distribution, where the occupancy is strongly distorted.](image)
5 Positron studies of CeB$_6$ and LaB$_6$

5.1 The hexaborides

The rare earth hexaborides (RB$_6$, R= La, Ce, Pr, Nd and Sm) provide an interesting subject for experimental and theoretical studies thanks to a variety of behaviours which can be ascribed to the special role played by their f-electrons. LaB$_6$ can be considered the reference non f-electron compound; CeB$_6$ is a Kondo lattice HF compound; PrB$_6$ and NdB$_6$ are local moment magnetically ordered metals and SmB$_6$ [defined as a "Kondo insulator", Aeppli et al (1992)] is a semiconductor with a narrow hybridisation band gap at the Fermi energy. As mentioned in §1.3 and §1.4, in CeB$_6$ the RKKY exchange interaction competes with the Kondo effect to produce a complex low-temperature magnetic phase diagram (Effantin et al, 1985). Two ordering transitions arise; a quadrupolar ordering at the temperature $T_q=3.2$K (phase II) and an antiferromagnetic ordering at the Neel temperature $T_N=2.3$ K (phase III). The low temperature behaviour of CeB$_6$ therefore differs from that of better understood dense Kondo-lattice systems (e.g. CeAl$_3$, CeRu$_2$Si$_2$, CeCu$_2$Si$_2$), where the hybridisation between the f-electrons and the conduction electrons leads to the wash-out of the f-electron magnetic moment below the Kondo temperature, $T_K$ (Fulde 1994, Cooper at al 1992). For CeB$_6$ $T_K \approx 5-10$ K according to Takase et al (1980)$^1$.

The dHvA and acoustic dHvA measurements (Ishizawa et al 1977, Joss et al 1987, Onuki et al 1989, Matsui et al 1993, Harrison et al 1993) of CeB$_6$, yielded similar FS features for CeB$_6$ and LaB$_6$. These experiments (at $T<T_K$) are therefore consistent with a model of the FS in which the f-electrons do not contribute to the Fermi volume. It is well known that the quantum oscillation experiments must be performed at very low temperature and under application of strong magnetic fields$^2$. As the dHvA measurements noted above were performed in phase II they can be fruitfully complemented by a 2D-ACAR measurement in the paramagnetic phase (I), at $T>T_K$.$^3$

Previous 2D ACAR results on the rare earth hexaborides [Tanigawa et al (1985),

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$^1$ The temperature dependence of the magnetic susceptibility of Ce$_x$La$_{1-x}$B$_6$ is reported in fig 1.3.

$^2$ The essential requirement for the dHvA effect to be visible is that $k_B T$, the thermal broadening of the FS, should be much less than $\hbar \omega_c = eB/m^*c$, the energy spacing between the Landau levels. Operating temperatures and B fields are usually $T=1K$ and $B=10T$. The high HF electron masses demand an increased ratio $B/T$ to fulfil the condition $B/T > (k_Bm^*c)/e$ so that millikelvin temperatures and stronger B fields (20-50 T) are required to detect quantum oscillations in HF systems.

$^3$ For normal metals the temperature effect of 30 K (2.5 meV) can be neglected as far the FS (defined at 0K) blurring is concerned but this might not be the case for HF systems.
(1989)] showed discrepancies with the results of theoretical calculations and with dHvA data. We therefore performed new high precision measurements on CeB$_6$. The 2D ACAR analysis was improved with the new filter procedures described in §4.4 which are designed to separate the FS signals from other structures present in the spectra [Biasini et al (1994)]. Here, the results are presented and compared with those obtained from measurements of the reference material LaB$_6$.

5.2 Fermi surface calculations

The unit cell of all the rare earth hexaborides (R-B$_6$), shown in figure 5.1, is simple cubic: it contains an R atom and a regular octahedron of six B atoms. The R atoms and the B octahedra form two interpenetrating simple cubic crystal lattices.

A very special feature of the rare earths is the fact that the radii of the elements shrink as the number of f-electrons increases. This is the famous "lanthanide contraction" [Kittel, (1986) p 403]. Consistent with this general rare-earth trend, the lattice constant, $a$, of LaB$_6$ ($a=4.156$ Å) is slightly larger than that of CeB$_6$, $a=4.139$ Å, (Langford at al 1990).

In § 1.4 it was mentioned how the FS predictions of a standard LDA band structure calculation for CeB$_6$ were in very poor agreement with the dHvA measurements mentioned in §5.1. The standard LDA calculation of Kubo et al (1989)$^4$ obtained a quite complex FS topology due to several bands, having mainly f-characters, crossing the Fermi energy $E_F$. The dispersion of those bands was $\sim 0.5$ eV, leading to band masses which were not in agreement with the low-temperature thermodynamic masses observed. The LDA spin polarised calculation [Gunnarson et al (1976)] of Langford

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$^4$ The band structure was calculated by means of the full-potential linearised augmented plane waves (FLAPW) method.
et al (1990) obtained FS sheets due to the majority spin bands (singly occupied), having mainly f-character, which were in no agreement with the experiments and FS sheets due to the minority spins, from bands having s, p and d characters, resembling the observed FS of LaB$_6$ (after a shift in the Fermi energy of more than 10mRyd). The authors speculated that the majority spin bands might not be seen by the dHvA experiments. However, the dHvA results of Harrison et al (1993) indicated that the up and down spin quasi-particles contribute equally to the Fermi volume and that the density of states at $E_F$ obtained from dHvA is in agreement with that obtained from the thermodynamic experiments.

With regard to other positron experiments on Ce systems, it is worth mentioning the 2D-ACAR measurements of Jarlborg et al (1989) on CeNi$_5$ and pure Ce (measured at room temperature), where a very poor agreement between calculated $k$-space density (via the LMTO band structure calculation) and measured LCW folded data was observed. In the case of pure Ce, an upward shift of 40 mRy of the f-like bands produced a considerable improvement in the agreement between calculation and experiment.

These results suggested that the standard LDA calculations had to be modified by some kind of adjustment which could account for an enhanced f-electron localisation. Recent band structure calculations [Norman et al (1986), Kubo et al (1992), Kitamura et al (1994), Itoh et al (1993)] were based on local models where the 4f orbitals were treated as incompletely occupied core states (abbreviated in the following as f-core-models), suggesting an FS topology for CeB$_6$ similar to that of LaB$_6$.

The latter consists of a set of nearly symmetrical, electron ellipsoids [Hasegawa et al (1977)] centred at the X points and connected by thick necks along the $\Gamma$- M ($\Sigma$) axes (Fig 5.2). The ellipsoids arise from a band having mainly La-5d character near the X points and B-2p character near the $\Gamma$ point. The conduction band, as shown in figure

![Fig. 5.2 The multiply connected ellipsoidal Fermi surfaces of CeB$_6$ (LaB$_6$). The ellipsoid radii assumed were 34% and 39% of the BZ for the XM and IX directions respectively. (Figure from Harima)](image-url)
5.4, exhibits a strong $k$-dispersion generating band masses which are lighter than the free electron mass $m_0$, in agreement with experimental results for the cyclotron masses $m^*$ ($m^* \sim 0.6m_0$, Onuki, 1989). In addition to this main FS sheet, a joint application of theory\(^5\) and experiments [Harima et al (1988)] established, in LaB$_6$, a second sheet of 12 smaller electron pockets along the $\Gamma$-M directions (shown by figure 5.3). This FS sheet was obtained by displacing the 4f level upward by 0.1 Ry\(^6\).

![Fig. 5.3](image1.png)

**Fig. 5.3** The 12 equivalent ellipsoidal electron pockets of LaB$_6$ (CeB$_6$) generated by the $\Sigma_4$ band. In the figure, ellipsoid sizes are not to scale.

![Fig. 5.4](image2.png)

**Fig. 5.4** The band structure of LaB$_6$ as calculated by Harima (1988). Note the $\Sigma_4$ band crossing the Fermi level, $E_F$, after the upward displacement of the 4f level. [(figure 5.3 and 5.4 from Harima (1988)]

The hypothesis of the second FS sheet solved previous inconsistencies regarding the shape and sizes of the ellipsoid necks. Recent acoustic dHvA measurements [Matsui et al (1993)] have detected frequencies corresponding to equivalent electron pockets in CeB$_6$ although they differ in size from those in LaB$_6$ (for a summary of the FS sizes for CeB$_6$ and LaB$_6$ as measured by dHvA, see Harrison et al, 1993).

The main sheet of the FS as calculated by Harima et al (1988) does not differ appreciably from a regular ellipsoid model FS. Figure 5.2 therefore shows a regular prolate ellipsoid's FS model. (The circular cross section of the ellipsoids is normal to the $\Gamma$-X direction.) Ellipsoid sizes were adopted from dHvA and acoustic dHvA

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\(^5\) via an FLAPW calculation

\(^6\) Though LaB$_6$ has no f-electrons, each eigenstate (expanded over the complete set of atomic eigenstates) has some f-character which contributes to the energy eigenvalue.
measurements of CeB₆ [Onuki et al (1989), Matsui et al (1993)]. The model was integrated along the experimental projection directions and convoluted with the assumed resolution function. Whereas the integration procedure along the highest symmetry axis <100> is obvious, along the <110> one must include the appropriate portion of BZ in order to reflect the \( k \)-space periodicity. The integration domain for the central slice (XX-ΓM-XX) of the obtained projected (110) occupancy is shown in figure 5.5.

Figures 5.6 and 5.7 show the resulting \( k \)-space electron occupancies in the first Brillouin Zone (BZ). It is worth noting that in the (100) projection the intensity of the four maxima surrounding the ΓX point (the 4 symmetric white areas at \( \sim(0.18, 0) \) a.u.), arising from the extent of the ellipsoid necks, coincides with the size of the BZ, if one neglects the effect of the experimental resolution (this results by applying a projection, to the 3D \( k \)-space density, as discussed in §2.5)⁷.

Fig. 5.6 Electron occupancies in \( k \) space obtained by integrating the Fermi surface model of figure 5.2 along the <100> direction. The result was convoluted with a resolution function of 0.084 a.u. corresponding to the average of the experimental resolutions along the two resolved momentum directions. The labelling describes the projected high symmetry points. In this and all following grey scale figures, white corresponds to high and black to low

Whereas in the case of LaB₆ the contribution to the \( k \)-space occupancy from the electron pockets, shown in figure 5.3, (as detected by acoustic dHvA) is negligible (after the convolution with the resolution function), it could be detected, by an ideal

⁷ All the BZ eigenstates along the integration direction are occupied in the \((k_x, k_y)\) regions corresponding to those maxima.
2D-ACAR experiment, in the case of CeB$_6$. Their effect is to soften the flat top character of the 4 maxima between $\Gamma X$ and XM in figure 5.6 and to distort the topology of the 2 main "mountains" at XX in figure 5.7. One can approximate the electron pockets by spheres having the same volume as that of the electron pockets observed by dHvA experiments (obtaining an overall radius $k_r = 5.4\%$ of $2\pi/a$) to assess their contribution. In figure 5.8 the occupancy of the model (convoluted with the experimental resolution) with and without the contribution of the electron pockets is shown on one slice of the (110) projection (parallel to the <1$\bar{1}$0> direction) where the effect is most visible.

We recently received from Dr Kubo the calculation of the electron occupancy of LaB$_6$, for integration along the <100> direction, modulated by the effect of the overlap of the electron-positron density (as described by eqn 2.55 of §2.7). The calculation yields the equivalent of folding the electron-positron momentum density back into the first BZ and will be abbreviated as LCW$_{th}$ (theoretical LCW). Details of the computational method (FLAPW) are described in Kubo et al (1989), (1992). Whereas to approximate the f-like bands as incompletely occupied core state severely alters the result of the calculation for CeB$_6$, in the case of LaB$_6$ (where the f-electrons are absent) the difference between a standard LDA and an f-core-model is very small (mainly affecting

\[ \text{Fig. 5.7: As figure 5.6 except that, here, the integral is along the <110> direction and has been convoluted with the asymmetric resolution of the spectrometer.} \]

\[ \text{Fig. 5.8 Upper curve: The CeB}_6\text{ (110) occupancy along one slice parallel to <1\bar{1}0> direction at 0.19 momentum a.u. from the centre of the LCW matrix, including the contribution of the electron pockets described in the text. Lower curve: same as the upper curve without that contribution.} \]
the small FS electron pockets). The LaB$_6$ LCW$_\text{th}$ is not severely distorted by the effect of the positron wave-function (with respect to a purely electronic occupancy). The results will be shown when discussing the experimental findings.

### 5.3 Experimental details

The CeB$_6$ sample was a single crystal of dimensions $3.6 \text{ mm} \times 2.9 \text{ mm} \times 2.4 \text{ mm}$, which displayed the typical Kondo effect in a resistivity measurement. The measurements were performed at a temperature of $\sim 30 \text{ K}$ and at a pressure of $\sim 10^{-6}$ torr. The estimated overall experimental resolution, obtained by combining the optical resolution (0.078 a.u.) with the intrinsic sizes of the positron source spot at the sample and the thermal motion of the positron (0.02 a.u.) for the $p_x$ and $p_y$ directions respectively (10% and 12% of the BZ size of CeB$_6$). We performed two measurements: the first, with integration along the $<100>$ crystal direction, to a total of $\sim 3.5 \times 10^8$ coincidence counts$^8$, the second, along $<110>$, to $1.1 \times 10^8$ counts. Data were accumulated in a $(256 \times 256)$ matrix with a bin size of $(0.1348 \times 0.1348)$ mrad$^2$.

The LaB$_6$ single crystal was similar in size to the CeB$_6$ one but the shape was of a rough semicircle with the diameter along the $<100>$ crystal axis. The measurements were performed at the same resolution, pressure, temperature and integration directions as for the CeB$_6$ experiment$^9$. The projection along the $<100>$ axis collected $\sim 2.1 \times 10^8$ coincidence counts. Because of experimental problems encountered, the second projection, along the $<110>$ axis, had to be stopped at $3 \times 10^7$ counts.

The spectra of both materials were subsequently MSF corrected, centred (see §4.1) and symmetrised, i.e. folded about the relevant crystal symmetry axes to further enhance the statistics (see §4.2).

### 5.4 Analysis of the anisotropies of the spectra

Because a display of the 2D ACAR data for a complex, multi-band system is seldom particularly illuminating, here the difference between the spectra and their angular average is shown (radial anisotropy). As described in §4.3, by this procedure one can eliminate the large isotropic part of the contribution originating from full valence bands and core electrons, and focus on the anisotropies in the spectrum arising mainly from the conduction electrons. The maximum magnitudes of the anisotropies (i.e. the difference between the maximum and the minimum of the anisotropy) in the twice-

---

$^8$The total counts reported for each acquisition refer to the "raw" data.

$^9$The acquisition was in a $288 \times 288$ bins matrix with the same bin size as for the CeB$_6$ measurement.
folded (with respect to the $p_x$ and $p_y$ axes) spectra for the (100) and (110) projections were 2.5% and 3.6% of the maximum, for the CeB$_6$ sample, and 3.9% and 5.7% of the maximum for the LaB$_6$ sample. For better comparison with the theoretical calculations and to increase further the effective statistics, the already twice folded (100) projection was folded again along the <110> symmetry axis. This removed the effect of the different resolution of the spectrometer along the x and y directions and restored the appropriate 4-fold symmetry. Figures 5.9, 5.10, 5.11 and 5.12 show the resulting anisotropy parts of the thrice-folded (100) and twice-folded (110) projections for CeB$_6$ and LaB$_6$. The anisotropies of the compounds display a very similar form in the corresponding projections. (To aid comparison, the borders of the projected first BZ in a repeated zone scheme are shown in the figures mentioned above).
Figure 5.9: Anisotropy of the measured and symmetrised (see text) momentum density of CeB₆ for integration along the <100> direction. The spectrum was smoothed with an equally weighted smoothing array of 0.67 × 0.67 mrad² (1 mrad = 0.137 a.u.). The borders of the projected first BZ in a repeated zone scheme are shown. The symmetrized structure present in the high momenta (10-15) mrad region (absent in figure 5.10) is due to a small artefact of known reason.

Fig. 5.10 As figure 5.9 for LaB₆ for the (100) projection

<table>
<thead>
<tr>
<th>Compound</th>
<th>Folding</th>
<th>dynamic/max (%)</th>
<th>dynamic/max (1^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeB₆ (100)</td>
<td>twice</td>
<td>2.5</td>
<td>8</td>
</tr>
<tr>
<td>CeB₆ (100)</td>
<td>thrice</td>
<td>1.8</td>
<td>9</td>
</tr>
<tr>
<td>CeB₆ (110)</td>
<td>twice</td>
<td>3.6</td>
<td>10</td>
</tr>
<tr>
<td>LaB₆ (100)</td>
<td></td>
<td>3.9</td>
<td>15</td>
</tr>
<tr>
<td>LaB₆ (100)</td>
<td>thrice</td>
<td>3.5</td>
<td>17</td>
</tr>
<tr>
<td>LaB₆ (110)</td>
<td>twice</td>
<td>5.7</td>
<td>9</td>
</tr>
</tbody>
</table>

Tab 5.1 Listing of the dynamic of the radial anisotropy in the two projections of CeB₆ and LaB₆.
In table 5.1 the dynamics of the different experiments are listed in terms of their ratio to the statistical error of the maxima. It appears that LaB$_6$ displays a stronger radial anisotropy. (The lower statistics of the LaB$_6$ (110) projection explains the less good figure of its ratio dynamic/max$^{1/2}$.) The stronger anisotropy of LaB$_6$ will be a recurrent issue in the data analysis.

In both projections, there are features reflecting the underlying (projected) BZ symmetry. The four minima (dark areas) at (2.9, 2.9) mrad in figures 5.10 and 5.9
reflect very well the lows shown at the corner of the projected Brillouin zone (MR) in
figure 5.6, which are expected from the FS model.

Other features agree with those of the radial anisotropy of a simulated spectrum
(figure 5.13). In the simulated spectrum, the contribution of the conduction electrons
was generated by modulating the appropriately projected electron occupancies (as
defined by the Fermi surface model of figure 5.2) in a multiply repeated zone scheme
by a Gaussian obtained by a fit of the experimental data. In the simulation,
appropriate consideration was
given to the symmetry group
character of the conduction band
and the associated contribution
(or lack of it) to $\rho(p)$, as
discussed in §2.8. A further
Gaussian function represented the
contribution from the filled bands
(which does not, however,
contribute to the anisotropy when
having radial symmetry). No
provision was made for
momentum wave function
anisotropies. The FS ellipsoid
sizes of the model were taken
from the dHvA experimental
values for CeB$_6$. The small
differences between the sizes of
the ellipsoidal FS of CeB$_6$ and the
corresponding ones for LaB$_6$,
(few percents of the BZ size, as
detected by dHvA) could certainly not be detected by this analysis.

The model spectrum featured both the observed minima at (2.9, 2.9) mrad and the
maxima at (0 ,4) and (4, 0) mrad. The further highs at (5, 5) mrad were less evident.
Nevertheless, the overall correspondence with the experiment was surprisingly good
for the (100) projection. One might think that the agreement between the simulation
and the experimental anisotropy was principally due to the symmetry of the BZ which
was forced into the simulation by repeating the electron occupancy according to the
reciprocal lattice structure of the system.

To check this possibility, the same simulation, using an incorrect FS model
(ellipsoids of different sizes and not connected by necks) and the same BZ topology,
was performed. The resulting radial anisotropy (RA) had no resemblance at all to the experimental RA. As regards the fact that the second series of highs (located at ∼(5, 5) mrad) in the RA of this "toy model" (figure 5.13) clearly have lower intensity than the experimental ones (shown in figures 5.9 and 5.10) one has to bear in mind that the (Gaussian) modulation function, which essentially transferred the simulation from \( k \)-space to \( p \)-space, was obtained by a fit of the overall momentum distribution. If the band generating the Fermi surface had (for example) a higher d-like character than other full bands, its high momentum components (HMC) would be enhanced, the approximating modulation Gaussian should be broader and clearly the second highs of the anisotropy of the model would be enhanced. Finally, one should realise that the empirical Gaussian function adopted to modulate the theoretical occupancy in a multiply repeated BZ scheme does not reflect the normalisation requirement of the coefficients of the expansion in plane waves of the \( k \)-electron eigenstates which generate the occupancy's HMC (see eqn 2.42, §2.6). In general, the normalisation is altered by the effect of the positron wave function, which reduces the LCW folded \( k \)-density by a factor which is proportional to the overlap integral of the positron density with the density of a given \( k \)-electron eigenstate (see eqn 2.55 in § 2.7). The application of the LCW procedure to this kind of simulation (not performed here) would introduce an unrealistic \( k \)-functional dependence.

In the (110) projections of both compounds (figures 5.11 and 5.12) the observed highs at (0, 7.5) mrad and the lows at (7, 0) mrad are not consistent with higher momentum images of the FS and must therefore be merely consequences of electron wave function momentum anisotropies. However, the topology of the anisotropies in the first BZ, with shallow minima at the centre of the distribution and at the corners of the zone, is not inconsistent with that of the theoretical (110) occupancy (figure 5.7). One can try to obtain further information by studying the difference between the corresponding projections for the two compounds when they are normalised to the same number of counts. From the definition of \( e^+ - e^- \) momentum density given by eqn 2.27,

\[
\rho^{e^+e^-}(p)dp = \frac{\pi r_{oc}^2 c}{(2\pi)^3} \sum_{k_{oc}} \left| \int dx \exp(-ip\cdot x)\psi^+_k(x)\psi^-_k(x) \right|^2 dp,
\]

it turns out that if the positron wave function is the same in the two compounds (CeB\(_6\), LaB\(_6\)), the difference CeB\(_6\)-LaB\(_6\) will be the momentum distribution of the f-electrons sampled by the positron. The positron wave function is the same if the crystal potential sampled by the positron is the same. This would be obtained if the f-electrons were sufficiently localised to shield the charge excess of the extra-proton of the Ce nucleus. As the positron wave-function calculations of Kubo et al (1989) seem to confirm that the positron tends to reside away from the R (Ce or La) sites, the
previous assumption is plausible and consistent with the f-core model. Obviously, if the overlap integral between f-electrons and positron were negligible the difference between the two momentum distributions should vanish. The difference between the momentum spectra for the two compounds when they are normalised to the same number of counts showed that the spectrum of CeB₆ was higher in the centre (p=0) with minima at intermediate (1 a.u.) values of p. The almost isotropic difference CeB₆-LaB₆, is shown in figure 5.14 after being radially averaged to improve its statistics. The conical shape of the peak (with a FWHM≈6.5 mrad) is not typical of a momentum distribution in electronic bands. If one assumes that the difference between the two projections is mainly due to the f-electrons, the maximum at $p=0$ is quite surprising as an f-electron should possess momenta higher than valence s,p,d electrons as discussed in §2.3 and shown for Gd in figure 2.2 [see also the analysis of CeCu₆ in the next chapter].

The meaning of such positive difference distribution at $p=0$ is not clearly understood. It is well known that the momentum distribution of electrons in open-space defects is peaked at $p=0$ (as discussed in §3.1, a positron can easily get trapped in voids or dislocations). The lifetime experiments performed on the two compounds could not, however, confirm or disprove that the difference peak was related to defects. Moreover, there is some evidence, listed in Appendix 3, that the high intensity at $p=0$ of the CeB₆ (100) projection might be caused by experimental artefacts (due possibly to annihilations outside the sample). The fact that the radial anisotropy of the two compounds was very similar (though of smaller dynamic in the case of CeB₆) is supportive of a difference which is due to some isotropic contribution and is independent of the FS of the compounds.

We further investigated the CeB₆ and LaB₆ (100) projections by monitoring the local anisotropy (band pass, §4.4) of the raw data of the spectra. The presence of a peak at $p=0$ in the band-pass data of CeB₆ (not shown), absent in the corresponding case for LaB₆, ruled out the possibility that the peak at $p=0$ in the difference spectrum
between the folded and corrected CeB₆ (100) and LaB₆ (100) (shown in figure 5.14) was due to artefacts arisen in the standard data processing.

5.5 LCW analysis and filtering techniques

5.5.1 LaB₆

In 2D ACAR studies of metallic solids the widely discussed LCW transformation is probably the most quantitative way of checking band structure calculations and theoretical models. Figures 5.15 and 5.17 show the LCW processed data for the (100) and (110) projections of LaB₆.

In case of the (100) projection, the experimental LCW data (lower part of figure 5.15) are compared to the electron-positron theory of Kubo (upper part of figure 5.15). In figure 5.16 the two major slices of the (100) occupancy, XM-Γ-XM and MR-XM-MR are compared with the electron-positron theory.

As one can see, the agreement between data and theory is quite satisfactory. However, the dynamic of the experimental LCW matrix (see §4.3) is 4.7%, equivalent to ~45 times the average error of the LCW intensity (for the twice folded data), as opposed to 6.6%, of the theory. Another discrepancy consists in the satellite structure, near to the maxima related to the ellipsoid necks, which appears in figure 5.16, at 0.07 a.u. from the centre of the LCW matrix (at channel ±4 of the kᵧ=0 slice). The satellite peaks are present in both the kₓ and kᵧ directions (although of different intensities) prior to the symmetrisation about the <110> axis (performed in figure 5.16) and, therefore, do not seem to be due to an experimental artefact. It is very unlikely that they are related to the small ellipsoidal FS pockets (from the Σ₄ band)

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10 If one defines the statistical uncertainty as 2 times the error δN (the uncertainty on each intensity N is N±δN), all the dynamics referenced are obviously reduced by a factor 2
because of their sizes and positions. The discrepancies could possibly be attributed to electron-positron interaction effects not properly accounted for by the theory [Kubo (1995)].

As the LCW\textsubscript{th} data were not very different from the purely electronic occupancy as calculated by Harima (1988), one could evaluate the Fermi volume under the assumption of a constant positron wavefunction. In this case, according to §2.7 and as shown in Fig 2.10, the contribution of the full bands is simply the constant given by the minimum of the LCW matrix. By recalling that the intensity of the four maxima surrounding the centres of the (100) LCW projection of figure 5.15 corresponds to the sizes of the BZ, the following steps can be performed:

1. Subtract the minimum from the LCW folded data.
2. Re-scale the LCW matrix so that the intensity of the 4 maxima mentioned above corresponds to the size of the BZ modulated by the smearing effect of the experimental resolution function (in our set-up the peaks are decreased to 96% of their original value). The re-scaling factor is, therefore, the ratio of the "decreased" size of the BZ to the value obtained by fitting the experimental maxima with a Gaussian (to avoid scatter due to noise and artefacts).
3. Compute the ratio $R$ of the total integral of the re-scaled matrix to the volume of the BZ.
4. The obtained ratio is $R=0.55\pm0.02$. The error is estimated from the uncertainties in the minimum subtracted from the LCW matrix and the total integral via the re-scaled statistical errors.

The same procedure applied to the (electron-positron) LCW\textsubscript{th} data, from Kubo, and the electronic theoretical occupancy, from Harima, yielded ratios of 0.53 and 0.49, respectively. Owing to the simplicity of the topology of LaB\textsubscript{6} this result can be interpreted immediately: only one band crosses the Fermi level (the contribution of the small electron pockets to the Fermi volume is negligible, being less than $10^{-4}$ of the BZ volume). As LaB\textsubscript{6} is an "uncompensated metal" (i.e. it has an odd number of electrons) and, assuming spin degeneracy, electrons fill the electronic bands two by two, the only conduction band will be semi-occupied (50% of the BZ is occupied).
The value obtained for the ratio $R$, $R=0.55\pm0.02$ suggests that in LaB$_6$ the positron wave-function does not play a significant role and supports a theory (LCW$_{th}$) yielding results not dissimilar to those of a purely electronic occupancy (i.e. assuming a constant positron wave-function).

The lower part of figure 5.17 shows the result of the LCW procedure for the (110) projection. In the absence of the electron-positron calculation, the LCW data are compared with the purely electronic occupancy, as calculated by Harima (1988), shown in the upper part of figure 5.17. Within the limits of the low statistical precision the agreement between data and theory is again quite satisfactory.

5.5.2 CeB$_6$

Figures 5.18 and 5.19 show the LCW processed data of the (100) and (110) projections for CeB$_6$. 

*Fig. 5.17* Upper part: Theoretical electron occupancy for the (110) projection of LaB$_6$, convoluted with the asymmetric experimental resolution. (Fermi surface calculation by Harima, 1988)

Lower part: Experimental LCW k-space density for the same direction. The BZ and labelling is as in figure 5.7. (Smooth: 2(-3)a.u.$^{-1}$).
The dynamics of the LCW matrices are 3.7% (∼60 times the statistical error) and 2.6% (∼20 times the statistical error) for the (100) and (110) projections, respectively.

The dynamics of the LCW matrices are 3.7% (∼60 times the statistical error) and 2.6% (∼20 times the statistical error) for the (100) and (110) projections, respectively.
The agreement with the theoretical data based on the f-core model is certainly only partial and consists essentially of the lows at the corners of the BZ (points labelled MR) in the (100) projection, the lows at XM and the saddle point at ΓM in the (110) projection. The predicted low at ΓX and surrounding four highs in the theoretical (100) projection (figure 5.6) are missing in the experimental corresponding data. It should be noted that the (110) projection shows a better agreement with the theoretical data of figure 5.7. The maximum in the centre (k=0) of the experimental CeB₆ (100) occupancy, in figure 5.18, is also incompatible with the recent fully relativistic spin polarised LMTO calculation performed by Suvasini et al (1995), mentioned in §1.4, with the f-electrons treated as itinerant. The main modification of that calculation with respect to the f-core model, is that additional singly occupied bands, having high f-character, cross the Fermi level, thus contributing to the Fermi volume. However, the resulting k-space (100) occupancy (not shown here), convoluted with the experimental resolution, also does not yield a maximum at the centre (k=0) of the projected BZ, but displays a structure with four highs located approximately in the same position as in the corresponding occupancy obtained from the f-core model (shown in figure 5.6).

One could conjecture (Biasini et al 1994) that the difference between the experimental and theoretical pictures is due to the modulation in k-space of the full bands generated by a non-uniform positron density. However, in the light of the recent LCW analysis on LaB₆, this explanation is less credible. In that case the positron wave-function effect could be considered only as a relatively small perturbation to the electronic occupancy.\footnote{One could otherwise speculate that the discrepancy leading to the double peaks in the ΓX-XM direction (in the (100) LCW of LaB₆ as shown in figure 5.16) is present also in CeB₆ but to much greater extent (and closer to the centre of the distribution), so as to obscure completely the main features of the integrated Fermi volume.} If the positron wave-function can be approximated to a constant, the f-electron contribution to the LCW folded data should be constant, assuming the f-core model (i.e. for a full f-band). Moreover, the fact that the f-band has a very narrow width does not support a strong k-dependent overlap integral between the f-electrons and the positron even for a non constant positron wave function. This can be understood by showing the contribution of the f-band to the k-space density $\rho_{LCW}^f(k)$, (see eqn 2.55),

$$\rho_{LCW}^f(k) = const \sum_n \theta(E_F - \varepsilon_{k,f,n}) \times \int d^3 r \left| \psi_{\varepsilon,k}^f(r) \right|^2 \\ \frac{\partial}{\partial k} \rho_{\varepsilon,k}^f(r)^2,$$

where the meaning of the symbols is the same as in eqn 2.55. In the f-core model, the energy eigenvalues $\varepsilon_{k,f}$ are almost degenerate (and less than $E_F$). Consequently, as
the eigenstates of the f-band can be viewed as atomic orbitals $\psi_k^f \approx \psi^f$, the result of the folding, $\rho_{LCW}^f (k)$, turns out to be almost $k$ independent.

The difference CeB$_6$-LaB$_6$ and the LCW of CeB$_6$ (100 projection) are both consistent with the fact that a high intensity isotropic contribution with a maximum at $p=0$ is superimposed on the FS signals. As another test of this hypothesis we applied the LCW transformation to an isotropic approximation of the experimental momentum spectrum. This comprised two Gaussian components having a FWHM of 9.8 mrad, (35% intensity) and 6.74 mrad (which is the FWHM of the peak observed in the difference distribution shown in figure 5.14), respectively.

The results (shown in figure 5.20) were very similar to those of the experimental LCW for the (100) projection and had a total amplitude variation of 4.8%.

We therefore applied the band-pass procedure (described in §4.4) to the momentum data prior to the LCW analysis. The spectrum to be filtered was initially smoothed (here with a simple equally weighted smoothing array of $15 \times 15$ channels, or $2. \times 2.$ mrad$^2$. The size of the smoothing array chosen was of the order of the distance (along the $k_x=0$, or $k_y=0$, direction) between the 4 peaks of the (100) projection shown in figure 5.6. The final light smoothing, applied to the difference spectrum to suppress the noise, had sizes of $(0.4 \times 0.4)$ mrad$^2$. The LCW spectra obtained from the filtered momentum spectra are shown in figures 5.21 and 5.22. The dynamic of the LCWs, considerably reduced by the effect of the filtering but still quite distinctly above the noise, is, in both cases, $\sim 13$ times the average statistical uncertainty of the LCW intensity. The improvement in the agreement between filtered experimental data and theory is clear: note, in particular, in the (100) spectrum (figure 5.21, lower part), the appearance of the predicted central plateau and the 4 surrounding highs (compare with the upper part of figure 5.21). These features are insensitive to the particular choice of the smoothing parameters. We assessed, for the (100) case, the effect of a variety of differently sized averaging masks with dimensions varying from 10 to 22 channels and obtained, in all cases, a very similar picture. A further test was performed on the unsymmetrized (100)
projection and the patterns that emerged after filtering were, increased noise and
decreased symmetry apart, consistent with those in the fully processed data. In a final
test the "maximum entropy" enhancement technique described in §4.4 was employed
(Dugdale and Alam, 1994). The result was the same. It should be stressed again that
the fact that (f-core) theory and band-pass filtering are in such good agreement
follows from the fact that a smooth isotropic contribution (discussed above) is
superimposed on the signals which are shown in Figures 5.21 and 5.22.

Figure 5.21 **Upper:** Electron occupancy of the (100) projection of CeB\textsubscript{6} from the geometrical
model described in the text, convoluted with the experimental resolution. Ellipsoid sizes are from
tab 5.2 **Lower:** Experimental LCW filtered (see text) k space density for the same integration
direction. The BZ and labelling is as in figure 5.6. (Smooth=3(-3)a.u.\textsuperscript{2})

In spite of the improvement in the agreement between 2D-ACAR "band passed"
data and the model predictions, discrepancies remain. In figure 5.22 (compare the
experimental data in the lower part with the model in the upper part) they are the local
slight minima at XR and XX and the fragmented highs around XX. The minima are,
almost certainly, an effect of the filtering process. They are typical of the filter
induced distortions as described by O'Brien, (1995) (see also figure 4.8 in §4.4).

We have deduced from an examination of the band-pass of the corresponding (110)
LCW of the original unsymmetrised data that the fragmentation of the highs at XX is
most probably a manifestation of symmetrised noise. In figure 5.21 (compare the
experimental data in the lower part with the model in the upper part) a further
discrepancy lies in the shape of the contour lines around MR, showing a distinct, sinuous pattern located at \(\sim(0.1, 0.35)\) a.u. (West, 1994 %). Such a deviation from the expected ellipsoidal form of the major Fermi surface sections cannot be explained.

The remaining predicted 12 small Fermi surface sections (centred approximately midway between \(\Gamma\) and M, as shown in figure 5.3) are inappropriately placed to account for this structure. The distortion is not typical of a filter artefact (O'Brien, 1995) and (after analysis of the unsymmetrized data) could not be related to symmetrized noise (being present also in the filtered, unsymmetrized data).

Finally, by supposing that the filtering described has highlighted the topology of the FS of CeB\(_6\), notwithstanding the residual uncertainties, we thought it appropriate to estimate, from our data, the radii of the main FS ellipsoids. In both projections (but more transparently in the (100) one) there is, in fact, enough information to deduce both radii of the ellipsoids, if the FS comes from a regular ellipsoid model. The two slices of the (100) occupancy at \(k=0\) and \(k=\pi/a\) of figure 5.23 show the second-order discontinuities which mark the size of the major ellipsoid semi-axis, \(\alpha_m\), and the minor ellipsoid semi-axis, \(\alpha_s\), in the case of a theoretical model un-convoluted with the experimental resolution. As the effect of the resolution smears these discontinuities we decided to compare the FWHMs of the band-pass data and of the model along the two mentioned slices of figure 5.23, using the following method: We first derived a figure for the ellipsoid diameter in the square Brillouin zone face containing the X, M and R points (see figure 5.2) through a simulation of the appropriate section (MR–XM–MR) of the filtered LCW for the (100) projection (figure 5.21). In that simulation, model occupancies with ellipsoids of different minor diameter were convoluted with the experimental resolution and the diameter adjusted until the FWHM of the section matched that of the experimental data. A similar model-
experiment comparison of the FWHM profile of the MM–XR–MM section of the (110) projection (figure 5.22) provided the same result. Finally, the ellipsoid major diameter (along the direction Γ to X in the Brillouin Zone) was determined by varying the major diameter (while keeping the minor diameter at the value deduced earlier) until the model and experimental profiles were in closest accord. Table 5.2 lists the ellipsoid parameters deduced.

As a consistency check one can compute the total (3 full ellipsoids) occupied fraction of Brillouin zone, neglecting the distortion due to the necks. The result (0.50±0.03), interestingly, is much closer to the ideal 0.5 than that deduced from the dHvA results (Harrison et al 1993). This figure is not altered by the addition of the further 0.01 for the volume of the suggested 12 small pockets along Γ–M (Harrison et al 1993).

![Figure 5.23](image)

**Fig. 5.23** The two BZ slices of the (100) model occupancy of CeB$_6$ at $k_y=0$ and $k_y=\pi/a$ show the discontinuities which define the sizes of the major semi-axis, $\alpha_m$ (from the label up to the border of the BZ) and of the minor semi-axis, $\alpha_s$ (from the label up to the centre of the slice) of the ellipsoidal FS. Note the flat top of the maxima of the $k_y=0$ slice due to the extent of the ellipsoids necks.

<table>
<thead>
<tr>
<th>Direction</th>
<th>% of $2\pi/a$</th>
<th>Evaluated through section</th>
<th>dHvA: % of $2\pi/a$</th>
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<tbody>
<tr>
<td>X-M</td>
<td>65±2</td>
<td>MR - MX - MR</td>
<td>68</td>
</tr>
<tr>
<td>Γ-X</td>
<td>75±2</td>
<td>MX - ΓX - MX</td>
<td>78</td>
</tr>
</tbody>
</table>

**Tab 5.2** Diameters of the FS ellipsoids of CeB$_6$, in percent of the BZ size, derived as described in the text. The values are compared with the dHvA results reported in Harrison et al, (1993).

To assume that the ideal result corresponds to a Fermi volume contributed by a semi-occupied band in the same manner as was obtained for LaB$_6$, implies the following: the f-core-model follows the application of the standard rare-earth-like picture, where the 4f orbitals are viewed as local atomic-like orbitals, regardless of the fact that the atomic 4f shells are only partially filled. In a band description, one can imagine that the rare earth bands split into two narrow parts: one fully occupied well below the Fermi level (in the case of CeB$_6$, the band is singly occupied) and the other
(unoccupied) pushed above the Fermi level by the Coulomb repulsion\textsuperscript{12}. The conduction band, being forced by the f-core model to have no f-character at all, can still be considered as doubly occupied (the energy eigenvalues of that band are degenerate with regard to the spin quantum number). When half-full, it will therefore accommodate one electron per formula unit\textsuperscript{13}.

On completion of the measurements of CeB\textsubscript{6} the picture which could be drawn from our experiments was that, at 30K, i.e. in the paramagnetic phase, the observed momentum distribution and the related \textit{k}-space densities were consistent with theoretical models of the Fermi surface obtained by treating the f electrons as localised. This conclusion was reached under the assumption that the adopted band-pass filter procedure was primarily eliminating the effect of a non uniform positron density from the momentum data. After the measurements of LaB\textsubscript{6}, the origin of the contribution which is filtered by the band-pass procedure is less clear, but possibly due to annihilations outside the sample (see Appendix 3). Without doubt, the LCW filtered data of CeB\textsubscript{6} and the radial anisotropy provide clear support of the f-core model. From the filtered spectra, our quantitative assessments of the main features of the Fermi surface of CeB\textsubscript{6}, (at 30 K) turn out to be in good agreement with those obtained by other experimental techniques (at T< T\textsubscript{K}). Further comments will be given in the concluding remarks, after the report of the measurements of CeCu\textsubscript{6} and LaCu\textsubscript{6}.

\textsuperscript{12} The validity of this rare-earth-like description of the f-bands in the case of HF compounds is certainly the object of discussion. Nevertheless, it is consistent with the FS results and the low temperature behaviour of the magnetic susceptibility of CeB\textsubscript{6}.

\textsuperscript{13} Note that if the f-electrons did contribute to the Fermi volume, CeB\textsubscript{6} would be a compensated metal, as the number of conduction electrons per formula unit is even, i.e. a metal with an equal volume of electrons and holes FS pockets.
6 Experiments on CeCu₆ and LaCu₆

6.1 The HF system CeCu₆

In the previous chapter we reported 2D-ACAR (above the Kondo temperature, \(T_K\)) and dHvA (below \(T_K\)) experiments on the 4f electron HF compound CeB₆, which undergoes magnetic ordering transitions upon cooling. The dHvA experiments yielded a FS topology very similar to that of the reference non-f compound LaB₆. Positron annihilation 2D ACAR experiments confirmed those findings. A localised f-electron model seemed therefore to be appropriate to account for the electronic structure of CeB₆. Similar conclusions were drawn from 2D-ACAR experiments on CeSb (Itoh et al. 1993). CeCu₆ is one of the most investigated HF compounds. It is regarded as the typical dense Kondo lattice material and displays one of the largest known low temperature specific heats \(\gamma \approx 1.6 \text{ J/mol K}^2\), (Stewart et al. 1984). Unlike CeB₆ or CeSb, it does not order magnetically but seems to approach a non-magnetic ground state, as inferred by specific heat measurements down to 0.05 K (Amato, 1987). The low temperature behaviour of the resistivity per mole cerium of CeₓLa₁₋ₓCu₆, shown in figure 6.1, has, for \(x>0.9\), the form \(\rho = \rho_0 + AT^2\), which is characteristic of Fermi liquid systems (see §1.1). The Kondo temperature for CeCu₆ is evaluated to be about 4–5 K (Onuki et al. 1987). The low temperature magnetic susceptibility, shown in figure 6.2, deviates from the Curie-Weiss law and tends to flatten out below 1K, reflecting the disappearance of the local moment due to the Kondo effect (Onuki et al. 1987). This suggests that in CeCu₆ the f-electrons should contribute to the Fermi volume. On the other hand, neutron scattering studies (Aeppli 1986) reveal that antiferromagnetic correlations develop below 1K, indicating the proximity of this HF compound to magnetic order. By alloying CeCu₆ with a heavier (Ag or Au) noble metal one can, in fact, obtain magnetic ordering as the increase in the lattice constant and in the Ce-Ce distance, by reducing the hopping probability of the f electrons.
favours the stability of local magnetic moments (Germann (1989), Gangopadhyay, (1988), Pietrus et al (1995), for pressure experiments in CeCu$_{6-x}$Au$_x$). CeCu$_6$ therefore seems to be a prototype system where the ground state depends critically on the competition between magnetic inter-site interaction, i.e. RKKY exchange interaction, and on-site Kondo exchange interaction. The appropriate description of the CeCu$_6$ 4f electrons, as either localised or itinerant, is still an open question as none of the calculations performed so far have shown agreement with experimental work (Chapmann et al 1990, Marabelli et al 1989, Harima et al 1992). Reasons of this discrepancy can also be due to its extremely complicated low-symmetry crystal structure: CeCu$_6$ is a 4 formula unit orthorhombic system where every Ce atom is surrounded by a cage of 19 Cu atoms (Cromer et al 1960). We therefore performed 2D ACAR experiments on CeCu$_6$ above $T_K$ and compared the results with those obtained for the reference non-$f$ standard material LaCu$_6$ in an attempt to contribute to the understanding of the electronic structure of CeCu$_6$ (Biasini et al, 1995).

6.2 Fermi Surface calculations

The 4 formula unit primitive cells of LaCu$_6$ and CeCu$_6$ at low temperature are monoclinic with lattice parameters differing by a few percent (Cromer et al 1960, Asano et al 1985). The CeCu$_6$ structure is orthorhombic at room temperature but undergoes a monoclinic transition at 200 K. In both compounds the departure from the orthorhombic structure is however very small, with a deviation from the 90° between basal plane and c axis of only $\sim 1.4°$. In the data analysis this small distortion was neglected and the orthorhombic lattice assumed.

\textsuperscript{1} To date, the departure of the traditional low temperature behaviour of the specific heat $C / T = \gamma$ to $C / T \propto -\ln(T / T_o)$ for CeCu$_{5.93}$Au$_{0.07}$ was taken as a sign of non-Fermi-liquid behaviour in that system. (Löhneysen, 1995)
A recent electronic structure LAPW calculation (in LDA) for LaCu$_6$ (Harima et al. 1990) predicted a complex many-sheet FS topology originating from the crossing of the Fermi level by four bands having mainly Cu 4s character. LaCu$_6$ is a compensated metal, i.e. possessing an equal volume of electrons and holes FS pockets. The electronic specific heat coefficient, $\gamma=6.4$ mJ/K$^2$ mol, calculated from the total density of states (Harima 1990), was in agreement with the experimental value, $\gamma=8$ mJ/K$^2$ mol, obtained by thermodynamic measurements. Although the extremal FS cross sections observed in dHvA (Onuki et al. 1986) agreed with some of those derived from the calculated FS, the sections predicted by the theory outnumbered those actually observed. The 2D $\mathbf{k}$-space electron density in the first BZ resulting from the theoretical multi-sheet FS is presented in figure 6.3. The theoretical 3D $\mathbf{k}$-space electron occupancy was integrated along the experimental $<001>$ projection direction and convoluted with the estimated experimental resolution function. After integration, the main features which remained quite evident consisted of cylindrical structures at the XU points and lows of small size at the corner of the BZ (RS points).

In the case of CeCu$_6$, LMTO (Chapman et al. 1990) and LAPW
(Harima et al. 1992) electronic structure calculations compared unsatisfactorily with the few dHvA experiments reported (Reinders 1987, Chapman et al. 1990). LMTO calculations were performed including the contribution from the Ce f-electrons as either band or core states. Both cases displayed a poor agreement with the experiments. The more sophisticated and computationally demanding LAPW calculation reported here was performed using the same standard LDA method discussed above for LaCu$_6$. The Ce f-electrons were treated therefore as itinerant (Harima et al. 1990). The topology of the FS was simpler than that of LaCu$_6$. The resulting 2D $k$-space density is displayed in figure 6.4 after the integration of the 3D $k$-space electron occupancy along the $c$ axis and its convolution with the experimental resolution. The main structure remaining after the integration is ridge-like along the $\Gamma Z$ - $X U$ direction.

6.3 Experimental details

Both samples were electroetched before the measurement and oriented with their $c$ axis along the integration direction selected by the spectrometer. This choice of alignment was suggested by the large size of the crystal unit cells along this direction ($c \approx 10.2 \, \text{Å}$), thus resulting in an almost two-dimensional BZ, and by the topology of the calculated FS.

Due to the small size of the projected BZ, it was decided to perform the measurements at the unusually small calibration of 0.0674 mrad/channel in a matrix of 512 $\times$ 512 channels. The ultimate resolution of the spectrometer, obtained combining the optical resolution with the intrinsic sizes of the source spot at the sample and the thermal spread of the positron, corresponded, in the case of the LaCu$_6$ sample, to 0.58 and 0.92 mrad for the $p_x$ and $p_y$ directions respectively (11.5% and 31% of the projected BZ sizes). Owing to the smaller sizes of the CeCu$_6$ sample, the estimated resolution on the $p_y$ direction was better than for LaCu$_6$ (0.78 mrad). The overall resolution for the CeCu$_6$ experiment corresponded to 11.5% and to 26% of the projected BZ for the $p_x$ and $p_y$ directions respectively.

The two measurements were performed at a temperature of 30 K and at a pressure of $10^{-6}$ torr. The resulting spectra, containing $3.3 \times 10^8$ and $1.3 \times 10^8$ (raw) counts for the LaCu$_6$ and CeCu$_6$ sample, respectively, were subsequently MSF corrected and symmetrised.

6.4 Results and discussions

The large number of valence bands (full and roughly isotropic) overwhelm the momentum density of the conduction electrons in such complex systems and render
the spectra quite featureless. Therefore, here again, only the RA (radial anisotropy) of each spectrum is displayed. The resulting anisotropies are shown in figures 6.5 and 6.6. The dynamic range of the two anisotropies is similar (4.4% of the maximum for CeCu$_6$ and 3.3% of the maximum for LaCu$_6$) and is equivalent to ~ 8 times the statistical uncertainty of the maxima. The anisotropies, more pronounced than in previous (unpublished) experiments on CeCu$_6$ (Manuel 1994) also have a very similar form. In both, there are features reflecting the underlying BZ symmetry, although those for LaCu$_6$ are somewhat better defined. Those structures could not, however, be related to the topology of the FS. The common, strong and extended maxima at (0, ±6) and minima at (±5.5, 0) mrad, for example, are the most likely structures arising from wave-function effects.
A study of the difference between the momentum spectra for the two compounds when normalised to the same number of counts showed that the spectrum of CeCu$_6$ was lower in the centre ($p=0$) and higher at intermediate values of $p$ (figure 6.7$^2$). To improve the statistics, the essentially isotropic difference spectrum (CeCu$_6$ - LaCu$_6$) was radially averaged. The first moment of the positive part of the radial distribution, shown in figure 6.8, was located at 1.39 (momentum) a.u. One may conclude from this relatively high momentum value and from the isotropy of the spectrum that the difference arises from deeper lying states. The f-electrons are a plausible source. By employing the uncertainty relation $\Delta x \Delta p = \hbar$, one deduces a figure of 0.72 a.u. for the spatial extent of the associated charge. This value is close to the maximum of the calculated radial density for the 4f electron in Ce (Kasuya et al. 1988). It would suggest that the f electrons in CeCu$_6$ are similarly tightly bound.

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$^2$ The difference was quite similar to that shown in appendix A3, between the (110) projections of CeB$_6$ and LaB$_6$, respectively.
As usual, the LCW transformation was attempted to derive information on the occupancy of the two systems. Its application gave total amplitude variations barely above the noise level (less than 1%). The complexity of the two compounds, with large bases and consequent small BZ, is the likely reason of these negative results (not shown).

In this regard, it is worth examining the ratio between the measured FWHM of the 2D-ACAR momentum distribution (which, after the Momentum Sampling Function correction is independent of the geometry of the spectrometer) and the size of the reciprocal lattice vectors. The comparison between the ratios of the present compounds, 3.3 and 2.1 for the p_y and p_x directions respectively, and the corresponding ratio for a transition metal, 1.4 for paramagnetic chromium (integrated along the <100> direction), shows that in the present case the momentum distribution extends over a considerably higher number of BZs. When the BZs are small, the FS breaks have correspondingly small extent (in momentum space). Moreover, their images (HMC of the FS), which are distributed over many BZs in the momentum density, may be relatively weak. Slight misalignments of the sample (or small errors in the experimental calibration), together with statistical noise, can bring them together incoherently during the LCW folding procedure and produce artefacts in the final k-space spectrum. Finally, even under ideal experimental conditions, the extremely high number of full bands present in these

Fig. 6.7: Normalised difference between the CeCu₆ and LaCu₆ momentum distributions projected along the <001> axis.

Fig. 6.8: As figure 6.7 after the radial average.
systems introduces in the LCW folded data a very high background, whose statistical precision can overwhelm the FS discontinuities.

It was therefore attempted to reduce the effects of the slowly varying trends present in the momentum distribution by means of the band-pass (§4.4) of the momentum data prior to the LCW analysis. At first a smoothed version of the spectra was subtracted from the spectra. The smoothing array used here was a $(2.2 \times 2.2)$ mrad$^2$ unweighted mask. The additional light smoothing used to reduce the amount of noise of the filtered data was $(0.47 \times 0.47)$ mrad$^2$. The results of the LCW procedure of the band-passed data are shown in figures 6.9 and 6.10 for LaCu$_6$ and CeCu$_6$, respectively. The total dynamic of the filtered LCWs corresponds to 12 and 10 times the average error of the intensity of the LCW matrix for LaCu$_6$ and CeCu$_6$, respectively. Interestingly, in the case of LaCu$_6$ the LCW data show very transparently the cylindrical features predicted by the theory (figure 6.3) at the XU points and the slight highs between the $\Gamma Z$ and the TY points. However, the small lows at the edges of the BZ are not displayed. Other features of the filtered LCW can be attributed to distortions induced by the filtering and by symmetrized noise. Given the small dynamics of the (filtered) LCW data, it is not surprising that all the other features of the theory (apart from the referenced highs) cannot be found in the experimental results. Their intensities are so low that they are probably lost within the noise. The same treatment of the CeCu$_6$ data results in a $k$-space density that deviates from the theoretical model proposed in figure 6.4. As the filtering algorithm could confirm the main features of the theoretical occupancy for LaCu$_6$, in the discussion which follows it will be hypothetically assumed that the discrepancy between

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3 The additional effect of the positron wave-function is unlikely to be the reason for the very small dynamic of the LCW matrix.

4 If one defines the statistical uncertainty as 2 times the error $\delta N$ (the uncertainty on each intensity $N$ is $N \pm \delta N$), all the dynamics referenced are obviously reduced by a factor 2.
Experimental results and theory is due to the inability of the theory to describe the system adequately (and not to poor experimental results). Beyond the LDA calculation adopted for comparison with the experiment, other possibilities, already described in §1.3, will be summarised below.

1) Standard LDA: In LDA the f-electrons are treated exactly in the same way as the other (valence or conduction) electrons. The f-like bands, crossing the Fermi level have a typical dispersion of $\sim 0.5$ eV ($\sim 6000$ K). The related FS sheets should also be observed at 30 K (the temperature of our experiments). It is, however, generally accepted (Zwicknagl 1992, Norman 1986) that the inappropriate description of many-body effects causes standard LDA calculations, such as those presented here for CeCu$_6$, to yield f-band widths which lead to underestimated values of the specific heat. The occupancy calculated by Harima (1993) disagrees with the experiment.

2) Renormalised band (RB) theory: According to the RB method (Zwicknagl, 1992) described in §1.3, an enhanced localisation of the f-electrons competes with the hybridisation between the f electrons and the conduction (s,p,d) electrons to yield narrow bands, having mainly f-character. Their small energy dispersion can account for the low temperature thermodynamic masses observed. The (parameterised) width of those bands is of the order of the Kondo temperature ($\sim 1$ meV). At $T_i=30$ K ($T_i>T_K$), any FS discontinuity contributed by those bands to the momentum density should be almost cancelled by thermal smearing. At $T_i>T_k$ the f-electrons would then behave as isolated atomic levels, carrying local magnetic moments (Zwicknagel, 1993). Though no calculation of the electronic structure of CeCu$_6$ with the RB method was performed, one could consequently expect, at 30 K, to find an electron occupancy more similar to that of LaCu$_6$.

3) F-core model: According to the f-core model (Kubo et al 1992, Norman et al 1986), at any temperature the f-bands are treated as incompletely occupied core
states. In analogy with the results obtained for LaB$_6$ and CeB$_6$, the hypothesis of localised Ce f-electrons should lead to a $k$-density similar to that observed for LaCu$_6$ (as for the RB model above $T_K$). The cylindrical features at the points XU of figures 6.3 and 6.9 were, in fact, also predicted by LMTO calculations performed including the contribution from the Ce f-electrons (in CeCu$_6$) as core states (Norman 1995).

It seems that none of the theoretical predictions is in agreement with our experimental results. Although there are some similarities between figures 6.9 and 6.10, the cylindrical features at the points XU of figures 6.3 and 6.9 do not appear in the filtered $k$-space occupancy for CeCu$_6$. The only trend which seems to be present above the noise are elevated regions close to the TY points. As mentioned in §6.1, a discrepancy between theory and experiment appeared also the previous dHvA experiment (Chapman 1990). It seems that a more careful investigation of the experimental and theoretical data is required to understand the electronic structure of this complex compound.
7 Concluding Remarks

The measurements described in this thesis were some of the very few performed with the 2D-ACAR technique on HF, or HF-related, compounds.

Given the limited number of experiments, it is probably premature to decide whether the technique is accurate enough to contribute to the many unsolved questions which these systems yield. This will be better understood when 2D-ACAR set-ups are upgraded in order to perform measurements above and below the temperature where coherency phenomena in HFs arise (the so-called coherence temperature, $T_{coh}$)\(^1\).

Up to now, the 2D-ACAR experiments performed on systems where the suggested FS is similar to the FS of the reference non f-electron compounds (CeB\(_6\)) here and CeSb by Itoh (1993) reported a fair agreement with the results of other experimental techniques and the f-core model. In the case of CeB\(_6\) the simplicity of the FS allowed one to obtain quantitative information on the FS topology and, consequently, on the Fermi volume.

According to the RB theory, as our measurements were performed above the Kondo temperature $T_K$ (which implies above $T_{coh}$), the observation of a momentum density related to a FS topology consistent with the f-core model would be an obvious piece of information. In fact, the f-electrons should always be described by the localised picture for $T>T_K$, regardless of the character of the ground state: magnetically ordered or non-magnetic because of the Kondo singlet formation\(^2\). This would be obvious if the experimental FS studies performed on HF compounds (above and below $T_K$) had been consistent with the RB assumption. Conversely, not a single measurement confirmed this hypothesis\(^3\) but, for example, angle resolved photoemission experiments performed by Arko et al (1990) suggest that the f-electron states in UPt\(_3\) are still itinerant at 300K (as discussed in §1.3, dHvA measurements on UPt\(_3\) below $T_K$ are consistent with an f-electrons-itinerant description)\(^4\). Since the RB assumptions must therefore still be considered as conjectures, our measurements on CeB\(_6\) provide a complement to the previous dHvA ones.

Less successful have been positron measurements of systems where the role played by the f-electrons is generally accepted to be itinerant (though still the object of discussion), such as CeCu\(_6\) or URu\(_2\)Si\(_2\) (Rozing et al 1990). The complexity of

\(^1\) As mentioned in §2.9, the only two 2D-ACAR experiments performed at different temperatures (Rozing 1991, Itoh 1993) have failed to detect differences in the momentum distribution and the $k$-space LCW folded data.

\(^2\) This was a comment from one of the referees of our paper on CeB\(_6\).

\(^3\) However, recall the experiments above and below the metamagnetic transition reported in §1.3.

\(^4\) Positron Annihilation experiments, because of their better resolution, could strongly contribute to this issue.
systems like CeCu$_6$ has, so far, prevented an agreement between electronic structure calculations (Harima et al, 1990, Chapman et al 1990) and experimental work (recall, in the case of dHvA experiments, Chapman et al 1990). Therefore, it is not clear whether the discrepancy between theory and 2D-ACAR experiments was due to inability of the theory to describe these systems or inability of the 2D-ACAR technique to separate the information related to the conduction electrons from that generated by the huge background due to valence (and core) electrons$^5$. 

With regard to the new data analysis tools used in this survey (simulations and filtering techniques), they proved to be useful in the cases described. In particular, the experiment on CeB$_6$ shows that the combination of some "a priori" knowledge of the symmetry and the topology of the Fermi surface of interest and the use of filtering procedures such as those described, can provide interesting information on the electronic structure of complex systems without a comprehensive and detailed calculation of the electron-positron momentum distribution. However, a careful check of the artefacts which can be generated by the filtering is indispensable. In particular, the application of the band-pass to the expected theoretical data is useful to predict the distortions induced by the algorithm.

In §1.4 it was mentioned that one of the main problems of heavy-fermion systems was a lack of universality. This prevented any theory from being able to explain simultaneously HF phenomena and the character of the ground state for more than few compounds. Sometimes, it appears that the word HF is given only to those systems which fulfil the so called "standard behaviour" described in §1.3 (which implies the hybridisation between f-electrons and conduction electrons and the Kondo singlet formation). Under this terminology, CeB$_6$, which orders magnetically and whose $\gamma$ constant is only 250 mJ/mole K$^2$, (as opposed, for example, to a $\gamma$ of $\sim$ 450 mJ/mole K$^2$ for UPt$_3$) would not enter into the HF category. However, as the band mass of LaB$_6$ is smaller than the bare electron mass, the mass enhancement of CeB$_6$ is bigger than that of UPt$_3$.$^7$. In a wider scenario, it is probably fair to conclude this survey by saying that a general understanding of HF systems is still missing.

$^5$ In general, the effectiveness of the 2D-ACAR technique is strongly established on relatively simpler systems such as elemental or binary alloys based on transition metals which were also measured in Bristol during the 28 months of the Bristol-Bologna joint venture.

$^6$ Among other 2D-ACAR measurements on systems of similar complexity it is worth remembering the successful observation of some FS sheets of YBaCuO (Haghighi 1991, Hoffmann 1993, Manuel 1993) which proved that not necessarily a high number of valence electrons must obscure the FS related signals.

$^7$ The mass enhancement of the cyclotron masses, as detected by dHvA, are 20 and 30 for UPt$_3$ and CeB$_6$, respectively.
Appendix 1  Saturation moment of Cubic Cerium in the presence of crystal field

Assuming that, for an isolated Cerium ion, only its \( f \) electron with total angular momentum \( J \) contributes to the magnetic moment, the total magnetic moment is

\[
\mu_T = g(J, L, S)\mu_B J,
\]

where

\[
g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}, \quad \mu_B \text{ is the Bohr magneton and } g \text{ is the Landé factor.}
\]

\( \mu_B \) is the Bohr magneton and \( g \) is the Landé factor. Assuming that the \( 2J+1 \) times degeneracy of the zero-field ground state is split by the action of the external magnetic field, one can derive the well-known Curie-Weiss law expressing the magnetic susceptibility as a function of temperature.

\[
\chi = \frac{N \mu_B^2 p^2}{V k_B T}, \quad \text{A1.2}
\]

where

\[
p = g(J, L, S)[J(J+1)]^{1/2}. \quad \text{A1.3}
\]

From A1.2 one can define the Curie constant as

\[
C = \frac{N p^2 \mu_B^2}{3 k_B}.
\]

Applying the Hund's rules to Ce, one sets \( L=3, \ S=1/2, \ J=5/2 \), obtaining \( g=6/7 \) and \( p=2.54 \).

This value is consistent with magnetic susceptibility measurements in the case of pure Ce and other Ce compounds like CeB\(_6\).

As \( T \to 0 \), for fixed field \( H \),

\[
M \to \frac{N}{V} g\mu_B J, \quad \text{A1.4}
\]
i.e. each ion should be completely aligned by the field, \( |J_z| \) having its maximum "saturation" value \( J \).

However, in the case of crystalline material, it is known that the action of the crystal electric field is responsible for breaking the total angular momentum \( J \) degeneracy (even in the absence of an external magnetic field).

In the case of a cubic crystal structure ([T Murao et al (1957)]), the \( J = 5/2 \) sixuplet is broken into a duplet,

\[
|2_{\pm}\rangle = -\sqrt{\frac{1}{6}}|J_z = \pm \frac{5}{2}\rangle + \sqrt{\frac{5}{6}}|J_z = \pm \frac{3}{2}\rangle
\]

and a quartet,

\[
|4_{1,2}\rangle = |J_z = \pm \frac{1}{2}\rangle
\]

\[
|4_{3,4}\rangle = \pm \left[ \sqrt{\frac{3}{6}}|J_z = \pm \frac{5}{2}\rangle + \sqrt{\frac{2}{6}}|J_z = \mu \frac{3}{2}\rangle \right]
\]

In the absence of an external magnetic field they are two times and four times degenerate, respectively. If the ground state is the duplet, the \( |J_z| \) "saturation" value at \( T=0 \) will be given by,

\[
\langle 2|J_z|2 \rangle = \frac{1}{6}\left( -\frac{5}{2}\right) + \frac{5}{6}\left( \frac{3}{2}\right) = \frac{5}{6}
\]

which when multiplied by the Landé g-factor gives a saturation moment of

\[
\frac{5}{6} \times 7 \mu_B = 0.714 \mu_B.
\]

If the ground state were the quartet, the \( |J_z| \) "saturation" value would be,

\[
\langle 4_3|J_z|4_3 \rangle = \frac{5}{6}\left( \frac{5}{2}\right) - \frac{1}{6}\left( \frac{3}{2}\right) = \frac{11}{6}
\]

which gives a saturation moment of
\[
\frac{116}{6} \mu_B = 1.57 \mu_B.
\]

Murao et al calculated the magnetic susceptibility as a function of the temperature\(^1\), obtaining a Curie constant value consistent with the high temperature region experimental results. The correction due to the crystalline field is, in fact, a factor which approaches unit at moderately high \(^2\) temperature.

\(^1\) Note that as the \(J_z\) operator does not commute with the Hamiltonian, \(H\), in a potential without rotational symmetry around the \(z\) axis (as in the case of a cubic crystal), the expression of the mean magnetic moment will include off diagonal matrix elements \(\langle n | J_z | n' \rangle\) if \(|n\rangle\) and \(|n'\rangle\) are eigenstates of \(H\).

\(^2\) at \(T=100\) K, the calculated effect of the crystalline field would be to reduce the Curie constant to 84% of its value.
Appendix 2 A fast method to calculate statistical errors of the band-passed data

This is attained in a two step procedure: i) the real errors of the corrected data are calculated via eqn 4.7 and approximated as invariant when taking the difference between data and smoothed, $W_{n,m}$, data.\(^1\) in eqn 4.14 ii) The error reduction due to the $W_l$ smoothing of eqn 4.14 is finally computed approximating the errors as constants within the smoothing array. Per each point of the error matrix $\sigma$ the following operations are performed:

$$v = \frac{1}{\sigma^2/N}, \quad A2.1$$

where $N$ is the number of elements of the smoothing array and $v$ is a "work" matrix. The smoothing of the work matrix $v$, (or its convolution with the smoothing array $W_l$)

$$v^{sm} = W_l \otimes v, \quad A2.2$$

and the division by $N$ in eqn A2.1 approximately equals the usual expression (Bevington, 1965 p 71) for the error of the mean $\sigma_{\mu}$ obtained from data having unequal errors $\sigma_i$,

$$\sigma_{\mu}^2 = \sum_i \left( \frac{1}{\sigma_i^2} \right). \quad A2.3$$

The error matrix $\sigma^{bp}$ of the band pass data is then

$$\sigma^{bp} = \frac{1}{\sqrt{v^{sm}}}. \quad A2.4$$

\(^1\) by neglecting the errors of the smooth version of the data (which is also correlated to the original data)
Appendix 3 Comparative analysis of the CeB₆ projections

In §5.3 it was reported that the normalised difference between the (001) projection of CeB₆ and LaB₆, had a maximum at $p=0$, in disagreement with the expectations about the role played by the f-electrons according to experiments (§2.3) and calculations (§5). New information was generated by applying the same procedure to the (110) projections of both compounds. Although the statistics (especially that of LaB₆) were lower, one should expect some kind of confirmation of the CeB₆ - LaB₆ (001) projections results. The almost isotropic difference, radially averaged, is shown in figure A3.1. The minimum at $p=0$ is in great contrast with respect to the (100) difference result shown in figure 5.14. There are two possible explanations of such different behaviour:

1) The 3D momentum distribution of the f-electrons is so anisotropic that, when projected along the $<001>$ direction, it contributes with a high intensity at $p=0$ and, when projected along the $<110>$ direction, it vanishes at $p=0$. This topological situation is ideally possible and can be realised, for example, by an f-sheet of the FS resembling the regular ellipsoids' FS model of figure 5.2 (but without ellipsoid necks). In that case, the occupancy due to the f band and, consequently, its contribution to the momentum distribution, would vanish at the centre of the BZ ($\Gamma M$) for the (110) projection but not for the (100) one (at $\Gamma X$). Therefore, as LaB₆ has no f-electrons, the difference CeB₆-LaB₆ would be different depending on the projection. Such a strong difference (as shown in Fig 5.14), realised by additional FS discontinuities, is in contrast with previous experiments and calculations. Moreover, these extra FS sheets should contribute, to some extent, to differences between CeB₆ and LaB₆ also in the radial anisotropy and should be observed in the LCW data. So far, no evidence in support of this hypothesis can be found.

Fig. A3.1 Normalised difference, radially averaged, between CeB₆ (110) projection and LaB₆ (110) projection.
2) The momentum distribution of CeB₆ (001) is affected by an artefact due to annihilations outside the sample (sample holder, glue, or wrapping kapton protecting the sample) which gives the high intensity at \( p=0 \).

One way of testing the second hypothesis consists of comparing in a suitable manner the two projections CeB₆ (001) and CeB₆ (110), performed a few days apart. These can be transformed in 1D-ACAR integrals. By rotating the (100) projection about the projection axis of 45° (here \( p_2 \)) and integrating along the \( <110> \) direction, that spectrum becomes identical\(^1\) to the (110) projection integrated along the direction \( <100> \) of the matrix. (see figure A3.2).

Any difference between the two spectra integrated as described in figure A3.2 should uniquely reflect differences in the \( p_x \) and \( p_y \) resolutions and in a correct alignment. The procedure was tested first on 3D simulated data: the result of the integration along the directions described above yielded identical 1D-ACAR spectra.

\(^1\) by assuming that the integration over the range -2.4 to 2.4 a.u. is a sufficient approximation to the infinity. (The FWHM of the distribution is 1.3 a.u.)
As the process of rotating the data affects the corners of the matrix, the difference between the corresponding 1-D spectra was restricted to the central 1.85 a.u. of the matrix. Figure A3.3 shows the normalised difference between the two spectra generated from the CeB$_6$ (100) and CeB$_6$ (110) projections, respectively. The dynamic of the difference corresponded to 2.2% of the maxima of the 1D-ACAR spectra.

The effect of having finite integration domains along two different directions for the 2 spectra (the <110> direction for the rotated spectrum and the <100> direction for the original (110) projection) was tested by cutting the original matrices to 95% of the original sizes and checking how the maxima of the two 1D-ACAR spectra were affected. The difference spectrum had a dynamic which differed of less than 0.5% with respect to the difference spectrum generated by matrices of the original sizes.

The positive intensity at $p=0$ of figure A3.3 might suggest that an extraneous signal is superimposed on the true signal in the CeB$_6$ (100) projection. It is useful to compare figure A3.3 with the difference between the CeB$_6$ (100) and LaB$_6$ (100) projections, respectively (shown in figure A3.4) when integrated along the <001> direction and normalised to the same number of counts as in figure A3.3. (Figure A3.4 is equivalent to the figure 5.14 of the main text, except for the fact that figure 5.14 arises from the radial average of the 2D difference spectrum CeB$_6$ (100) - LaB$_6$ (100)). It appears that the dynamic of figure A3.3 is even stronger than that in the latter spectrum.

A further test was obtained by comparing the LCW matrices relative to the unfiltered CeB$_6$ (110) and (100) projections transformed in 1D-ACAR spectra by integrating along the directions specified by figure A3.2. In $k$-space the (100) occupancy is periodic and therefore, when performing the integration along the <110> direction, it must be extended according to the prescriptions specified by figure 5.5. As the rotation introduces an interpolation and therefore a smoothing in the (100) projection, the 1D-ACAR spectrum of the (110) (un-rotated) projection was also smoothed by a

![Figure A3.5](image)

**Fig. A3.5. Curve a):** normalized 1D-ACAR LCW obtained by integrating along <001> the LCW matrix of the unfiltered CeB$_6$ (110) projection. **Curve b):** normalized 1D-ACAR LCW from the rotated unfiltered LCW CeB$_6$ (100) projection as described in the text.
comparable amount. Further, the (110) un-rotated projection was convoluted with an additional Gaussian resolution along the $p_x$ direction to (conservatively) over-compensate for the difference in the resolution of the (100) LCW data. Figure A3.5 shows the two processed spectra normalized to the same number of counts. The fact that the 1D-ACAR spectrum obtained from the (100) projection is considerably higher at the centre than the corresponding (110) one confirms the previous conjectures.

Though this analysis is not conclusive, it would suggest that the isotropic contribution in CeB$_6$ (100) projection discussed in the main text is not due to intrinsic differences between the electronic structure of CeB$_6$ and that of LaB$_6$. This would also explain why the CeB$_6$ (110) unfiltered LCW is clearly in better agreement with the theory and why the LaB$_6$ (100) projection highlights major information on the topology of the FS (with respect to the CeB$_6$ (100) one) without the need of the band-pass procedure.

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2 The same procedure, applied for internal check to the two projections of LaB$_6$, showed a structure of much smaller ($\sim$1/3) intensity with a low at the centre of the distribution. However, the method is still under study. It appears that the operation of taking differences between processed spectra must be checked with great care.
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