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Infrared Reflectivity of Doped InSb and CdS*

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The coupling of free carriers and lattice-vibrational modes in CdS and InSb was investigated by using reflectance measurements. When the free-carrier concentration is such that the longitudinal-optical-mode frequency is at or near the plasma frequency, the longitudinal mode takes on a mixed character and is shifted in a manner similar to that described by Varga in 1965, while the transverse mode remains fixed. The electron effective masses in such a situation can be determined with the lattice effects excluded. In the case of CdS, the polaron mass and additional absorption in the plasma mode above the longitudinal-optical-phonon frequency must be taken into account.

THE subject of this paper is the coupling of free carriers and lattice-vibrational modes in polar semiconductors. This condition is most apparent when the concentration is such that the plasma frequency ω_P is at or near the longitudinal-optic-mode frequency ω_L. The authors examined the dielectric function for the coupled system of plasma and phonon modes by infrared reflectance from surfaces of suitably doped single crystals. This dielectric function was formerly derived by Varga[1] and expanded upon by Singwi and Tosi,[2] but it had been assumed and empirically used earlier by Collins and Kleinman[3] in the reflectance of ZnO in the long-wavelength limit.

Measurement of the room-temperature reflectance of a Ga-doped single crystal of CdS was made with the electric vector parallel and perpendicular to the c axis. The concentration of free electrons ($N=1.32\times10^{18}$ cm^{-3}), as measured on a Hall bar taken from the reflectance sample, fixed ω_P at $1.12\omega_L$. The principal transverse-optic-mode frequency ω_T defines ω_L by the Lyddane-Sachs-Teller relation

$$\omega_L=(1+\delta\epsilon/\epsilon_\infty)^{1/2}\omega_T\,, \tag{1}$$

when damping and weaker modes are neglected.[4] Here $\delta\epsilon$ is the principal mode strength and ϵ_∞ is the high-frequency dielectric constant. In all cases, the angle of incidence was 30°, and the data were analyzed using this value.

Polarized reflectances of two Te-doped single crystals of InSb were made in which the free-electron concentrations of $N=1.43\times10^{17}$ cm^{-3} and 3.96×10^{17} cm^{-3} fixed ω_P at $0.85\omega_L$ and $1.41\omega_L$, respectively. Most of the effective-mass variation with concentration in InSb that had been discussed by Spitzer and Fan[5] can be explained in terms of this coupling.

The validity of Varga's dielectric function has been substantiated through Raman scattering in n-type GaAs by the work of Mooradian and Wright,[6] Mooradian and McWhorter,[7] and Tell and Martin.[8] They have verified the longitudinal-optic-mode frequency shifts and in some cases the lifetimes.

A comparison of the lifetime as calculated from the Hall mobility is made with the plasma lifetime in the Drude free-electron term of the dielectric function. In CdS, which has the larger polaron coupling constant with a value of 0.58,[9] the effect of an additional polaron mode absorption is very noticeable at frequencies just greater than ω_L as calculated by Gurevich *et al.*[10] Analysis of the polaron effective mass is made in the same weak coupling approximation,[9] and with no additional parameters, the fit of the reflectance data is greatly improved. Polaron effects were considered negligible in InSb as the coupling constant has a smaller value of 0.034.

A reflectance minima relation has been derived[11] and found to work quite well when applied to these and other doped samples of ZnO,[3] InSb,[5] GaAs,[12,13] and CdS.[14]

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EXPERIMENTAL PROCEDURES

The experimental reflectance values were calculated from a comparison of sample reflected fluxes with the flux obtained by replacing the sample with an evaporated aluminum mirror (assumed to be 100% reflecting). For energies greater than 210 cm^{-1}, a Beckman IR-12 was used in double-beam operation where the angle of incidence was 30°. Wire-grid polarizers,[15] purchased from the Perkin Elmer Corporation, were placed at the entrance slit where no depolarization would occur between the polarizer and samples (AgCl substrate for energies greater than 450 cm^{-1} and polyethylene substrate for energies less than 450 cm^{-1}).

For energies less than 210 cm^{-1}, a single-beam vacuum (used here at 150×10^{-3} Torr) spectrometer, with a high-pressure GE UA-2 mercury lamp[16] as a source, was used. Visible and near-infrared radiation were eliminated by being scattered from a rough aluminum surface and by being transmitted through black polyethylene[17]—one piece at room temperature and another at 4.2°K at the detector—and crystal quartz[18] at the detector. The light was chopped at 10 cps by a semidisk blade and detected by a Texas Instruments Ga-doped germanium liquid-helium-temperature bolometer.[19,20] The bandpass regions were narrowed in the appropriate wave-number regions before they reached the echelette gratings which were used in a Czerny-Turner geometry, by being reflected from KBr,[21] transmitted through a 0.5-mm thickness of fused quartz,[22] and by having the relative grating efficiencies applied for the various orders and harmonics. The samples were placed at 60° angle in the brass light pipe—the assumed angle of incidence being 30°—with the wire-grid polyethylene polarizer situated in a 4-mm gap.[23] The distance between the polarizer and sample was minimized to $\frac{1}{2}$ in. to reduce depolarization.

The Ga-doped CdS sample was purchased from the Clevite Corporation. A Hall bar had been cut directly from the center of the polished face of the sample. The c axis of the sample was parallel to the reflecting surface and was oriented in the plane of incidence with polarized reflectances made by rotating the polarizer. Room-temperature Hall measurements showed a concentration of n-type carriers at 1.32×10^{18} cm^{-3}. The resistivity was 1.37×10^{-14} stat Ω cm.

The Te-doped InSb samples A and B were supplied by the Monsanto Company. Hall measurements of these samples showed concentrations of 1.43×10^{17} and 3.96×10^{17} cm^{-3}. Their resistivities were 0.058×10^{-14} and 0.041×10^{-14} stat Ω cm, respectively. The (111) planes were in the polished faces. The π polarizations were used rather than no polarization in order to make an exact calculation.

ANALYSIS

The analysis was made by using the dielectric function, restricted to a principal axis direction, discussed by Varga[1] and derived in a fashion as follows in Born and Huang[24]:

$$\epsilon(0,\omega)=\epsilon_\infty-\frac{4\pi Ne^2}{m^*(\omega^2+i\omega/\tau)}+\sum_{\text{modes}}\frac{\delta\epsilon^i}{1-(\omega/\omega_0{}^i)^2-i\omega\Gamma^i/(\omega_0{}^i)^2}, \tag{2}$$

where the zero in $\epsilon(0,\omega)$ denotes the long-wavelength limit, ω the frequency of that Fourier component examined, ϵ_∞ the high-frequency dielectric constant, $\delta\epsilon^i$ the strength of the ith mode, and $(\omega_0{}^i)^2$ the restoring force on the ion masses in the ith mode divided by the reduced mass of the + and − ions usually taken to be $(\omega_T)^2$ when Γ^i, the velocity-dependent damping parameter of the ions in the ith mode, is small. N is the parameter for the concentration of free electrons with charge e and effective mass m^*, and τ the collision time of this plasma mode. These parameters were used to make a fit of the reflectance curve.

This dielectric function is related to the optical constants in the usual way by

$$n^2-\kappa^2=\text{Re}[\epsilon(0,\omega)]$$

and (3)

$$2n\kappa=\text{Im}[\epsilon(0,\omega)],$$

where n and κ, and thus ϵ, depend on the crystalline direction considered. In the case of CdS, the authors chose the principal directions to be those of the electric vector. Thus, they could use the modified equations of Mosteller and Wooten[25] for the reflectance of the uniaxial absorbing crystals. In the σ configuration, where the electric vector is perpendicular to the plane of incidence, the reflectance is given by

$$R_\sigma=[(\cos\theta-a)^2+b^2]/[(\cos\theta+a)^2+b^2], \tag{4}$$

where

$$2\binom{a^2}{b^2}=[(n_\perp{}^2-\kappa_\perp{}^2-\sin^2\theta)^2+4n_\perp{}^2\kappa_\perp{}^2]^{1/2}\pm(n_\perp{}^2-\kappa_\perp{}^2-\sin^2\theta), \tag{5}$$

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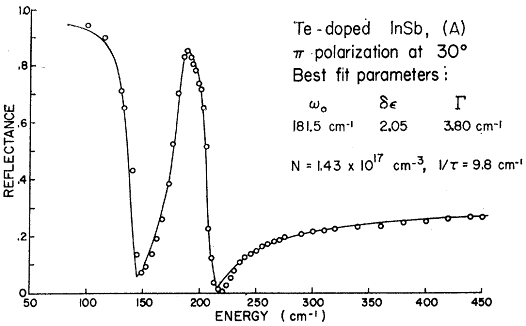

FIG. 1. Te-doped InSb, sample A.

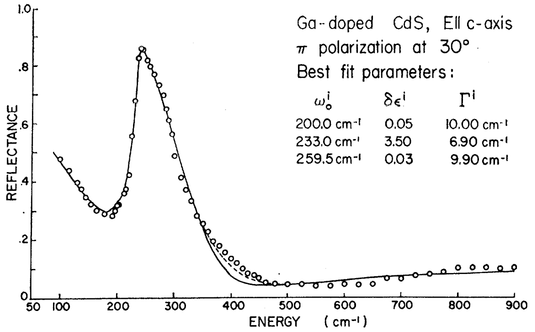

FIG. 3. Ga-doped CdS, E parallel to c axis. Solid line, $N=1.32\times10^{18}$ cm^{-3} and $1/\tau=265$ cm^{-1}; dashed line, improved fit from considerations of section on polaron mass and absorption, $N=1.42\times10^{18}$ cm^{-3} and $1/\tau=255$ cm^{-1}.

and in the π configuration, where the electric vector is in the plane of incidence, the reflectance is given by

$$R_\pi=\frac{(c\cos\theta-a)^2+(d\cos\theta-b)^2}{(c\cos\theta+a)^2+(d\cos\theta+b)^2}, \tag{6}$$

where

$$c=n_\perp n_\parallel-\kappa_\perp\kappa_\parallel$$

and $$\tag{7}$$

$$d=n_\perp\kappa_\parallel+n_\parallel\kappa_\perp.$$

These equations are altered from those of Mosteller and Wooten[25] to describe the geometry where the uniaxial direction lies in the face and not as they had with this direction oriented perpendicular to the face. In the CdS crystal, the uniaxial direction (the c axis) was in the plane of incidence, and, as mentioned, θ was 30°.

The InSb samples were analyzed in the π configuration by assuming that $n_\parallel=n_\perp$ and $\kappa_\parallel=\kappa_\perp$ and by applying the R_π relation.

RESULTS

Reflectances of the InSb samples A and B in Figs. 1 and 2 were fitted by assuming the Hall values of $N=1.43\times10^{17}$ cm^{-3} and 3.96×10^{17} cm^{-3}, respectively, and $\epsilon_\infty=15.68$,[26] and then by adjusting ω_0, $\delta\epsilon$, Γ, m^*, and τ to obtain the best fit. The values of ω_0 and $\delta\epsilon$ were in agreement with the values found for pure InSb.[27] This indicates no shift in the transverse-mode frequency. The value of Γ in these doped samples was 3 to 4 times that found for the pure samples. The free electrons showed effective masses $m^*=0.030m_e$ and $0.031m_e$ in samples A and B, respectively. These masses are not as low as, nor do they vary as much as, would be predicted if the lattice vibrations were not included in the dielectric function as in Ref. 5. The data of Ref. 5 indicate a more rapid decrease in effective mass with smaller concentrations, because the analyzed minimum, which is attributed to the plasma edge at higher concentrations, becomes a result of the coupled plasma-phonon system as ω_P nears ω_L. In the reflectance minima section, a value of $m^*=0.030m_e$ was used in the theory to fit the minima frequencies of Ref. 5 and the author's data.

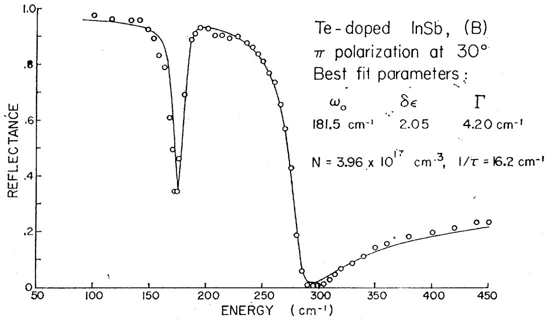

FIG. 2. Te-doped InSb, sample B.

In sample A (or sample B), the Drude relaxation time $\tau_{\text{opt}}=5.4\times10^{-13}$ sec (or 3.3×10^{-13} sec) that is made at optical frequencies is a little less than the values obtained by a static Hall measurement, $\tau_H=m^*/\rho Ne^2=6.6\times10^{-13}$ sec (or 3.4×10^{-13} sec). Values of τ_{opt} could be determined with a 5% accuracy, and values of m^* were more precise with a 2% accuracy.

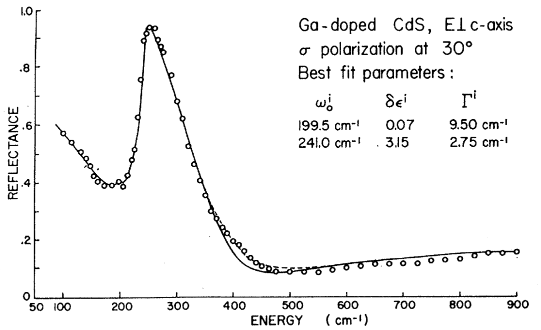

FIG. 4. Ga-doped CdS, E perpendicular to c axis. Solid line, $N=1.32\times10^{18}$ cm^{-3} and $1/\tau=265$ cm^{-1}; dashed line, improved fit from considerations of section on polaron mass and absorption, $N=1.42\times10^{18}$ cm^{-3} and $1/\tau=255$ cm^{-1}.

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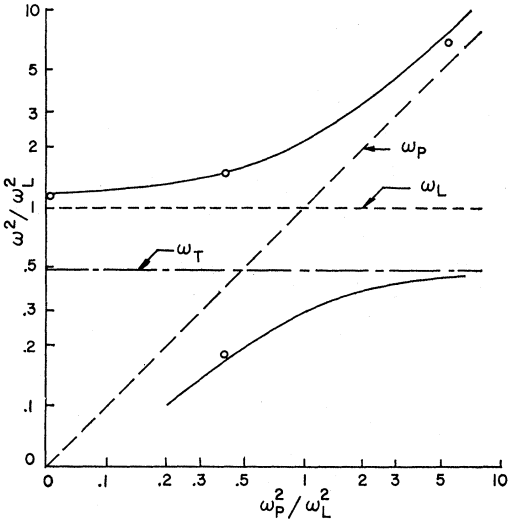

FIG. 5. Reflectance minima for n-type ZnO. Solid line, ω_{min} from Varga dielectric function; o, Collins and Kleinman (Ref. 3).

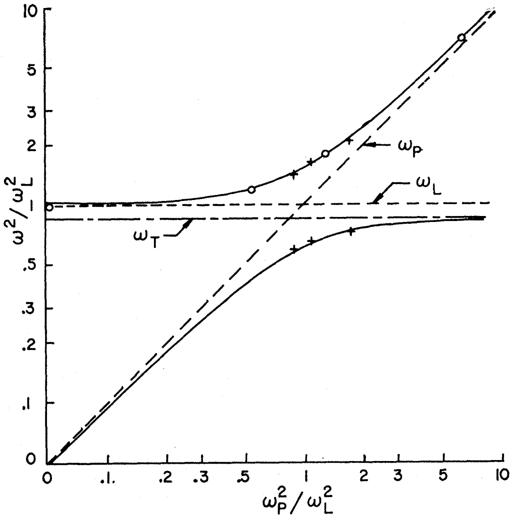

FIG. 7. Reflectance minima for n-type GaAs. Solid line, ω_{min} from Varga dielectric function; o, Spitzer and Whelan (Ref. 12); +, Olson and Lynch (Ref. 13).

Figures 3 and 4 show the data for the CdS sample measured in both polarizations, which were normalized in the range of the IR-12 at 1950 cm^{-1} to the dielectric constant parallel to the c axis $\epsilon_\infty{}^\pi = 5.17$ [28] and perpendicular to the c axis $\epsilon_\infty{}^\sigma = 5.23$,[28] because part of the surface was not perfectly polished. The reflectances taken in the 100–210-cm^{-1} range were direct ratios with aluminum. The lattice parameters compare favorably with the values found for pure CdS [29] in both polarizations, with the exception of Γ for the main peak in the π polarization. Using the Hall value for $N = 1.32 \times 10^{18}$ cm^{-3}, the effective mass is found to be $m^* = 0.20 m_e$, which is in agreement with others.[30,31] The fit (solid line) to the reflectance data is poor in the 300–600-cm^{-1} range and could not be improved without destroying the fit elsewhere as will be discussed below.

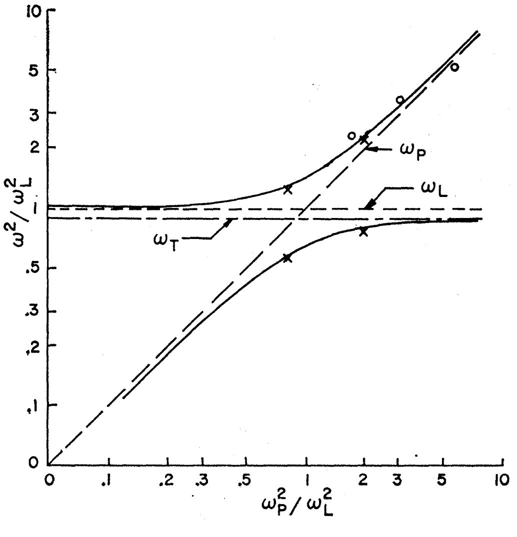

FIG. 6. Reflectance minima for n-type InSb. Solid line, ω_{min} from Varga dielectric function; o, Spitzer and Fan (Ref. 5); X, from Figs. 1 and 2.

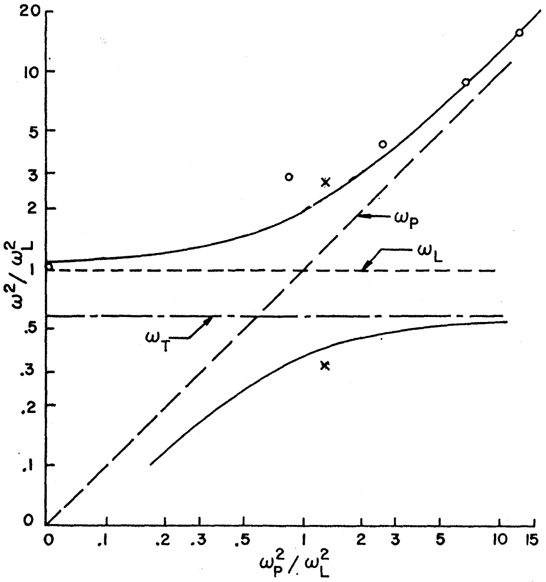

FIG. 8. Reflectance minima for n-type CdS. Solid line, ω_{min} from Varga dielectric functions; o, Piper and Marple (Ref. 14); X, from Fig. 4.

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For CdS, the optical value of $\tau_{\text{opt}}=2.1\times10^{-14}$ sec is smaller than the value $\tau_H=4.3\times10^{-14}$ sec that was obtained from a Hall measurement.

Though the transverse frequencies are unshifted, the longitudinal-mode frequencies, usually noted as those frequencies at which the real part of the dielectric function vanishes when the imaginary part is small, are shifted in a manner as described by Varga.

POLARON MASS AND ABSORPTION

The polaron coupling constant for CdS, α,[9] was calculated as 0.58, and while large enough to be noticeable, it is small enough to apply perturbation methods to the mass and absorption. The polaron mass treatment was mentioned in the data on ZnO [3] and is the change in mass on passing to frequencies above the longitudinal-optic-phonon frequency, where the lattice is no longer polarized by the moving electrons. So at frequencies below ω_L, where the lattice is polarized, the polaron mass $m_P=(1+\frac{1}{6}\alpha)m^*$ is used as calculated by Frohlich.[9]

There is also a new relaxation process available to the electrons at frequencies above ω_L because a plasma mode may exchange energy with the lattice modes. The addition to the imaginary part of the dielectric function calculated by Gurevich *et al.*[10] is

$$\epsilon'=\frac{8\pi Ne^2\alpha}{3m^*\omega\omega_L}(\omega_L/\omega)^{5/2}(1-\omega_L/\omega)^{1/2}. \tag{8}$$

It has the effect of increasing the imaginary part of the dielectric function from 2.43 to 2.80, where it has its maximum effect at $\omega=(8/7)\omega_L=355$ cm^{-1}.

In order to best fit the two polarizations, N had to be increased to 1.42×10^{18} cm^{-3} because of the 10% increase in the effective mass at frequencies less than ω_L. Also $1/\tau$ had to be decreased to 255 cm^{-1}. With no additional parameters, these new considerations produce essentially the same reflectances except in the 300–600-cm^{-1} range, where the fit was improved considerably as shown by the dashed lines in Figs. 3 and 4. In the case where $\alpha<1$, the use of Gurevich's perturbation expression is shown to be applicable.

This absorption process was used in the case of SrTiO[3] by Barker[32] and found not to apply. A less reliable small polaron theory[33] had to be used.

REFLECTANCE MINIMA

Without an analysis of mode frequencies, the most obvious change in the reflectance spectra for the coupled system from that of the pure lattice system—providing that the electron mobility is not too low—is the additional minimum. Physically, such minima, whose reflected fluxes approach zero, occur at frequencies which are just those points on dispersion curves where the free space photon curve crosses the coupled photon–transverse-optical-phonon curves. This coupled transverse mode is sometimes referred to as a polariton mode, and its crossing point with the photon curve is clearly shown on p. 91 of Ref. 24. This minimum has been studied in the case of CdS,[34] from the viewpoint of Murray *et al.*,[35] but the relationship fails as ω_P approaches ω_L because the dielectric function was assumed to be composed of a frequency-dependent plasma term that was added to a frequency-independent lattice term, i.e., no coupling. A slightly more complicated but more applicable minima relation, including the coupling effects, was derived[11] by using the above property as stated below. That is, these frequencies are values at which $\epsilon(0,\omega)=1$, and when absorption is neglected, they are

$$\omega_{\min}{}^2=\frac{\epsilon_0(1+\omega_P{}^2/\omega_L{}^2)-1\pm\{[\epsilon_0(1+\omega_P{}^2/\omega_L{}^2)-1]^2-4\epsilon_0(\epsilon_\infty-1)\omega_P{}^2/\omega_L{}^2\}^{1/2}}{2(\epsilon_\infty-1)/\omega_T{}^2}. \tag{9}$$

This equation works quite well as shown in Figs. 5–8 for CdS and much better for the cases of ZnO, GaAs, and InSb, where the mobilities are much higher.

Just as in a description of the longitudinal-mode frequencies, the lower curve in this minima plot starts with complete plasma character at small N. As ω_P approaches ω_L, the minimum becomes a result of a mixture of these two modes, and finally as ω_P becomes much greater, it becomes a result of the lattice mode. A description of the upper curve follows in a reverse manner.

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