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ABSTRACT

We investigate fine structure in energy derivative reflectance (EDR) spectra near 20-21 eV in GaP, GaAs, and GaSb, and near 18-20 eV in InP, InAs, and InSb. Derived energy values for X_1^c thresholds in GaP and GaSb, and L_1^c and X_1^c thresholds in GaAs, agree well with previous Schottky barrier electroreflectance (ER) results. L-X structure splittings in EDR spectra of InAs and InSb, for which Schottky barrier ER measurements cannot be performed, are 0.29 eV and 0.44 eV, respectively. Estimates of expected locations of these structures, based on XPS and absorption data and band structure calculations, indicate energy deficits of 0.2 eV for In4d$-L_1^c$ and 0.5 eV for In4d$-X_1^c$ transitions, respectively.

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In a series of papers[1-4], Aspnes, Olson, and Lynch developed a model that described the electroreflectance (ER) spectra of the Ga3d core level to lower conduction band transitions in GaP, GaAs, and GaSb in terms of the one-electron conduction band structures of the compounds. Dominant features near 20 eV were assigned to the X_1^c final states, and the moderate energy deficits, of the order of 0.1 eV relative to XPS core-level data[5], were attributed to excitonic effects[4]. Fine structure observed in the GaAs ER spectrum could only be interpreted within this model by assigning it to L_1^c[6], which required placing L_1^c below X_1^c in opposition to the then accepted ordering of the $L_1^c - X_1^c$ minima of this material. The validity of the model,

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however, appeared to be confirmed as several new experiments[7] verified not only the revised ordering but also the ER-determined energy separation of 170 ± 50 meV between L_1^c and X_1^c. Further support came from low-temperature reflectance measurements[8] which correlated well with the ER results.

We report here high-resolution energy derivative reflectance (EDR) measurements for InP, InAs, and InSb, as well as for GaP, GaAs, and GaSb, that also show fine structure in the core-threshold region. This structure and the correspondingly derived energy threshold values of X_1^c for GaP and GaSb, and of X_1^c and L_1^c for GaAs, are in excellent agreement with the previous Schottky barrier ER work on these compounds, with the L-X splitting in GaAs well resolved. This result is significant because EDR is a more general technique than ER, and the observation of equivalent fine structure by EDR opens the possibility of performing indirect-threshold determinations via core-level spectroscopy on a wide class of materials. For example, core-level ER spectra cannot be obtained on the In-V compounds, and because their direct gaps are so small the standard intraconduction band absorption or alloying techniques cannot be used. Thus the energies of these minima have not been measured previously. We find our EDR results to be consistent with a band model interpretation, but only if an anomalously large excitonic binding energy of 0.5 eV is assumed for the In4d $-$ X_1^c transitions.

Room temperature reflectance data were taken on single-crystal samples of GaP, GaAs, GaSb, InP, InAs, and InSb at the DORIS storage ring using a 3 meter monochromator with energy resolution 0.01 eV[9]. The carrier concentration of all samples was less than 4×10^{17} cm^{-3}, so impurity effects were negligible. Surfaces were prepared by Syton polishing, and residual oxides were stripped chemically before mounting in the sample chamber to reduce the effect of oxide overlayers. After initial measurements were completed, the samples were etched in Br-methanol (I-methanol for InSb) and remeasured to test for possible surface damage. Only InAs showed any improvement, and because nothing essential was changed only pre-etched data are given. To check the effect of surface quality we also measured cleaved (110) surfaces of GaAs and InAs. Further measurements on cleaved surfaces were performed

at low temperature[9].

The reflectance data and their second derivatives for the polished and etched samples are shown in Fig 1 and 2, respectively. The gross features of the reflectance spectra agree with those reported by Cardona et al[10]. Noise is well under the structural details shown in the vicinity of the main peaks. The energies of the corresponding transitions for the Ga-V compounds, as determined from ER data, are shown by arrows in Fig. 2. The expected positions of critical point thresholds for the j=5/2 transitions are indicated by the dashed lines labeled according to the respective conduction band minima. These positions are determined by adding the core level binding energies relative to the Γ_8^v valence band edge, as determined by XPS,[5] to the energies of the indirect minima relative to Γ_8^v, as determined by conventional techniques or band structure calculations. We use XPS data[5] as the core level reference; analogous UPS data[11] agree with these to within about 0.1 eV if the XPS Ga3d data are assumed to give the weighted average energy of both j=5/2 and j=3/2 core levels and if the In4d data are assumed to give the j=5/2 energy alone. The difference in interpretation between Ga3d and In4d energies in XPS is simply a consequence of instrument resolution (0.55 eV) with respect to the spin-orbit splittings (0.44 eV for Ga3d, 0.88 eV for In4d), and can be inferred directly from data shown in ref. 5.

For GaP, the Γ_1^c and X_1^c conduction band minima relative to the valence band edge are determined from absorption data[12], and the L_1^c point located by means of recent TER measurements by Kyser and Rehn[13]. The lower conduction band structures of GaAs and GaSb have been discussed in refs. 6 and 3, respectively. Data for InP are from Onton et. al.[14] and Pitt et. al.[15] Data for the indirect thresholds for InAs and InSb are not available; we have indicated in Fig. 2 the predictions of the nonlocal pseudopotential results of Chelikowsky and Cohen[16]. For the latter two compounds Γ_1^c is off scale to the left and not shown. Figure 3 shows the second derivative reflectance spectra of cleaved (110) surfaces of GaAs and InAs. The structure observed is basically the same (with some distortion) as that reported in Fig. 2 except for the "surface exciton" peaks E^s.[8]

The energies of the negative peaks in the second derivative EDR spectra are given in Table I and compared where possible to threshold values determined from ER spectra.[4] The 110K ER values of ref. 4 are corrected by the 50 meV reduction in threshold observed for GaP upon going to room temperature.[17] The values agree to within the experimental uncertainties of both methods. For GaSb, the ER X_1^c structures at 19.8 and 20.2 eV are sharper than their EDR counterparts, and the 20.6 eV structure seen in Fig. 2 does not exist. This probably represents a combination of angle-of-incidence effects and a different sensitivity of response of the various thresholds to electric field modulation. The average Ga3d spin-orbit splitting of 0.43 ± 0.03 eV from Table I is in agreement with the best ER value of 0.43 ± 0.02 eV. Thus the previous results[4] on threshold values, splittings, and binding energies are recovered.

We consider next the In-V compounds. Of these, direct experimental values for higher thresholds are available only for the X_1^c minima of InP. Onton, Chicotka, and Yacoby[14] obtained 0.960 ± 0.005 eV for this separation at 8K by intraconduction band absorption measurements. For comparison, the Chelikowsky-Cohen prediction[16] is 0.94 eV. Using the 1.34 eV $\Gamma_8^v - \Gamma_1^c$ direct threshold at room temperature[18], and increasing the $\Gamma_1^c - X_1^c$ gap by 0.02 eV to approximate the change from 8K to 300K by that for GaAs[6], we expect to find the $4d - X_1^c$ structure at 19.12 ± 0.15 eV instead of the actual 18.61 ± 0.05 eV. Thus the "excitonic binding energy" for X_1^c in InP, 0.51 ± 0.20 eV, is much larger than the corresponding value, 0.17 ± 0.15 eV, in GaP. Although the L_1^c structure is not seen, we can calculate its expected location from the 0.35 eV room-temperature $L_1^c - X_1^c$ separation inferred by Pitt, Vyas, and Mabbit[15] from pressure-induced level crossing measurements on $Ga_{1-x}In_xP$ alloys. For comparison, the Chelikowsky-Cohen predicted $L_1^c - X_1^c$ separation, corrected to room temperature[6], is 0.28 eV. Thus the $4d - L_1^c$ structure should appear at 18.77 eV in InP, although it is not seen for reasons that will become clear from the results for InAs and InSb.

For InAs and InSb, the expected locations can be obtained only through band structure calculations.[16] Reducing the L_1^c values by 0.11 eV and the X_1^c values by 0.08 eV to account approximately[6] for temperature shifts we expect $4d - L_1^c$ structures at 18.51 eV and 18.21 eV,

and $4d - X_1^c$ structures at 19.29 eV and 18.92 eV, for InAs and InSb, respectively. Comparing to Table I we find "excitonic binding energies" of 0.17 ± 0.18 eV and 0.21 ± 0.18 eV for the $4d - L_1^c$ transitions and of 0.66 ± 0.18 eV and 0.48 ± 0.18 eV for the $4d - X_1^c$ transitions in InAs and InSb, respectively. The error limits refer only to the experimental, not theoretical, uncertainties, and these reflect mainly the uncertainties in determining the core binding energies. To the extent that the band structure calculations are accurate, the result suggests that the energy deficit associated with L_1^c is only half that of X_1^c. We note that if the expected energy of $4d - L_1^c$ for InP were lowered by 0.2 eV, the L_1^c energy deficit for InAs and InSb, then the $4d - L_1^c$ structure for InP would fall at 18.57 eV, i.e. within 0.04 eV of the observed X_1^c structure in Table I. This would explain completely the apparent absence of this structure in the InP spectrum of Fig 2.

The In4d spin-orbit splitting of 0.88 ± 0.03 eV from Table I is about 10% smaller than the 0.95 eV value calculated by Wepfer, Collins, and Euwema[19]. A similar decrease was also found for the Ga3d spin-orbit splitting.[4]

While the band structure interpretation appears to be supported at least qualitatively, the new In-V data provide evidence of an additional complication and emphasize several details that also were not understood in the Ga-V compounds. The complication is the apparent breakdown of the previous assumption of a fixed energy deficit valid for all conduction band minima. We now examine the implications for the Ga3d transitions. Supposing an approximate 2:1 ratio between the X:L "binding energies" based on the In-V results and using the measured low-temperature $X_1^c - L_1^c$ separation of 0.34 eV in GaP[13] corrected to 0.37 eV for room temperature, we calculate that the $3d_{5/2} - L_1^c$ structure should fall 0.45 eV above $3d_{5/2} - X_1^c$. This is precisely the location of the stronger $3d_{3/2} - X_1^c$ structure, whence the lower L_1^c structure would not be seen. However, the $3d_{3/2} - L_1^c$ should appear 0.44 eV above $3d_{3/2} - X_1^c$. The existence of such a structure has been suggested[2,20] but it is ill-defined and in any case would have to have relatively weak matrix element.

For GaAs, a similar calculation predicts that the room-temperature $L_1^c - X_1^c$ separation

would increase by 0.05 eV because L_1^c is below X_1^c in the observed spectrum. Thus the $\Gamma_1^c - L_1^c$ level would drop to 0.24 ± 0.05 eV. While the change is not large, it moves the value out of good agreement with that obtained by other methods although the regions of estimated uncertainty still overlap.

We have noted that a consistent interpretation for GaP requires a relatively small $3d - L_1^c$ matrix element compared to $3d - X_1^c$. For the unambiguous cases InAs and InSb, Fig. 2 shows in fact that the L_1^c strength doubles with respect to X_1^c from InAs to InSb, suggesting it well may be small in the III-P compounds. Pseudopotential matrix elements[21] show the X_1^c value larger than L_1^c in about the correct proportion to explain the GaAs ER and EDR data. OPW calculations[21] for GaAs are in essential agreement and show further a $In4d - L_1^c$ matrix element about twice as large for $In4d - X_1^c$, suggesting again that the L_1^c strength increases for increasing anion atomic number. However, a comprehensive treatment is required.

Finally, the "exciton binding energies" of all Ga3d and $In4d - L_1^c$ transitions appear to be similar and much smaller than that for $In4d - X_1^c$ transitions. In all cases the shifts are so large that appreciable L-X mixing should occur in the final state. Owing the differences in deformation potentials among Γ_1^c, L_1^c, and X_1^c, uniaxial stress measurements should be useful in probing the mixing as well as the local vs. band character and the validity of the band interpretation.

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Table 1. Minima in the second derivative spectra of GaP, GaAs, GaSb, InP, InAs, and InSb in the region of 3d- or 4d-core to conduction band transitions. Electroreflectance thresholds from ref. 4, corrected to room-temperature values, are shown in parenthesis for comparison for the Ga-V compounds. All entries are in eV.

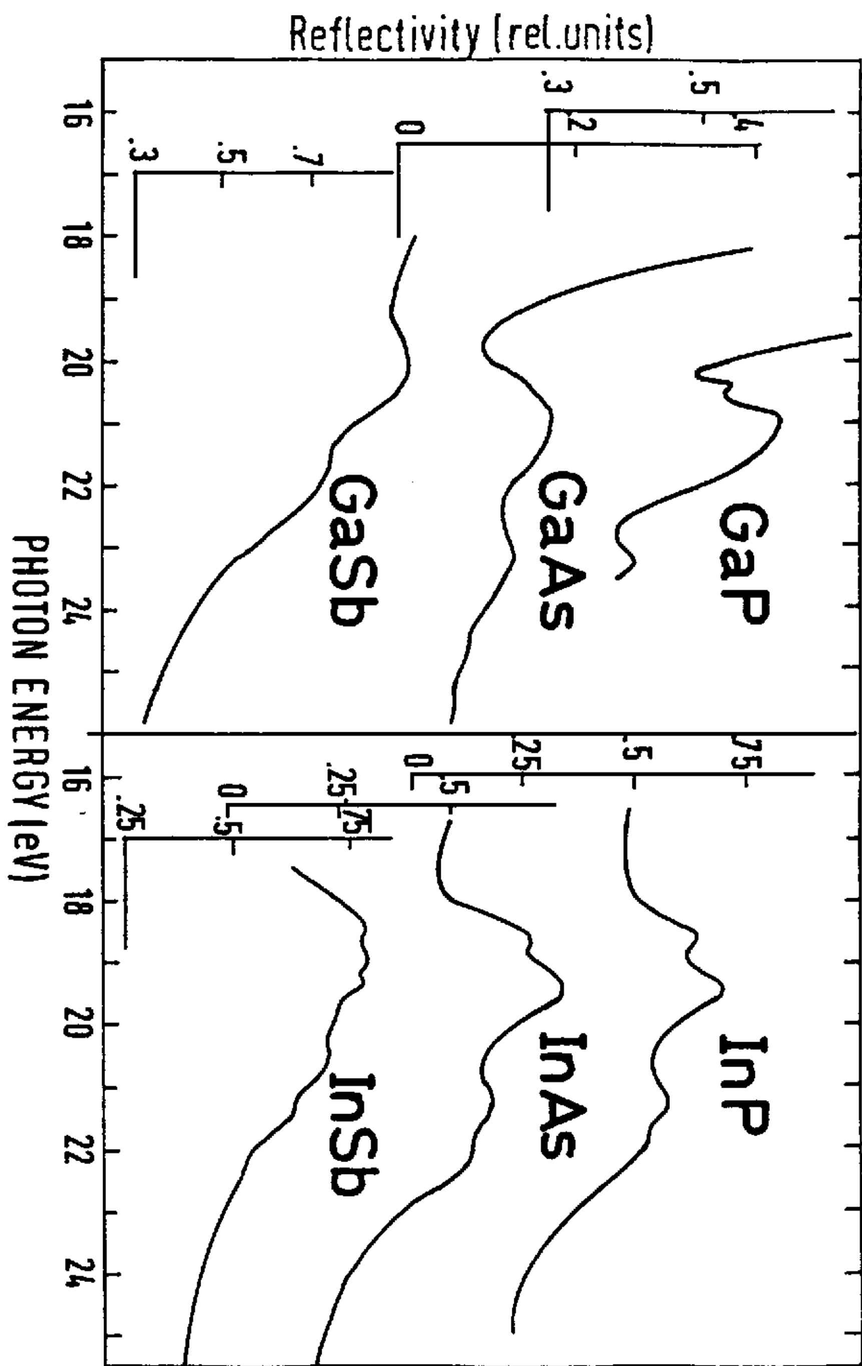
Compound	j = 5/2		j - 3/2		EDR
	L_1^c	X_1^c	L_1^c	X_1^c	Uncertainty
GaP		20.48 (20.45)		20.92 (20.89)	±0.05
GaAs	20.23 (20.27)	20.44 (20.44)	20.71 (20.71)	20.92 (20.88)	±0.03
GaSb		19.79 (19.77)		20.16 (20.21)	±0.03
InP		18.61		19.52	±0.05
InAs	18.34	18.63	19.20	19.50	±0.02
InSb	18.00	18.44	18.87	19.31	±0.03

FIGURE CAPTIONS

Fig. 1. High resolution reflectance data associated with d-transitions for several III-V compounds.

Fig. 2. Second derivative of the reflectance data calculated from Fig. 1. Arrows for Ga-V compounds indicate ER-determined thresholds; dashed lines show expected locations of lower conduction band minima. Horizontal bars indicate spin-orbit splitting of Ga 3d and In 4d.

Fig. 3. Reflectance and second derivative reflectance spectra for GaAs and InAs cleaved (110) surfaces. E^s denotes additional structure due to surface excitons.[8]



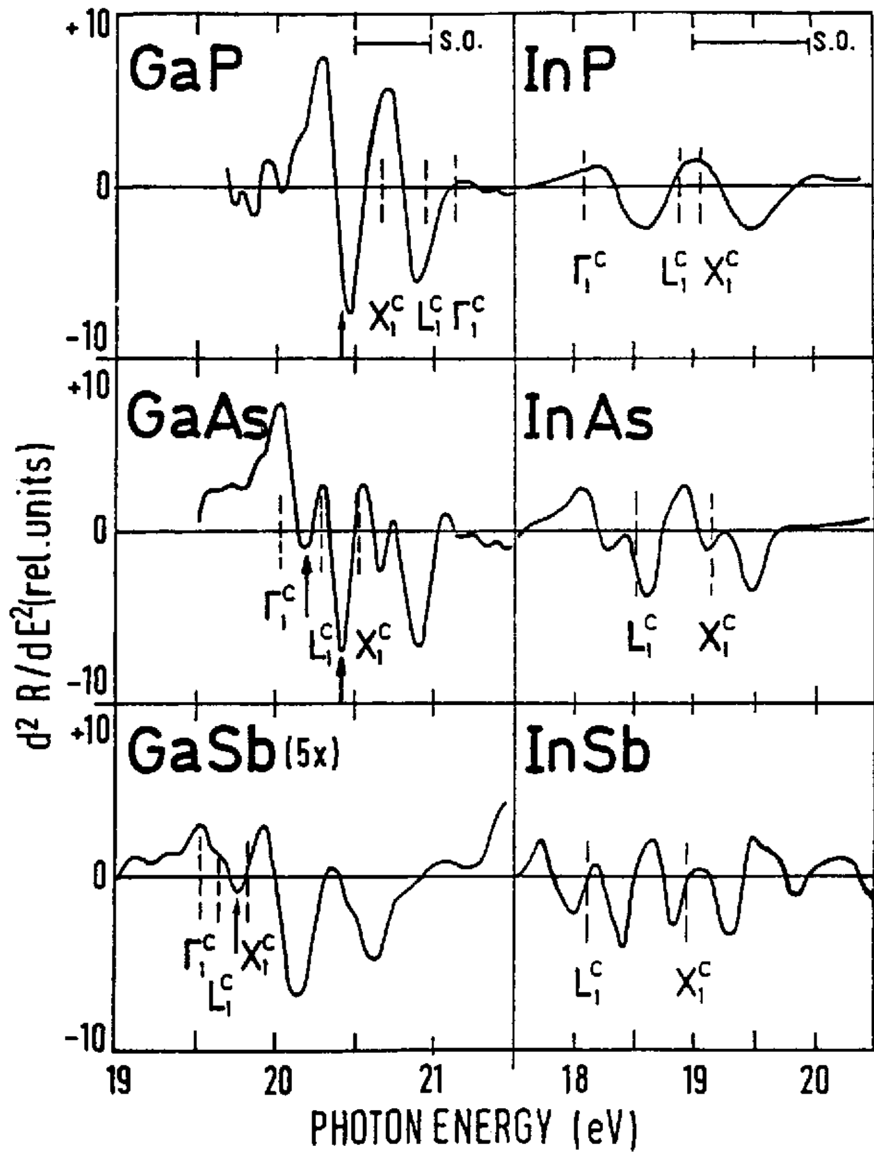


Fig. 2

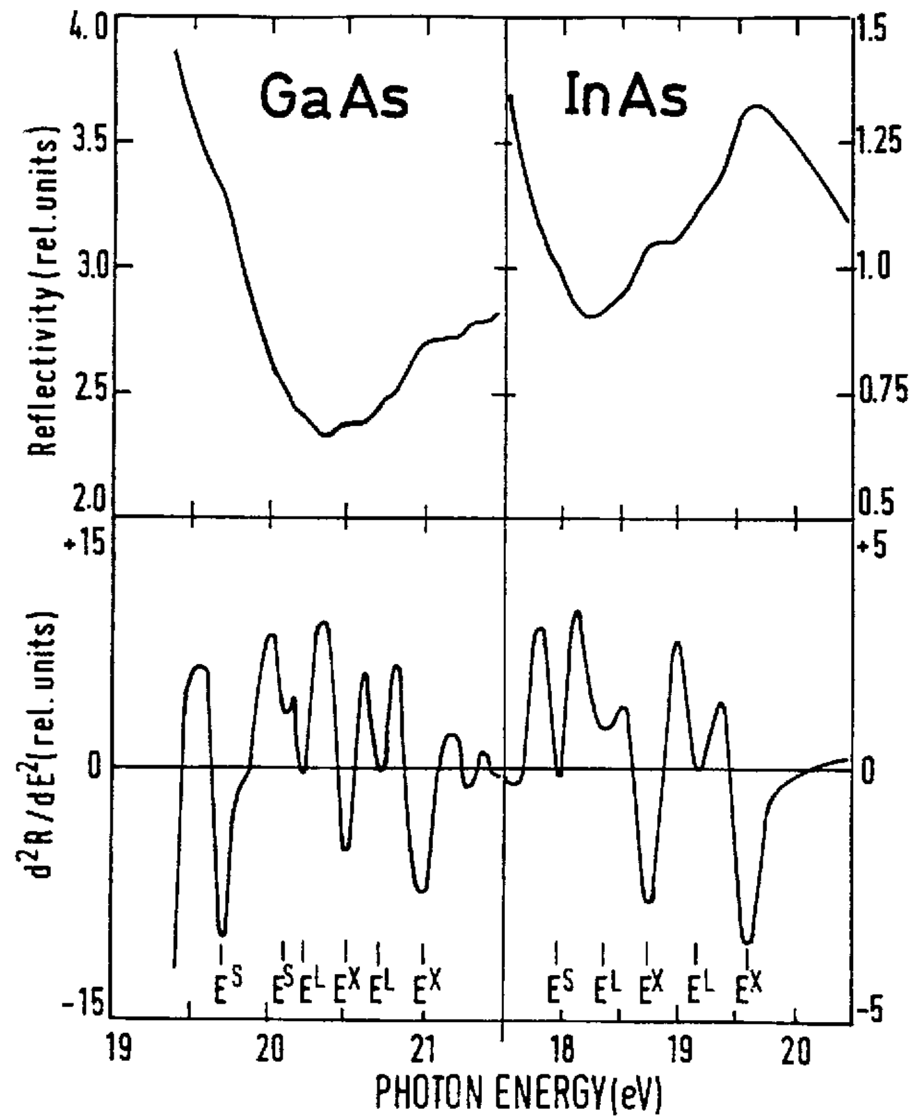


Fig. 3