Observation of Differences between Low-Energy Electron- and Positron-Diffraction Structural Determinations of the Cleavage Faces of CdSe

T. N. Horsky,[1] G. R. Brandes,[1] K. F. Canter,[1] C. B. Duke,[2] S. F. Horng,[3] A. Kahn,[3] D. L. Lessor,[2] A. P. Mills, Jr.,[4] A. Paton,[5] K. Stevens,[3] and K. Stiles[3]

[1]*Department of Physics, Brandeis University, Waltham, Massachusetts 02254*

[2]*Pacific Northwest Laboratory, Richland, Washington 99352*

[3]*Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544*

[4]*AT&T Bell Laboratories, Murray Hill, New Jersey 07974*

[5]*Xerox Webster Research Center, Webster, New York 14580*

(Received 14 November 1988)

Low-energy positron diffraction (LEPD) is used in conjunction with low-energy electron diffraction (LEED) to determine the relaxed atomic geometries of the CdSe cleavage surfaces. The LEPD analyses yield optimal fits at smaller top-layer perpendicular relaxations than LEED for both cleavage faces, and significantly better agreement between theoretical and experimental intensity profiles.

PACS numbers: 61.14.Hg, 61.14.Dc, 68.35.Bs

During the past decade, low-energy electron diffraction (LEED) has become a powerful tool for the structural determination of ordered surfaces.[1-3] In spite of the success of LEED in determining the surface structure of compound semiconductors, the agreement between observed diffracted-beam profiles $I_{ex}(V)$ and calculated profiles $I_{th}(V)$ has not been as good as for metal and adsorbate-on-metal surfaces. Although the reason for this is not yet fully understood, the higher degree of complexity due to relaxations extending below the outermost one or two atomic layers is commonly regarded as a major factor. Because of the large differences between diffracted-beam intensity profiles observed via LEED and low-energy positron diffraction (LEPD),[4-6] comparison of LEED and LEPD structural determinations of a compound semiconductor surface would provide additional insight into this issue and could yield a more accurate structural determination than one using LEED alone. Accordingly, we have carried out LEPD and LEED structural determinations of the relaxed atomic geometries of the recently determined[7] $(10\bar{1}0)$ and previously undetermined $(11\bar{2}0)$ cleavage faces of CdSe. We find that both the LEPD and LEED results are consistent with the relaxation predicted by Wang and Duke.[8] In addition, the agreement between $I_{ex}(V)$ and $I_{th}(V)$ for LEPD is, surprisingly, observed to be significantly better than for LEED. For both cleavage faces, we also find smaller top-layer perpendicular relaxations for the LEPD structure analyses than for the LEED analyses, although the differences may be viewed as lying barely within the uncertainty of the analyses. We have established that the LEPD-LEED differences are not experimental artifacts by obtaining both LEPD and LEED data from the same sample surfaces in the same apparatus at Brandeis University. The validity of the Brandeis LEED results was then checked by comparison with LEED data and structural analyses carried out at Princeton University.

The LEPD intensities were obtained with the brightness-enhanced, slow positron beam at Brandeis.[9] A 230-mCi ^{58}Co positron source produced a final positron beam of 5000 s^{-1}, monochromatic within 0.2 eV and having a phase space of 1 mm deg over the energy range 20–200 eV. The beam optics also produced a 1-mm-deg electron beam, allowing the collection of LEED intensities from the same sample surfaces as the LEPD. The normal-incidence diffractometer incorporated a channel electron multiplier array and resistive anode encoder. Details of the diffractometer and beam design are given elsewhere.[10,11] The CdSe$(10\bar{1}0)$ and CdSe$(11\bar{2}0)$ samples were high-purity, Cd-rich, low-resistivity single-crystal boules of 5 mm diam. Both the Brandeis and Princeton data utilized samples from the same supplier,[12] and in the experiments both were cleaved *in situ* at 10^{-10} Torr. With the exception of the room-temperature LEPD $(10\bar{1}0)$ data, all data used in the analyses were collected at ~ 100 K.

The Brandeis $I_{ex}(V)$ profiles were produced by repeatedly ramping beam energy in 2 eV increments from 20 to 160 eV and integrating the digitally recorded spot intensities minus background. Normalization to incident current was accomplished by electrostatically mirroring the positron (electron) beam back into the detector array and monitoring incident current as a function of beam energy. The symmetry-equivalent beams $[(hk)=(\bar{h}k)$ for $(10\bar{1}0)$ and $(hk)=(h\bar{k})$ for $(11\bar{2}0)]$ were then averaged to produce the final experimental $I(V)$ curves. The Princeton $I_{ex}(V)$ profiles were obtained from 20 to 240 eV using a spot photometer. In this case, symmetry equivalence was checked for several pairs of beams at various energies, but the equivalent beams were not averaged. Instead, three complete sets of $I(V)$ profiles were collected and then averaged. Normalization was accomplished by monitoring the current leaving the electron gun. Ten (twelve) beams comprised the LEPD (LEED) data for $(10\bar{1}0)$ while fourteen (thirteen) beams

comprised the LEPD (LEED) data for $(11\bar{2}0)$. Four of the Brandeis LEPD and Princeton LEED beam profiles from CdSe$(11\bar{2}0)$ are displayed in Fig. 1, illustrating the best fits we obtained between calculated and measured intensities.

The LEED and LEPD intensities were calculated using a multiple-scattering program which previously has been applied to the study of numerous[1] compound semiconductor surfaces including CdSe$(10\bar{1}0)$.[7] The interaction of the incident electron or positron with the solid is described by complex phase shifts describing its scattering from the individual vibrating Cd or Se species, whereas its propagation in between these species is simulated by a uniform complex potential. A detailed account of the mathematical model of this interaction is given by Weiss *et al.*[5] The rigid-lattice phase shifts are obtained from a muffin-tin potential constructed from self-consistent solutions to the Dirac equation as described by Ford, Duke, and Paton[13] for electrons and adapted for positrons as indicated by Weiss *et al.*[5] An important aspect of this adaptation is the absence of an exchange interaction for positrons, leading to positron-solid phase shifts which are electrostatic in origin. The effects of positron–core-electron correlation have also been demonstrated to have a negligible effect on diffracted positron intensities.[14] In accordance with previous LEED-LEPD studies of Cu,[5,6] we used an energy-independent inelastic mean free path λ_{ee} for the LEED analysis and one that varied as $E^{1/2}$ for LEPD.[11] At 35 eV, the positron λ_{ee} was found to be roughly half the electron λ_{ee} with both being equal at 140 eV, for example. In both the LEED and LEPD analyses, we verified that the λ_{ee} used optimized the agreement between $I_{ex}(V)$ and $I_{th}(V)$.

The structural variables for the $(10\bar{1}0)$ and $(11\bar{2}0)$ faces were parametrized according to the relaxation model of Wang and Duke[8] as bond-length-conserving rotations of the topmost Cd-Se dimers [in the $(10\bar{1}0)$ case] or of the Cd-Se-Cd and Se-Cd-Se triplets [in the $(11\bar{2}0)$ case], as also discussed by Duke *et al.*[7,11] A detailed description of the structural variables associated with the bond-length-conserving rotation angle ω is given in Ref. 11. As ω was varied over the range of values for which the bond lenghts could be preserved, the resultant calculated intensities were compared with the experimental intensities via an R-factor methodology.[15,16] This analysis minimizes the value of the x-ray R factor[16] R_X (which directly compares the intensity line shapes in a point-by-point manner) as a function of ω, as shown in Fig. 2. R_X has been demonstrated to be a reliable figure of merit for the determination of compound-semiconductor surface structure[17] and has been used in a large body of previous work.[1,3] We have also incorporated into the analysis the integrated beam R factor R_I, which for a given beam is simply a measure of the difference in the areas under the two curves [i.e., $I_{ex}(V)$ and $I_{th}(V)$] being compared. R_I has proven useful[15] in discriminating between two local minima in R_X, but has not been used to determine surface structure by itself due to its insensitivity to the intensity line shapes. The

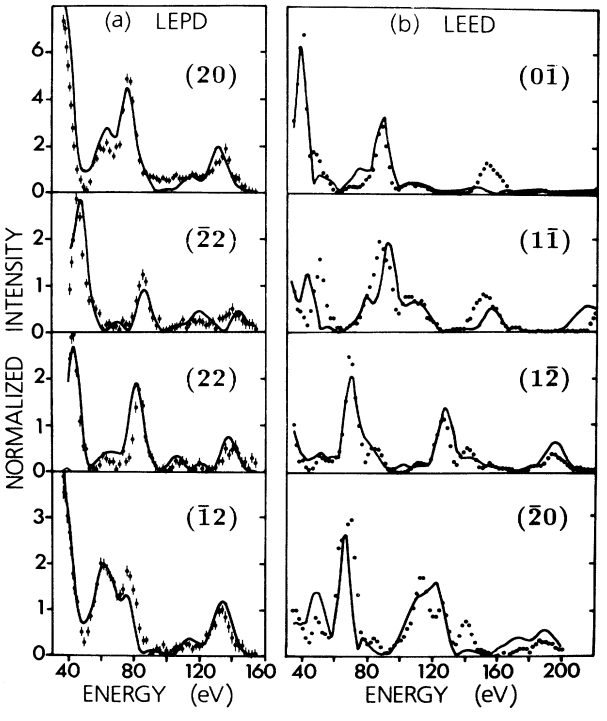

FIG. 1. Data (points) and theory (lines) for four beams diffracted from the CdSe$(11\bar{2}0)$ surface, utilizing the best-fit structures of (a) LEPD and (b) LEED. Intensities are given in absolute reflectivity multiplied by 10^4 for (a) and in arbitrary units for (b).

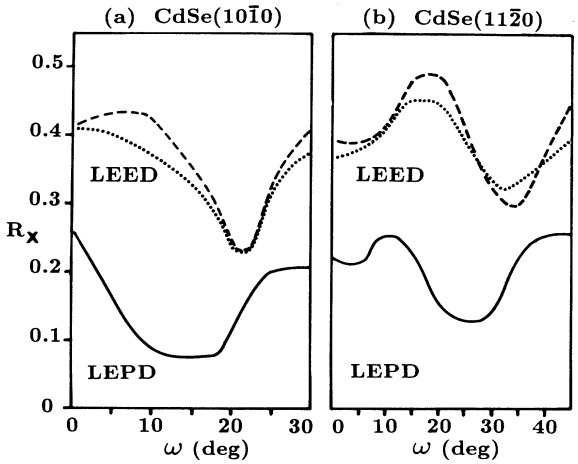

FIG. 2. X-ray R factor R_X as a function of the bond-rotation angle ω for the (a) CdSe$(10\bar{1}0)$ and (b) CdSe$(11\bar{2}0)$ surfaces. Solid lines: LEPD. Dashed lines: Princeton LEED. Dotted lines: Brandeis LEED.

TABLE I. Anion-cation perpendicular shear $\Delta_{1,\perp}$, first interlayer spacing $d_{12,\perp}$, and bond-rotation angle ω for the best-fit structures for LEED and LEPD from both CdSe cleavage faces, and their associated R factors. Uncertainties in ω are given in the text, while those of $\Delta_{1,\perp}$ and $d_{12,\perp}$ are nominally ± 0.1 Å.

	ω (deg)	$\Delta_{1,\perp}$ (Å)	$d_{12,\perp}$ (Å)	R_X	R_I
		CdSe($10\bar{1}0$)			
Bulk	0	0	1.24	···	···
LEPD	15	0.68	0.65	0.08	0.05
Theory[a]	17.7	0.78	0.64	···	···
LEED[b]	21.5	0.96	0.45	0.19	0.05
LEED[c]	21.5	0.96	0.45	0.21	0.03
		CdSe($11\bar{2}0$)			
Bulk	0	0	2.15	···	···
LEPD	27	0.61	1.62	0.12	0.04
Theory[a]	32	0.71	1.52	···	···
LEED[b]	33	0.73	1.51	0.32	0.22
LEED[c]	34	0.76	1.47	0.29	0.12

[a]Reference 8.
[b]Brandeis data.
[c]Princeton data.

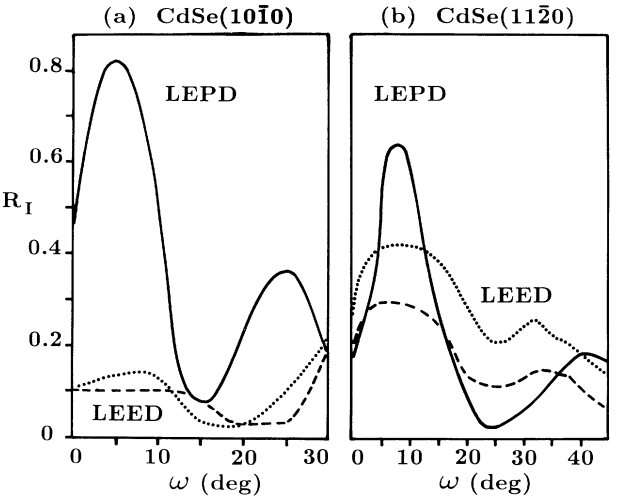

FIG. 3. Same as Fig. 2, but for the integrated beam R factor R_I.

minimum values of R_X for $(10\bar{1}0)$ appear at $\omega = 15° \pm 5°$ LEPD and $\omega = 21.5° \pm 3°$ for both the Brandeis and Princeton LEED analysis. The minimum R_X values for $(11\bar{2}0)$ appear at $\omega = 27° \pm 5°$ for LEPD and $\omega = 33° \pm 4°$ and $34° \pm 3°$, respectively, for the Brandeis and Princeton LEED analyses. Although the R_X minima appear broad, particularly for LEPD, it is evident that the LEPD analyses suggest systematically smaller ω values (and hence smaller perpendicular top-layer displacements $\Delta_{1,\perp}$) than the LEED analyses. These results are summarized in Table I, where the predicted[8] structures are included for comparison. The predicted values of the structural variables fall between the values giving the best fits to the LEED and LEPD intensities for both cleavage faces.

The variation of R_I with respect to ω is shown in Fig. 3. We observe that R_I in LEPD exhibits a strong dependence on ω, and that the location of its minimum is consistent with the LEPD minimum in R_X for both cleavage faces. In an attempt to understand the sensitivity of R_I to ω, we compared the energy-dependent elastic scattering cross sections $\sigma(E)$ for positrons and electrons from Cd and Se atoms in the wurtzite crystal. We found, as expected,[3] large differences (up to 400%) between the Cd and Se $\sigma(E)$ for electrons, but remarkably less than 10% difference for positrons was observed. This situation is likely due to the repulsive Hartree potential for positrons adding to the repulsive centrifugal barrier, as opposed to having a canceling effect for electrons. Consequently, the degree to which the scattered positron samples the iron cores is reduced. This repulsion also contributes to the aforementioned insensitivity of LEPD to positron–core-electron correlation.[14,18] Thus, the small scattering differences between cation and anion in LEPD could explain the strong dependence of R_I on surface structural variables. Indeed, one can view the unrelaxed, bulk-terminated surface to a first approximation as consisting of effectively one species of scatterer for LEPD. In this case, the surface possesses a higher degree of symmetry, leading to reduced scattering into certain beams. As the surface relaxes, this artificial symmetry is broken, so that the relative beam strength in LEPD would be highly sensitive to the degree of relaxation: a prediction compatible with our observation of a factor of 4–15 reduction in I_{th} for the (01), $(0\bar{1})$, (11), and $(1\bar{1})$ beams for the $(10\bar{1}0)$ surface as ω is reduced towards zero.

Although the differences in the locations of the minima in R_X vs ω may be viewed as minor, the agreement between $I_{th}(V)$ and $I_{ex}(V)$ differs markedly for LEED and LEPD, as can be seen in Fig. 1. A more quantitative distinction is provided in Table I; i.e., the minimum R_X values for LEPD are significantly lower than they are for LEED. This implies that $I_{th}(V)$ can be calculated more accurately, i.e., in better agreement with experiment, for LEPD than LEED, perhaps because the positron sees a simpler electronic and/or atomic distribution when scattering from CdSe. In addition to the reduced positron–core-electron correlation, it may also be possible that the positron is relatively insensitive to the nonspherical nature of the valence-electron spatial distribution within the Cd-Se bonds. Further, we cannot yet rule out the possibility of complex relaxations involving more than the outermost two atomic layers, as modeled in the $I_{th}(V)$ calculations, and that the electron samples the subsurface layers to a greater depth than the positron due to its larger penetration depth. It is possible, however, to draw some inferences from the observed improve-

ments in $I_{th}(V)$ for LEPD without having definitively established the reasons for the improvement. The fact that just dropping the exchange-correlation interaction and reversing the sign of the Hartree potential yields accurate values of $I_{th}(V)$ for positrons is an indication that the basic LEED theory affords a quantitative description of such fundamental effects as inelastic collision damping on wave diffraction from a vibrating lattice.

In summary, we have performed both LEPD and LEED structural determinations of the cleavage faces of CdSe which are in reasonable agreement with theoretical predictions. The LEPD profiles are found to be insensitive to the exact form of the scattering potential, and to a lesser degree, also to elemental specificity. This results in absolute scattering intensities which display an enhanced sensitivity to variations in the surface structural parameters for compound semiconductors. We also find a significantly improved goodness of fit between experimental and theoretical beam intensity profiles for LEPD relative to LEED. Although it may be premature to interpret this improvement in goodness of fit as evidence of a more reliable structural determination, our results demonstrate that further study of this issue is well warranted.

We wish to acknowledge helpful discussions with S. Berko and E. Jensen, and the data analysis performed by S. Levine. This work was supported in part by NSF Grants No. DMR-8519524 and No. DMR-8709531. Pacific Northwest Laboratory is operated by Batelle Memorial Institute for the Department of Energy under Contract No. DE-AC-6-76RLO 1830.

[1]C. B. Duke, in *Surface Properties of Electronic Materials,* edited by D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1988), pp. 69–118.

[2]*Determination of Surface Structure by LEED,* edited by P. M. Marcus and F. Jona (Plenum, New York, 1984).

[3]A. Kahn, Surf. Sci. Rep. **3**, 193 (1983).

[4]I. J. Rosenberg, A. H. Weiss, and K. F. Canter, Phys. Rev. Lett. **44**, 1139 (1980).

[5]A. H. Weiss, I. J. Rosenberg, K. F. Canter, C. B. Duke, and A. Paton, Phys. Rev. B **27**, 867 (1983).

[6]R. Mayer, C. S. Zhang, K. G. Lynn, W. E. Frieze, F. Jona, and P. M. Marcus, Phys. Rev. B **35**, 3102 (1987).

[7]C. B. Duke, A. Paton, Y. R. Wang, K. Stiles, and A. Kahn, Surf. Sci. **197**, 11 (1988).

[8]Y. R. Wang and C. B. Duke, Phys. Rev. B **37**, 6417 (1988).

[9]K. F. Canter, G. R. Brandes, T. N. Horsky, P. H. Lippel, and A. P. Mills, Jr., in *Atomic Physics with Positrons,* edited by J. W. Humberston and E. A. G. Armour (Plenum, New York, 1987), pp. 153–160.

[10]T. N. Horsky, Ph.D. thesis, Brandeis University, 1988 (unpublished).

[11]C. B. Duke, D. L. Lessor, T. N. Horsky, G. R. Brandes, K. F. Canter, P. H. Lippel, A. P. Mills, Jr., A. Paton, and Y. R. Wang, J. Vac. Sci. Technol. A (to be published).

[12]Cleveland Crystals, Cleveland, OH.

[13]W. K. Ford, C. B. Duke, and A. Paton, Surf. Sci. **112**, 195 (1982).

[14]F. Jona, D. W. Jepsen, P. M. Marcus, I. J. Rosenberg, A. H. Weiss, and K. F. Canter, Solid State Commun. **36**, 957 (1980).

[15]C. B. Duke, S. L. Richardson, and A. Paton, Surf. Sci. **127**, L135 (1983).

[16]E. Zanazzi and F. Jona, Surf. Sci. **62**, 61 (1977).

[17]C. B. Duke, A. Paton, W. K. Ford, A. Kahn, and J. Carelli, Phys. Rev. B **24**, 562 (1981).

[18]R. Feder, Solid State Commun. **34**, 541 (1980); M. N. Read and D. N. Lowy, Surf. Sci. **107**, L313 (1981).