Resonance structure in PbSnTe reflection spectra due to charge-carrier localization

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A resonance structure has been found in the reflection spectra of PbSnTe solid solutions near a residual-ray band. This structure is attributed to a localized state of free carriers.

A study of the conductivity of solid solutions of lead-tin chalcogenides has shown that at high temperatures ($T > 300$ K) the conductivity decreases to the extent that there is a deviation from the Ioffe-Regel' relation, according to which the mean free path of an electron must be greater than its wavelength.[1] This result is evidence of a localization of some of the electronic states. Localization effects may be caused by states that arise as a result of the deformation which an electron causes in the immediate crystal surroundings of an intrinsic structural defect[2,3] in PbSnTe. An electron-lattice interaction of this sort is promoted by the softness of the phonon spectrum of PbSnTe solid solutions. A "softening" of phonon modes, which causes a structural phase transition, has been discovered in these solutions.[4,5] There has also been a report of an observation of lattice solitons,[6] which may by themselves promote a localization of carriers.

In this letter we report an observation of a resonance structure caused near a residual-ray band by localized carriers.

We studied reflection spectra of epitaxial films and bulk samples of the solid solutions $Pb_{0.8}Sn_{0.2}Te$ over the wavelength range from 25 to 1000 μm (using a Bruker IFS-113V Fourier spectrometer). The spectra are recorded at temperatures over the range 10–500 K for p-type samples with Hall free-carrier concentrations of 10^{16}–10^{19} cm^{-3} (as measured at $T = 77$ K). The samples were not deliberately doped.

Figure 1 shows the temperature dependence of the reflection spectra. At low temperatures we see a reflection due to plasma oscillations of free carriers. This reflection can be described well by the classical Drude theory. The oscillations in the reflection at frequencies above the plasma frequency (ω_p) result from an interference of the light in the film. There is a pronounced decrease in the reflection coefficient at $\omega < \omega_p$, and we also see the appearance of a resonance structure, marked in this figure by the arrow, in the temperature interval 200–400 K. This structure disappears as the temperature is raised further.

As the concentration of free carriers is varied, we can observe the appearance of a corresponding structural feature in the spectra. Figure 2 shows reflection spectra of samples with various carrier concentrations recorded at room temperature. At a low concentration ($N = 10^{16}$ cm^{-3}) we see a residual-ray band in the spectrum, which lies in the frequency interval (ω_{TO}, ω_{LO}), i.e., between the frequencies of transverse and

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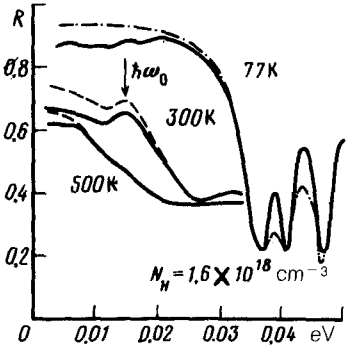

FIG. 1. Infrared reflection spectra of a $Pb_{0.8}Sn_{0.2}Te$ sample with a Hall concentration $N_H = 1.6 \times 10^{18}$ cm^{-3} as recorded at various temperatures. Dot-dashed line—calculated from the Drude theory; dashed line—calculated for the case with localized states.

longitudinal optical oscillations of the lattice. According to Ref. 7, we have $\hbar\omega_{TO} = 0.004$ eV and $\hbar\omega_{LO} = 0.014$ eV; these figures correspond well to the residual-ray region in Fig. 2. Samples with $N \gtrsim 10^{19}$ cm^{-3} have a clearly defined plasma reflection edge without structural features. In the intermediate case, as the number of carriers increases, the reflection coefficient in the residual-ray band initially drops to $\simeq 0.4$ and then increases upon the appearance of a resonance structure at a photon energy $\simeq 0.015$ eV.

The shape of the reflection spectra of samples with a carrier concentration of 10^{17}–10^{18} cm^{-3} at temperatures of 200–400 K thus cannot be explained by the Drude theory, in which lattice oscillations and plasma oscillations of free charge carriers contribute to the dielectric constant. The observed structure of the reflection spectra

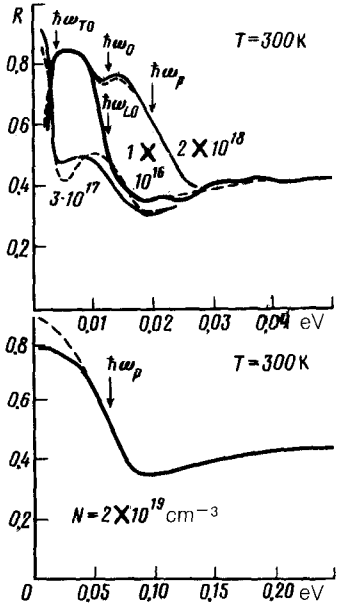

FIG. 2. Infrared reflection spectra of $Pb_{0.8}Sn_{0.2}Te$ recorded for samples with various concentrations of free carriers. The numbers labeling the curves are the values of the Hall concentration. In the calculation of the dashed lines, the localized states were taken into account by means of expression (1).

can be described by incorporating the contribution of a resonant state. In a first approximation we take this resonance state to be the dielectric constant of a linear oscillator having a parabolic potential. We have no grounds for considering any other, more complicated model, since we have no data to give us information on the shape of the localization potential. In light of the results which we found in Ref. 1, this resonant state may be a consequence of localized electrons. The dielectric constant of the crystal can then be written

$$\epsilon(\omega) = \epsilon_\infty \left[1 + \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\omega\Gamma} - \frac{\omega_p^2}{\omega^2 - i\omega/\tau} + \frac{\omega_{LOC}^2}{\omega_0^2 - \omega^2 - i\omega\gamma} \right], \qquad (1)$$

where ϵ_∞ is the high-frequency dielectric constant, Γ is the damping of the lattice oscillations, and τ is the momentum relaxation time of the carriers. The last term in (1) is the contribution of localized states characterized by a frequency ω_{LOC}, a resonant frequency ω_0, and a damping γ. The dashed lines in Figs. 1 and 2 are reflection spectra calculated from (1). These results are seen to give a good description of the experimental spectra. The energy corresponding to the frequencies of the phonon spectrum was assumed to be equal to the values cited above, while the resonant energy of the localized states turned out to be $\hbar\omega_0 = 0.014$ eV. The calculation parameters, which vary from sample to sample and with the temperature, are the frequencies $\omega_p = \omega_{\text{LOC}}$ and the damping values Γ, $\hbar/\tau$, and γ. The values of Γ and $\hbar/\tau$ increase with increasing concentration of free carriers and with the temperature; Γ reaches the value of $\hbar\omega_{\text{LO}}$ (a similar effect has been observed in a study[8] of the IR reflection of PbTe). The damping characterizing the localized state remained essentially the same.

The values of ω_p and ω_{LOC} are related to the numbers of free and localized electrons, respectively. It turns out that ω_p decreases with increasing temperature, while ω_{LOC} increases. The observed change in the numbers of free and localized carriers with the temperature is evidence that the local level lies against a background of allowed states. The extent to which this local level is filled can be estimated from the well-known relation which gives the single-particle filling of an impurity level by electrons[9]:

$$N_L = \frac{N_{s0}}{1 + \frac{1}{2}\exp\left(\frac{E_0 - E_F}{kT}\right)}, \qquad (2)$$

where N_{s0} is the maximum possible number of localized states in the lattice of the semiconductor, and E_0 is the energy of the localized state. This relation couples the number of localized electrons to the number of free electrons through the Fermi energy E_F. Expression (2) ignores the distribution of electrons among levels in the well; that distribution leads to an insignificant change in the coefficient of the exponential function at high temperatures.

Figure 3 shows the temperature dependence of the concentrations of free (N) and localized (N_L) carriers as determined from the reflection spectra and as calculated

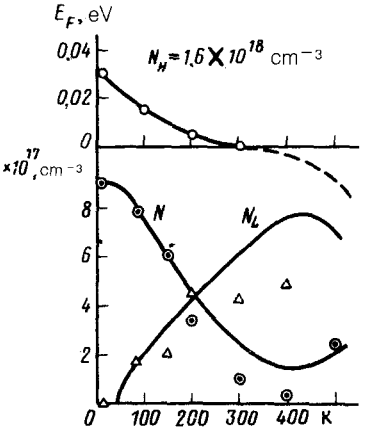

FIG. 3. Temperature dependence of the concentrations of (circles) free charge carriers and (triangles) localized charge carriers, found by fitting the spectra calculated from (1) to the experimental reflection spectra. The curves were calculated from (2) with the parameter values $N_{s0} = 2 \times 10^{18}$ cm^{-3} and $E_0 = 0.04$ eV. The temperature dependence of the Fermi energy, as determined with the help of the Moss-Burstein effect, is shown in the upper part of the figure.

from (2). The free-carrier concentration is related to ω_p by $\omega_p^2 = 4\pi e^2 N / m_s \epsilon_\infty$, where m_s is the effective conduction mass, whose temperature dependence was measured in Ref. 10. The values of ϵ_∞ were determined from the magnitude of the reflection coefficient in the high-frequency part of the spectra, and the Fermi energy was determined from the Moss-Burstein shift. The concentrations of the localized carriers are shown in arbitrary units in Fig. 3, since we do not know the specific relationship between ω_{LOC} and N_L (we evidently have $\omega_{\text{LOC}}^2 \sim N_L$). It follows from this figure that as the temperature is raised, there is an increase in the number of localized carriers and therefore a decrease in the number of free charge carriers. The curves calculated from (2) give a satisfactory description of the observed temperature dependence of N and N_L. The temperature dependence of the parameters which determine the shape of the IR reflection spectra thus agrees with the assumption that localized electronic states appear in the PbSnTe crystal lattice.

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