POLARIZATION DEPENDENCE OF THE FAR ULTRAVIOLET OPTICAL TRANSITIONS IN CdS

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The far ultraviolet reflection spectrum of CdS displays a number of distinct features in the range 5 to 18 eV which have been attributed, by analogy with the spectra of diamond and zinc blende materials, to direct valence-to-conduction band transitions.[1,2] From a low-temperature study in polarized light out to 6 eV, Cardona[3] attributed the complex 5.6-eV peak to the doublet $(\Delta_5, \Delta_6) \to (\Delta_1\Delta_3)$ at 4.95 to 5.03 eV and a single transition analogous to $L_3' \to L_3$ of the zinc blende structure at 5.58 eV. In addition, Phillips[4] assigned the 9.5-eV peak to $\Gamma_6^v \to \Gamma_5^c$. The author[1] has observed this latter peak to be double with maxima at 9.2 and 9.6 eV and suggested, it now appears erroneously, an identification of the 9.6-eV peak with the second member of the spin-orbit split $\Gamma_5^v \to \Gamma_1^c$ (upper) transition. A series of three high-energy peaks at 14.4, 16.1, and 17.4 eV have been attributed to transitions originating on the cadmium 4d band.[1]

Recent photoemissive studies by Kindig and Spicer[5] have raised doubts concerning the exclusive role of direct transitions in explaining the above features of the optical spectrum. Maxima in the photoelectron energy distribution at electron energies of 0.6 and 1.8 eV which are independent of the exciting photon energy were interpreted as due to transitions to final states consisting of two maxima in the conduction-band density of states at 6.8 and 8.2 eV, respectively, above the valence-band maximum. A shoulder appearing in the energy distribution for photon energies exceeding 9.6 eV and whose position was linearly dependent on the photon energy was attributed to transitions from an initial state at a maximum in the valence-band density of states located 1 eV below the top of the valence band. This interpretation is consistent with the optical data, provided we ignore the doublet nature of the 6-, 8-, and 9-eV peaks and postulate a third conduction-band density-of-states maximum about 5 eV above the top of the valence band. The optical transitions below 10 eV could then be accounted for by transitions from the single valence-band density-of-states maximum to the three conduction-band maxima. The three peaks at 14.4, 16.1, and 17.4 could then be attributed to transitions from another valence-band density-of-states maximum located about 9.3 eV below the top of the valence band to the same three conduction-band maxima. The neglect of the fine structure is reasonable since a fairly wide (twenty-Angstrom) bandwidth was employed in the photoemissive measurements. This interpretation requires, however, that k-nonconserving transitions occur with transition probabilities comparable to direct transitions.

In an attempt to clarify this situation the room-temperature reflection spectrum of a cleaved single crystal of CdS was measured in the hitherto inaccessible region 6-11 eV with radiation polarized perpendicular and parallel to the C axis. It was hoped that if k-conserving transitions were dominant, they would show a polarization dependence through the crystal selection rules. A recently developed pile-of-plates polarizer[6] constructed from LiF plates was employed. It gave a polarization of 80% near 1216 Å (10 eV) and 70% near 1680 Å (8 eV). Figure 1 shows the reflection spectrum for the two orientations. Since the angle of incidence, 25°, was not zero, $R_\perp$ was expected and observed to be larger than $R_\parallel$ in the absence of specific crystalline anisotropy effects. Only two crystalline effects were observed in this region. These were a strong enhancement of the 7- and 9.2-eV peaks for $E \perp C$. These effects are interpreted as due to the crystalline selection rules governing the interband transition rather than a decrease in R for $E \parallel C$ associated with an approach to the Brewster condition for two reasons. (1) A strong reduction in R for $E \parallel C$ for an incident angle of 25° would occur only for $n \sim 0.5$. Since preliminary measurements by the author show that n is well above unity in this region, this effect is ruled out. (2) The polarization results show a definite enhancement at the two peaks in question for $E \perp C$ compared to data for unpolarized radiation. The 7-eV peak in CdS and a corresponding one at 6.3 eV in CdSe were interpreted by Phillips[4] as due to $\Gamma_5^v \to \Gamma_5^c$ with the selection rule $E \parallel C$. This assignment was made on the basis of measurements using unpolarized light.[2] The present results clearly show that the selec-

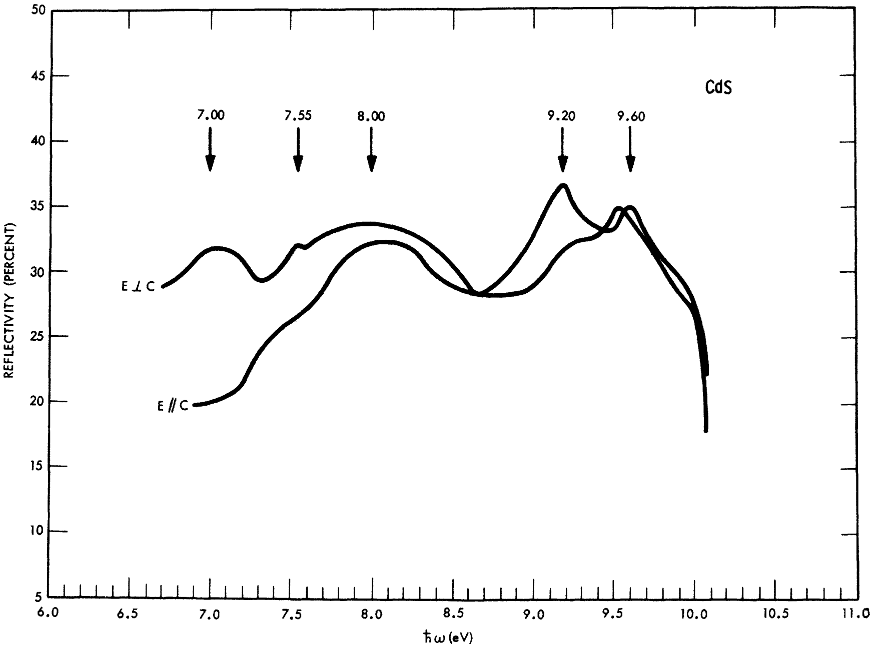

FIG. 1. Ultraviolet reflection spectrum of CdS in light linearly polarized perpendicular ($E\perp C$) and parallel ($E\parallel C$) to the C axis.

tion rule for the 7-eV transition is $E\perp C$. If this transition takes place at the center of the Brillouin zone, the only likely transition, neglecting the small (0.02-eV) spin-orbit splitting, would be $\Gamma_5^v \to \Gamma_1^c$. Preliminary calculations by Herman[7] for ZnS, however, would favor assigning $\Gamma_5^v \to \Gamma_1^c$ to the 9.2-eV peak with $E\perp C$. It has not been possible to arrive at an assignment of the peaks below 10 eV in terms of transitions only at the Γ point which will agree with the polarization measurements.

The lack of polarization effects in the 8.0-eV peak and the complex nature of the 9-eV peak indicate that the situation in CdS is much more complex than in the zinc blende materials. Thus, while a strong k-conserving transition such as $\Gamma_5^v \to \Gamma_1^c$ may contribute to the polarization-dependent part of the 9-eV peak, nonvertical transitions between other density-of-states maxima degenerate in energy with this transition may be responsible for the bulk of both the 8- and 9-eV peaks. Evidence for the violation of k conservation for certain transitions for which the initial electron state is strongly coupled to the phonon field seems to exist for several materials.[8] Further polarization studies at low temperature on CdS and CdSe, where spin-orbit effects may aid in the interpretation, should help clarify this complex situation.

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