DIELECTRIC CONSTANT BEHAVIOR NEAR BAND EDGES IN CdTe and Ge†

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Optical reflectance measurements[1] have been used to obtain the frequency-dependent dielectric constants $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ in semiconductors at 300°K. In order to obtain a more complete understanding of $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ near band edges, these quantities were measured for Ge and CdTe at low temperatures (25°K) as well as 300°K. These data are presented here together with an elementary theory which accounts for the essential features of the observations.

It will be shown that the structure associated with a band edge may resemble that for an oscillator or exciton. This feature is important not only in connection with the present data, but also in relation to some controversy[2] associated with the interpretation of transitions at the point X in Ge, Si, and the III-V compounds.

The data are shown in Fig. 1. Data on CdTe were obtained on cleaved faces of single crystals of high-resistivity CdTe,[3] exposed to air for less than an hour after cleaving. The results for Ge were obtained on etched HF-rinsed samples.[4] The dielectric constant was measured by an ellipsometric method described by Roberts.[5] The reflectance of CdTe calculated from the results in Fig. 1 agrees with our measurements of the reflectance (not reported here), but differs in absolute value from previous observations.[1,6] Except for the appearance of the shoulder in ϵ_2, the results for Ge show the structure already reported.[2]

The observed shoulder in ϵ_2 at 2.5 ev in CdTe, Fig. 1(a), is identified as the $\Gamma_7 \rightarrow \Gamma_1$ transition. Since the $\Gamma_8 \rightarrow \Gamma_1$ gap is 1.6 ev,[7] the valence band

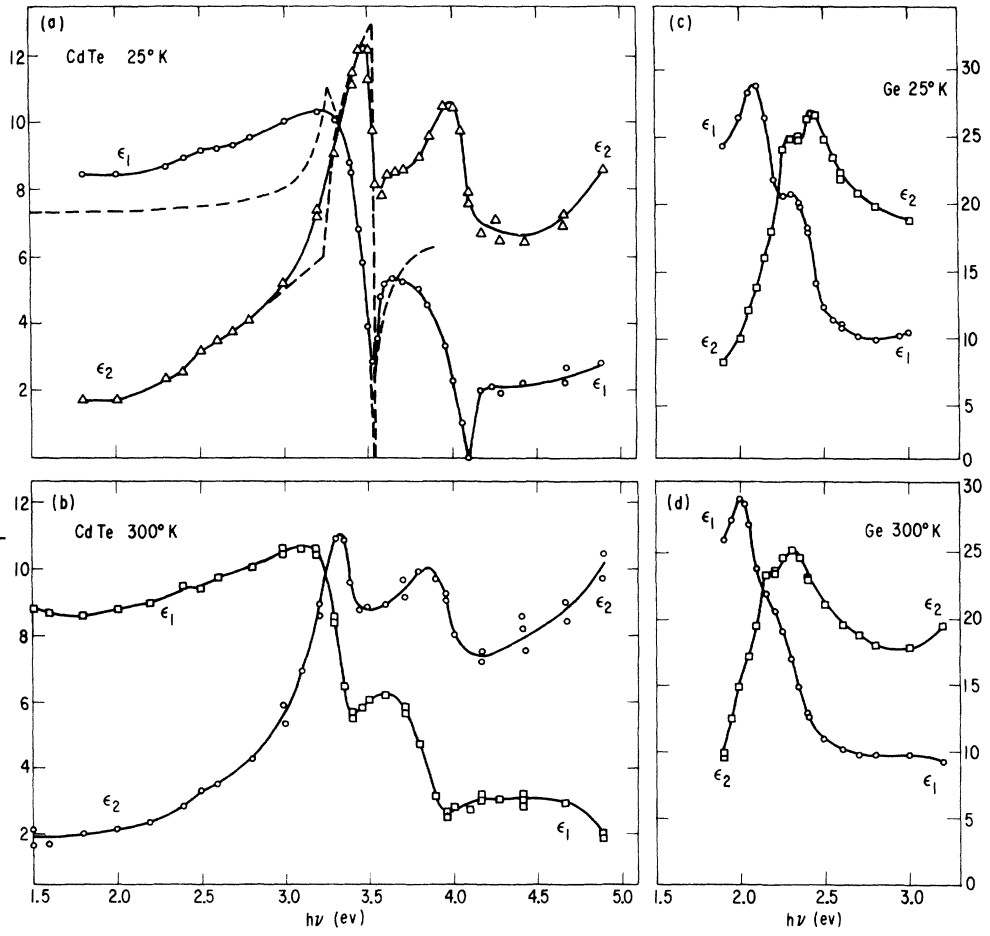

FIG. 1. Dielectric constant $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ observed for CdTe and Ge at 25°K and 300°K vs $h\nu$. Dashed curves are calculated values.

spin-orbit splitting at Γ is 0.9 ± 0.1 ev. This is consistent with the observed splitting[1] of $L_{3'}$. The corresponding splitting in Ge (see Fig. 1), 0.2 ev, agrees with reflectance results.[8]

The structure in CdTe at 3.45 and 4.0 ev might be identified with exciton formation at L. Qualitatively the dielectric constants vary as for oscillators and the structure sharpens as the temperature is reduced. If the weak edge at 3.65 ev is associated with interband transitions, the binding energy would correspond to 0.2 ev. These excitons would be comparable to those observed in alkali halides[9] rather than those at Γ in covalent semiconductors.[10] An exciton picture, however, is not compelling since there are marked deviations from pure oscillator-like behavior in $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$. Since the great similarity of the reflectivity of CdTe and other semiconductors having the diamond and zinc blende structures suggests that the band structures of all these materials are very much alike, the existence of tightly bound excitons in CdTe would be rather surprising.

It is indeed possible to explain the observed structure in terms of interband transitions. Korovin's theory,[11] which applies only when the two bands involved in a transition remain essentially parabolic for energies rather larger than the band gap E_G, must be modified since bands in fact become appreciably nonparabolic in this region. More general results can be obtained from the expressions for $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ given by Ehrenreich and Cohen.[12] For an insulator

$$\epsilon_1(\omega) = 1 + m^{-1}(e/\pi)^2 \sum_{ll'}{}' P \int d^3k f_0(E_{kl}) f_{l'l}(\omega_{l'l}{}^2 - \omega^2)^{-1}, \tag{1}$$

where $\omega_{l'l} = (E_{kl'} - E_{kl})/\hbar$ in terms of the energies E_{kl} of an electron in band l having wave number k, $f_0(E_{kl})$ is the Fermi distribution function, and P indicates that the principal value is to be taken. It is seen from Fig. 2(a), in which $\omega_{l'l}(k)$ for the $\Lambda_{3'}$ and Λ_1 bands in[13] Ge is sketched as an example, that $\omega_{l'l}(k)$ can have an extremal value $\omega_{l'l}(k_0)$ at some point k_0 in the Brillouin zone. When $\omega = \omega_{l'l}(k_0)$, the integrand has a singularity and $\epsilon_1(\omega)$ is negative and possibly singular. Since $\nabla_k \omega_{l'l}(k_0) = 0$, k_0 corresponds to a singularity in the joint density of states for bands l and l'. The singularity will be removed if damping effects are introduced. If $\omega_{l'l}(k_0)$ is energetically close to E_G, it is possible to obtain the sharp structure shown in Fig. 1(a) for CdTe at 25°K.

As a simple model, one can approximate $\omega_{l'l}$ near a single band edge by a single parabola truncated at k_0 as illustrated in Fig. 2(a). The actual

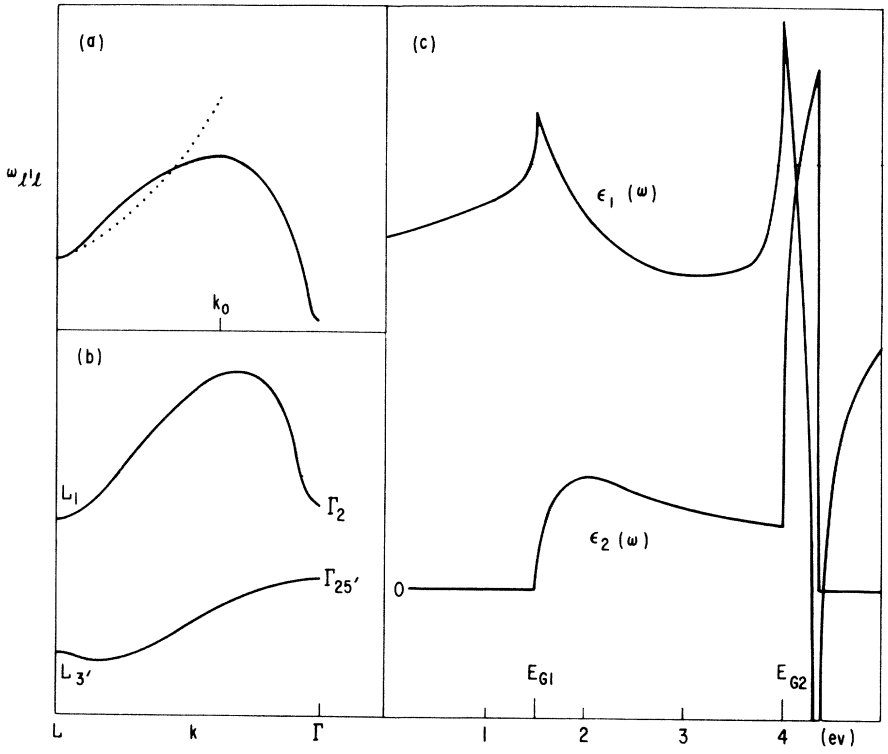

FIG. 2. (a) Solid curve: $\omega_{l'l} = (E_{kl'} - E_{kl})/\hbar$ vs wave number. Dotted curve: parabolic approximation. (b) Schematic diagram of the valence and conduction bands along the [111] axis. (c) Sketch of ϵ_1 and ϵ_2 vs $h\nu$ including two band gaps.

band structure is then replaced by two simple parabolic bands with reduced mass m_γ. Equation (1) and the corresponding equation for $\epsilon_2(\omega)$ then yield $\epsilon_1(\omega) = \epsilon_0 + \gamma g(\omega, x_0)$ and $\epsilon_2(\omega) = \gamma(\beta - 1)^{1/2}/\beta^2$ for $1 \leq \beta \leq 1 + x_0^2$ and 0 otherwise, where

$$\beta = \hbar\omega/E_G, \quad x = (\hbar^2 k_0^2/2m_\gamma E_G)^{1/2},$$

and

$$g(\omega, x_0) = (2/\pi\beta^2)$$

$$\times\{-s(\omega, x_0) - (1+\beta)^{1/2}\tan^{-1}[x_0(1+\beta)^{-1/2}] + 2\tan^{-1}x_0\},$$

with

$$s(\omega, x_0) = (1-\beta)^{1/2}\tan^{-1}[x_0(1-\beta)^{-1/2}], \text{ for } \beta \leq 1$$

$$= \tfrac{1}{2}\ln\left|[(\beta-1)^{1/2} + x_0]/[(\beta-1)^{1/2} - x_0]\right|, \text{ for } \beta \geq 1.$$

Also $\gamma = 4\nu(m_\gamma/m)^{3/2}(E_P/E_G)^{3/2}$ for $E_P = (2/m)|P|^2$ and E_G in rydbergs. Here ν is the number of equivalent valleys and P is the momentum matrix element connecting the two bands. The parameter ϵ_0 is a slowly varying contribution due to other regions in the Brillouin zone, if E_G is well isolated. The singularity at k_0 is seen to be logarithmic in this particular model.

Figure 2(c) illustrates an extension of the theory to two band edges, such as those at Γ and L, for which k_0 is the same point. The structure associated with E_{G2} is sharp due to the close proximity of $\omega_{l'l}(k_0)$. The behavior near E_{G1} is similar to that predicted by Korovin's theory.[11] An explicit fit to the lower of the two $L_{3'} \rightarrow L_1$ transitions in CdTe is shown in Fig. 1(a). It was assumed that E_G is the energy at which $\epsilon_1(\omega)$ is maximum and that the singularity occurs at the cusp; γ was determined by requiring the maximum of the theoretical and experimental values of $\epsilon_2(\omega)$ to agree; ϵ_0 was obtained from the known dielectric constant above the lattice bands; the transitions at Γ were neglected. Assuming $E_P = 25$ ev as in Sn and Ge,[14] and four valleys, one finds the reasonable values $m_\gamma/m = 0.2$ from γ, and $k_0 = 1.2\times10^7$ cm^{-1} as measured from the point L.

It is noteworthy that Ge, Fig. 1(c), does not exhibit cusps in ϵ_1. This may be because $\omega_{l'l}(k_0)$ is rather larger than E_G, as is indeed suggested by the sketch in Fig. 2(a). The behavior of $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ indeed resembles that around E_{G1} in Fig. 2(c). Another possibility is that the excited electron states in Ge may have a shorter lifetime due to Auger transitions, which are possible in Ge but probably not in CdTe since the band gaps at both Γ and L are considerably larger.

A quantitative theory of the structure of the dielectric constants must include the energy surfaces realistically and broadening effects. In particular, it requires a detailed knowledge of the singularities of the joint densities of states in the Brillouin zone.

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