EXCITONS AT THE L ABSORPTION EDGE IN ZINC BLENDE-TYPE SEMICONDUCTORS

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Reflectivity measurements in semiconductors with zinc blende structure have shown the existence of a very strong absorption edge at photon energies considerably larger than the energy gap.[1] This edge corresponds to transitions at the L point of the Brillouin zone and shows a splitting due to the spin-orbit splitting Δ_1 of the L_3 valence band state.

In the present work, we observed the L edges by transmission in thin films obtained by evaporation on a heated substrate. Due to the large absorption coefficient at the top of this edge (between 10^5 and 10^6 cm^{-1}), it was not possible to prepare by grinding and polishing films thin enough for transmission studies. The substrate temperature, velocity of evaporation, and subsequent annealing were adjusted in order to optimize the steepness of the absorption edge. Films of GaAs, GaSb, InAs, InSb, ZnSe, HgSe, ZnTe, CdTe, and HgTe were prepared. They all showed absorption edges and spin-orbit splittings in good agreement with those found from reflectivity measurements. When the temperature was lowered, exciton effects appeared which, as expected, were especially noticeable in those materials with a large spin-orbit splitting (InSb, GaSb, HgTe, CdTe, and ZnTe). Figure 1 shows the log of the absorbance of an InSb film at several temperatures as a function of photon energy. The film thickness is 0.3 micron as determined by the Tolansky method. The substrate was heated to 180°C during the evaporation. The excitonic nature of the absorption spectrum appears clearly at 78 and 20°K.

We have attempted to fit the absorbance immediately above the first exciton peak with Elliot's formula for allowed direct absorption above the energy gap[2] which takes into account the electron-hole Coulomb interaction:

$$\alpha = Ke^{x}/\sinh x, \text{ with } x = \pi E_{ex}/(\hbar\omega - E_g), \qquad (1)$$

where α is the absorption coefficient, E_{ex} the exciton binding energy, E_g the energy gap, and K a constant. The best fit was obtained for $E_{ex} = 0.04$ ev. The increase in absorption beyond 3 ev is due to the existence of a maximum in the absorption coefficient at 4.1 ev.[1] Attempts to prepare samples thin enough for the observation of the maximum were not very successful: A broad maximum was always obtained due to the presence of pinholes. No attempt was made to fit with Eq. (1) the absorption of the high-energy exciton since there is no way of subtracting from the experimental data the absorption of the low-energy exciton.

Figure 2 shows $\log(I_0/I)$ for a 0.25-micron thick CdTe film evaporated on a substrate at 300°C and annealed for 24 hours at the same temperature. The presence of exciton absorption is also seen clearly at 78 and 20°K. The smallness of the fundamental absorption edge observed around 1.6 ev gives a clear idea of the relative magnitude of the fundamental and the L absorption edges. While the shape of the 4.05-ev peak is probably determined by the poor resolution (due to the low light intensity available), the shape of the 3.5-ev peak should be real. The best fit for the absorption above the first exciton peak was obtained with Eq. (1) for $E_{ex} = 0.035$ ev.

Table I lists the energy of the exciton peaks E_1 and $E_1 + \Delta_1$ found by transmission in evaporated films at several temperatures and the energy of the corresponding reflectivity peaks of bulk ma-

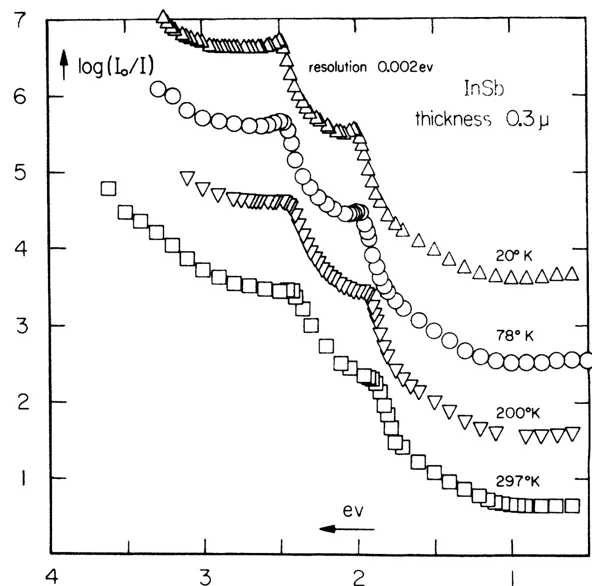

FIG. 1. Absorption in an InSb film as a function of photon energy. (The vertical scale corresponds to the measurements at 297°K. The vertical scales for the curves at 200, 78, and 20°K have been shifted by 1, 2, and 3 units, respectively.)

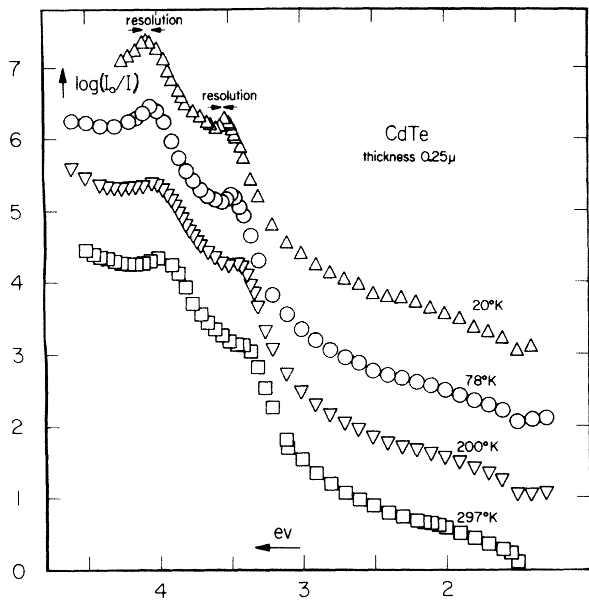

FIG. 2. Absorption in a CdTe film as a function of photon energy. (The vertical scale corresponds to the measurements at 297°K. The vertical scales for the curves at 200, 78, and 20°K have been shifted by 1, 2, and 3 units, respectively.)

terial at room temperature.[1] The agreement between transmission and reflection data is excellent.

The absorption edges reported in this work are due to transitions between electronic states with $\vec{k}_e = (\pi/a, \pi/a, \pi/a)$, where a is the lattice constant. The hole left in the valence band after absorption of one photon has $\vec{k}_h = -\vec{k}_e$ and the crystal momentum of the resulting exciton is $\vec{k} = \vec{k}_e + \vec{k}_h = 0$. The exciton binding energies obtained are an order of magnitude larger than the values found for the direct and indirect excitons in Ge,[3] but comparable to the binding energies obtained for the cuprous halides.[4] However, the meaning of the binding energy obtained from Eq. (1) is questionable, since this equation was derived for nondegenerate bands with spherical symmetry. The poor crystal structure may also alter the shape of the absorption curve and thereby change the value of E_{ex} obtained from Eq. (1). A theoretical estimate of the bound levels of these excitons, according to the method of Dresselhaus,[5] is not possible since the effective-mass parameters of the valence and conduction bands at the L point are not known. Moreover, the polar nature of these compounds makes it difficult to estimate the dielectric constant to be used in the effective Coulomb interaction between electron and hole.[6]

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Table I. Energies (in ev) of the exciton peaks of thin films and of the corresponding reflectivity peaks of bulk material for zinc blende-type semiconductors.

	E_1 transmission				$E_1+\Delta_1$ transmission				E_1 reflection	$E_1+\Delta_1$ reflection
Material	20°K	78°K	200°K	297°K	20°K	78°K	200°K	297°K	297°K	297°K
ZnSe	4.94	4.92	4.89	4.80	5.20	5.19	5.14	5.10	4.75[a]	5.10[a]
ZnTe	3.66	3.64	3.57	3.52	4.19	4.18	4.14	4.10	3.57	4.13
CdTe	3.53	3.49	3.44	3.38	4.07	4.05	4.02	3.96	3.29	3.84
HgSe	3.00	2.97	2.92	2.87	3.30	3.28	3.23	3.20	2.82	3.13
HgTe	2.26	2.24	2.20	2.14	2.88	2.86	2.81	2.78	2.08	2.77
GaSb	2.18	2.16	2.11	2.07	2.62	2.60	2.58	2.56	2.02	2.48
InSb	2.00	1.98	1.95	1.89	2.49	2.48	2.47	2.44	1.82	2.38

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