OBSERVATION OF *d* BANDS IN 3-5 SEMICONDUCTORS

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(Received December 29, 1961)

We have observed the indium *d* bands in InSb and InAs and the gallium *d* bands in GaAs and GaP as structure in the vacuum ultraviolet reflectance at photon energies above 16 ev. The reflectance for energies below about 10 ev is associated with interband transitions.[1] At larger energies, when the f-sum rule for valence band states is nearly exhausted, the reflectance due to the valence electrons exhibits free electron-like behavior as described qualitatively by Drude theory.[2] Deviations from this behavior, shown in Fig. 1, were observed for energies above 16 ev for the 3-5 compounds studied here. It will be shown here that this structure is associated with the *d* band. In Si, where *d* bands are absent, the reflectance continues to fall as in the case of an ideal metal. The dielectric constants $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ and the absorption coefficient $\alpha = 4\pi k/\lambda$ were evaluated by applying the Kramers-Kronig relations to these data.[3] Results for InSb are shown in Fig. 2. Corresponding plots for the other materials are similar.

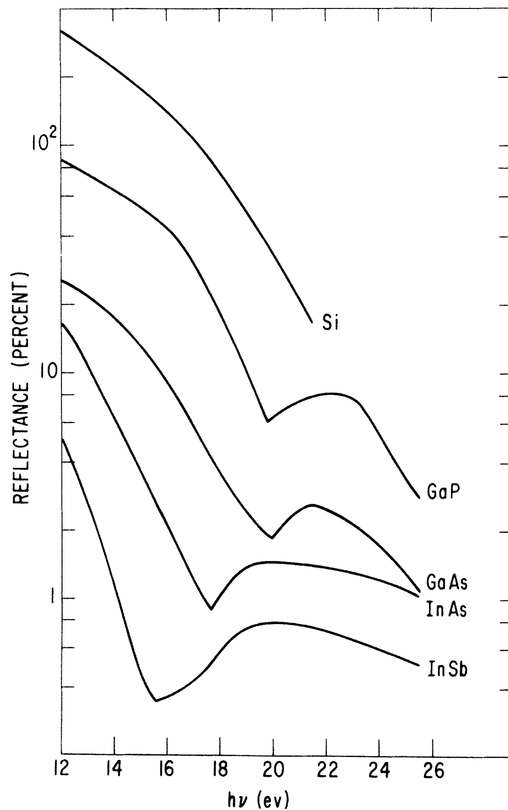

FIG. 1. Spectral dependence of the reflectance at 300°K of several semiconductors. Observed reflectances correspond to multiplying the ordinate by 2 for InSb, 1 for InAs, $\frac{1}{2}$ for GaAs, $\frac{1}{4}$ for GaP, and $\frac{1}{10}$ for Si.

An expression for the complex dielectric constant $\epsilon(\omega)$ for an insulator in the band approximation, which includes damping effects, can be obtained as a generalization of previous theoretical results[4]:

$$\epsilon(\omega) = 1 - m^{-1}(e/\pi)^2 \int d^3k \sum_{ll'} f_0(E_{\vec{k}l}) f_{l'l} \times (\omega - \omega_{ll'} + i/\tau)^{-1} (\omega + \omega_{ll'} + i/\tau)^{-1}. \quad (1)$$

Here $\omega_{l'l} = (E_{\vec{k}l'} - E_{\vec{k}l})\hbar$ in terms of the energy $E_{\vec{k}l}$ for an electron in band l having wave number k, $f_0(E_{\vec{k}l})$ is the Fermi distribution, $f_{l'l}$ is an oscillator strength, and τ is the single, possibly frequency-dependent, relaxation time which provides an heuristic description of the damping effects. This expression contains the physical features just discussed. For frequencies greater than those corresponding to essential exhaustion of the f-sum rule it reduces to a Drude-like formula which can be fit quantitatively to the experimental dielectric constants in Si. Asymptotically, $\epsilon_1(\omega)$ approaches unity from below and $\epsilon_2(\omega)$ approaches zero. Equation (1) also predicts a rise of $\epsilon_1(\omega)$ above unity due to *d* bands for materials in which they exist. Figure 2 shows that this behavior is in fact observed.

Additional structure might be expected in the high-energy reflectance peaks since the transitions from the *d* bands terminate at different energetically close conduction bands. The fact that this structure is not observed may be due to experimental difficulties in measuring small values of reflectance in this energy region and also to broadening effects, resulting from the electron-electron interaction, which are associated with such highly excited electronic states.

The reason for expecting to observe only the Ga and In *d* bands is that the As and Sb bands lie below those of Ga and In by roughly 23 and 13 ev, respectively, according to atomic data.[5] It is noteworthy that the behavior of the reflect-

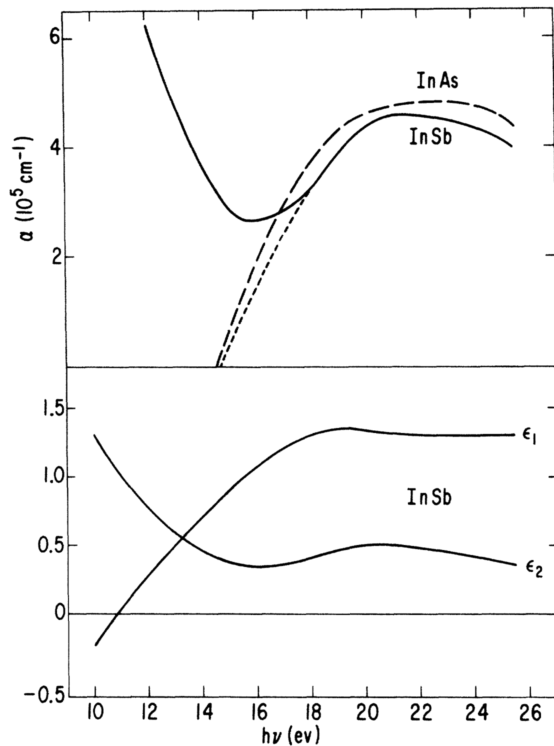

FIG. 2. Dielectric constants $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ and absorption coefficient $\alpha = 4\pi k/\lambda$ for InSb (and InAs) vs $h\nu$.

ance (Fig. 1) is quite similar for the pairs InSb, InAs and GaAs, GaP. This similarity is also observed in the absorption coefficient, illustrated in Fig. 2 for InSb and InAs in this energy range. This observation is all the more striking since the only d band possible in GaP is due to Ga.

Naively, one might identify the minimum d-band conduction band separation $E_{cd} = \hbar\omega_{cd}$ with the onset of additional optical absorption, as indicated by the dashed lines in Fig. 2. However, it is possible that absorption occurs at energies about 4 ev smaller than this minimum separation because of broadening effects caused by electron interactions.[6] This situation corresponds to a partial breakdown in the band approximation and foreshadows the even more serious deviations from the one-electron picture encountered in x-ray spectroscopy.[7] More appropriately, the gap should be assumed to lie somewhere between the energies where $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are maximum.[8] This corresponds to about 21 ev in InSb and InAs, and to about 22 ev in GaP and GaAs. Because of the inaccuracy of the Kramers-Kronig analysis in this energy range due to inadequate extrapolation of the reflectance data beyond the last experimental point, it is not possible to give these values more precisely.

Another way of verifying that it is indeed the d band that is responsible for the structure observed above 16 ev is by application of a sum rule due to Nozières and Pines.[9] This general theorem states that for a single, energetically well-isolated group of electrons (such as, for example, the valence electrons in Si) which are characterized by a plasma frequency $\omega_p = (4\pi ne^2/m)^{1/2}$, where m is the free electron mass and n is the number of electrons per unit volume, $\int_0^\infty \omega\epsilon_2(\omega)d\omega = \pi\omega_p^2/2$. An analogous relation for a finite range of integration, applying in the one-electron approximation where several bands are contributing, can be obtained from Eq. (1). This can be written in the form

$$\int_0^{\omega_0} \omega\epsilon_2(\omega)d\omega = (2\pi^2e^2/m)n_{\text{eff}}, \qquad (2)$$

where n_{eff} is the effective density of electrons contributing to the integral between the limits 0 and ω_0. From the explicit expressions for n_{eff}, to be given elsewhere,[10] it can be shown that n_{eff} increases monotonically to a value corresponding to four electrons per atom when ω_0 ranges from zero to a frequency somewhat larger than the valence bandwidth. Equation (2) predicts

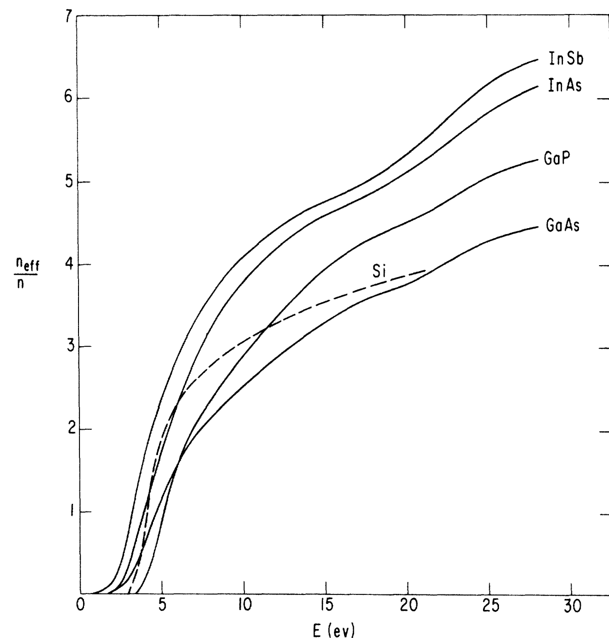

FIG. 3. Effective number of electrons per atom (n_{eff}/n) vs $h\nu$ obtained from Eq. (2) and data.

a further increase in n_{eff} when ω_0 approaches ω_{cd}. If the cation d band is sufficiently well separated from the anion band, n_{eff} will saturate at a value of 9 electrons per atom for ω_0 such that the f-sum for the anion d band is exhausted.

Because of broadening effects the d band will again contribute at energies somewhat below ω_{cd}. Figure 3 shows the results, expressed in terms of n_{eff}/n, where n is the number of atoms per unit volume, obtained from numerical integration of the experimental values of $\omega\epsilon_2(\omega)$. The curves for the 3-5 compounds all exhibit a characteristic break near 20 ev and values of n_{eff}/n greater than 4. Since the valence bands contain only 4 electrons per atom, the additional structure in the reflectivity, responsible for the behavior shown in Fig. 3, must be due to the d band. In contrast, the curve for Si does not show this structure and appears to saturate for $n_{\text{eff}}/n = 4$ as expected.

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[2]For example, L. G. Schulz, Suppl. Phil. Mag. 6, 102 (1957)
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[7]For example, L. G. Parratt, Revs. Modern Phys. 31, 616 (1959).
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[10]H. Ehrenreich and H. R. Philipp (to be published).

BONDING AND ANTIBONDING SPIN-ORBIT SPLITTINGS*

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(Received December 29, 1961)

Ehrenreich, Philipp, and Phillips have reported[1] the identification of several new interband transitions in semiconductors, notably $L_{3'} \rightarrow L_3$. The spin-orbit splitting $\Delta_{\text{SO}'}$ of bonding $L_{3'}$ is already known in a large number of semiconductors[1,2] through the splitting of the transition[3,4] $L_{3'} \rightarrow L_1(s)$. The new measurements yield Δ_{SO}, the spin-orbit splitting of antibonding L_3. The pertinent energy levels are shown in Fig. 1.

Here we calculate Δ_{SO} and $\Delta_{\text{SO}'}$ in several different ways, and show that the results have far-reaching implications for the choice of representations of crystal wave functions. We begin with the simplest approximation, which is to set $\Delta_{\text{SO}} = \Delta_{\text{SO}'} = \Delta_{\text{atomic}} = 0.12$ ev in neutral Ge.[5]

Because of the strong covalent bond, we know there must be substantial overlap between the wave functions of nearest neighbors. This effect can be included in the tight-binding approximation by forming linear combinations of atomic orbitals (LCAO's). For the L_3 and $L_{3'}$ levels the relevant nearest neighbor overlap integrals are

$$\pi = (pp\pi) = 0.56,$$
$$\sigma = (pp\sigma) = -0.11. \qquad (1)$$

The numerical values were obtained by fitting

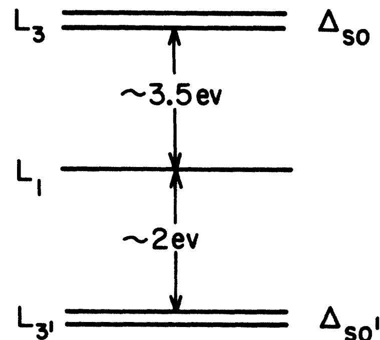

FIG. 1. A sketch of the important energy levels at $\vec{k} = \vec{L} = \pi a^{-1}(1, 1, 1)$ in diamond- and zinc-blende-type semiconductors.