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Reflectivity of Semiconductors with Wurtzite Structure

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The room-temperature reflection spectrum of hexagonal ZnS, CdS, and CdSe has been measured. A number of reflection peaks have been seen and identified with the peaks predicted for these materials when crystallized in the cubic (zincblende) modification. It is concluded that the band structures corresponding to these two crystal modifications are very similar.

IT has been suggested by Birman[1] that the band structure of wurtzite-type crystals can be derived by perturbation theory from the band structure of the corresponding zincblende-type material. So far, experimental verifications of the validity of such approach have been confined to the fundamental absorption edge.[2] We have performed reflectivity measurements on hexagonal ZnS, CdS, and CdSe crystals in order to show the close connection between the wurtzite and zincblende band structures. A number of reflection peaks have been seen at the energies at which reflection peaks for the corresponding zincblende-type materials should exist. It is concluded that the difference between the wurtzite and the zincblende crystal potentials perturbs the combined density of states for direct optical transitions only very slightly: The same peaks and edges are seen in zincblende and wurtzite and their energies differ only by a small amount (~0.1 eV).

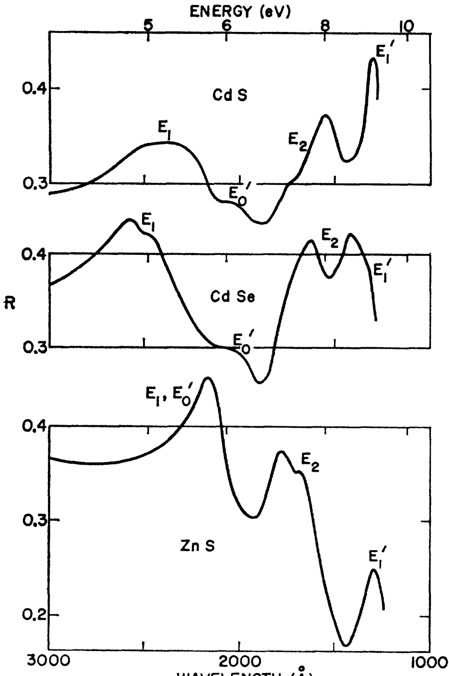

FIG. 1. Reflection spectrum of CdS, CdSe, and ZnS.

Figure 1 shows the room-temperature reflection spectrum of ZnS, CdS, and CdSe. Only relative reflectivities were measured. The measurements were performed on the surface of growth of platelets grown from the vapor phase. The light was unpolarized except for the polarization introduced by the spectrometer grating. Since the shift in the fundamental absorption edge with direction of polarization found in ZnS,[2] CdS,[3] and CdSe[4] is less than 0.03 eV, it is believed that variations in the normal incidence reflection spectrum with polarization direction should be unobservable due to the broad nature of the peaks.

The low-energy peak (E_1) of CdSe shows a splitting of 0.28 eV. This splitting is two-thirds of the splitting observed at $k=0$.[4] This relationship has also been observed in many zincblende-like materials[5] and has lead to the identification of the transitions causing the peak with direct transitions at the L point of the Brillouin zone ([111] direction, edge of the zone). It has been suggested later[6] that these transitions do not take place at the edge of the zone but at a saddle point in the energy separation between the bands, somewhere inside the zone in the [111] direction (Λ point). Since the crystal-field splitting produced by the trigonal field in CdSe at $k=0$ is much smaller than the spin-orbit splitting,[4] one can treat the spin-orbit perturbation neglecting the crystal-field splitting. Under these conditions, the spin-orbit splitting along the hexagonal axis at a point remote from $k=0$ should also be two-thirds of the splitting at $k=0$. It is, therefore, reasonable to identify this peak in CdSe with transitions at a point of k space somewhere along the trigonal axis between the top of the valence band (Λ_3 in zincblende, A_3 in wurtzite) and the lowest conduction band (Λ_1 in zincblende, A_1 in wurtzite). In order to identify the other peaks in the reflectivity structure we used Herman's perturbation scheme for correlating energy gaps of semiconductors of the same isoelectronic sequence.[7] Any energy gap of a polar zincblende-like semiconductor is given by

$$E_{\text{polar}}=E_{\text{nonpolar}}+A\lambda^2, \quad (1)$$

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[1] J. L. Birman, Phys. Rev. **115**, 1493 (1959).

[2] J. A. Beun and G. J. Goldsmith, Helv. Phys. Acta **33**, 508 (1960).

[3] D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).

[4] J. O. Dimmock and R. G. Wheeler, Suppl. J. Appl. Phys. **32**, 2271 (1961).

[5] M. Cardona, Suppl. J. Appl. Phys. **32**, 2151 (1961); M. Cardona and D. L. Greenaway, Phys. Rev. **125**, 1291 (1962).

[6] D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters **9**, 94 (1962).

[7] F. Herman, J. Electronics **1**, 103 (1955).

where E_{nonpolar} is the corresponding gap of the group IV element of the same isoelectronic sequence, A is a constant, $\lambda=0$ for group IV materials, $\lambda=1$ for III–V materials, and $\lambda=2$ for II–VI materials. Gaps involving X_1 states ([100] direction, edge of the zone) will in addition split, since the double degeneracy of X_1 in the diamond structure is split in the zincblende structure. The splitting is proportional to λ. Equation (1) is only valid for $A\lambda^2 \ll E_{\text{nonpolar}}$. A more general equation can be derived if the initial and final states of the gap interact through an antisymmetric potential. Neglecting all other interactions we obtain by diagonalizing exactly the perturbation matrix:

$$E_{\text{polar}}=E_{\text{nonpolar}}(1+2AE_{\text{nonpolar}}^{-1}\lambda^2)^{1/2}. \tag{2}$$

Figure 2 shows a plot of the various reflectivity peaks of the ZnS, CdS, and CdSe sequences as a function of λ^2. The gaps of the nonexisting group IV materials have been assumed to be the average of gaps of the existing group IV materials, i.e., the gaps of the group IV material of the CdSe sequence is obtained by averaging the gaps of Ge and α-Sn. The reflectivity spectrum of GaP and InAs has been reported previously.[5,8,9] The reflectivity peaks of InP have been measured by the author.[10] The experimental points have been fitted with Eqs. (1) and (2), using for the II–VI compounds the peaks of the wurtzite instead of the zincblende materials. Equation (1) has been used for gaps between states which do not interact through an antisymmetric potential ($X_4 \rightarrow X_1$, $L_{3'} \rightarrow L_1$), Eq. (2) for interacting gaps ($L_{3'} \rightarrow L_3$, $\Gamma_{25'} \rightarrow \Gamma_{15}$). The good fit obtained establishes the similarity between the zincblende and wurtzite band structures, confirms the identification of the E_1 peak in CdSe, and suggests the same identification for the E_1 peak in CdS. The low-energy peak in ZnS must be a superposition of the E_1 peak and the E_0' peak, due to transitions at the center of the Brillouin zone between the highest valence band ($\Gamma_{25'}$ for diamond structure, Γ_{15} for zincblende, Γ_1 and Γ_5 for wurtzite) and a degenerate conduction band minimum (Γ_{15} for diamond and zincblende structures, Γ_1 and Γ_5 for wurtzite). A similar phenomenon occurs in other materials of the ZnS sequence such as GaP[5] and CuCl.[11] The E_2 peaks are due in the diamond-like materials to transitions between the X_4 valence band and the X_1 conduction band points. The X_1 point splits into two (X_1 and X_3) in the zincblende structure. The splitting seen in ZnS, CdS, and CdSe at the E_2 peak is related to the X splitting. However, since the X point of the zincblende lies inside the Jones zone of the wurtzite and does not have any particularly high symmetry, an additional splitting of this point by the trigonal field may cause a large discrepancy between the wurtzite and zincblende splittings.

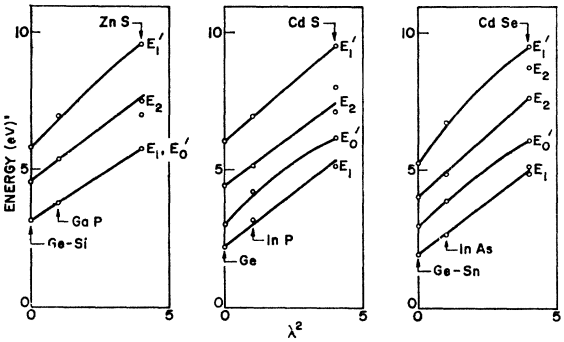

FIG. 2. Reflection peaks of the CdS, CdSe, and ZnS isoelectronic sequences as a function of polar perturbation parameter λ.

TABLE I. Energies (in eV) of the reflectivity peaks in ZnS, CdS, and CdSe.

	E_1	E_0'	E_2	E_1'
ZnS	5.7	5.7	7.0 7.5	9.5
CdS	5.1	6.1	7.1 8.0	9.5
CdSe	4.8 5.08	6.1	7.6 8.7	9.5

The E_1' peak is due, in zincblende-like materials, to transitions between the L_3 valence band and the L_3 conduction band.[9] Figure 2 indicated that this is also the case in the wurtzite materials where the equivalent of the L_3 point is the Γ_5' point. The energies of the observed reflectivity peaks in the wurtzite-like materials are listed in Table I.

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[8] J. Tauc and A. Abraham, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 375.

[9] H. Ehrenreich, H. R. Phillipp, and J. C. Phillips, Phys. Rev. Letters **8**, 59 (1962). The energy of the $\Gamma_{15} \rightarrow \Gamma_{15}$ peak given in this paper for InAs seems incorrect. A better fit is obtained in Fig. 2 by attributing to these transitions the 3.9-eV hump in the reflectivity of InAs.

[10] M. Cardona, J. Appl. Phys. **32**, 958 (1961); also (unpublished).

[11] M. Cardona, Phys. Rev. **129**, 69 (1963).