Determination of a phase transition temperature in a PbSnTe solid solution from the softening of a long-wavelength plasmon-phonon mode

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A long-wavelength plasmon-phonon mode was observed for the first time in the reflection spectra recorded in the reststrahlen band for crystals with a high degree of ionicity (PbSnTe). This made it possible to determine the frequency of a transverse optical phonon ω_{TO}. The temperature dependence of ω_{TO} indicated that a structural phase transition occurred below 150 K. The critical temperature of this transition was found to be $T_c = 20 \pm 2$ K.

Lead-tin telluride ($Pb_{1-x}Sn_xTe$) solid solutions crystallize in a fcc lattice of the rocksalt type.[1] A structural phase transition is exhibited by SnTe ($x = 1$) at $T_c \approx 100$ K: at this temperature the cubic lattice is modified to the rhombohedral structure.[2,3] On the other hand, capacitance measurements[4] indicate that the phase transition temperature of PbTe ($x = 0$) is negative, i.e., that this phase transition is unattainable. Clearly, the phase transition in the PbSnTe solid solutions should occur at some intermediate temperature. There has been much evidence that a structural phase transition does take place in these solid solutions (see the bibliography in Refs. 5 and 6, and also Ref. 7). However, reliable information on the phase transition temperature of PbSnTe solid solutions is lacking. For example, in the case of the most widely used composition with $x = 0.2$ the critical temperature estimated by various methods lies within the range — 20–25 K. This situation is due to the fact that it has not yet been possible to determine the transverse optical phonon frequency at temperatures close to the critical value. Vanishing of this frequency is an indication of a structural phase transition.[8]

The phonon frequencies can be determined accurately from Raman scattering, neutron spectroscopy, or reflection spectra in the reststrahlen band. The first-order Raman scattering in PbTe crystals and their solid solutions is forbidden by symmetry considerations.[9] There are no published neutron spectroscopy data at temperatures near the phase transition.

We determined the frequencies of optical phonons of a PbSnTe solid solution from reflection spectra recorded at wavelengths up to 1000 μ. This made it possible to observe for the first time a long-wavelength plasmon-phonon mode (ω_-) in crystals with a high degree of ionic binding. It was found that the frequency ω_- varied with temperature because of the *TO* phonon softening, which indicated the occurrence of a structural phase transition.

EXPERIMENTAL METHOD AND PREPARATION OF SAMPLES

We investigated *n*- and *p*-type $Pb_{0.8}Sn_{0.2}Te$ films grown by thermal evaporation in vacuum on BaF_2 substrates. The carrier density was determined from the Hall effect and was within the range 10^{16}–10^{19} cm^{-3}, depending on the sample. Electrophysical parameters of the samples determined at $T = 77$ K are listed in Table I. The carrier density in sample 1 was close to the intrinsic value and increased with temperature. In the case of other samples the carrier density was practically independent of temperature.

The reflection spectra were recorded using an IFS-113V Fourier spectrometer (made by Bruker, West Germany); the temperature dependence of the reflection coefficient was determined using a CF-1104 cryostat (made by Oxford Instruments). The signal/noise ratio was increased by averaging 100 spectra.

DISCUSSION OF RESULTS

The reflection spectra of PbSnTe were recorded in the temperature range 4.2–295 K. Figure 1 shows, by way of example, the reflection spectrum at $T = 77$ K. Oscillations observed in the short-wavelength part of the spectrum were due to interference of light in a film. The increase in the reflection on reduction in the wavelength was due to crystal lattice vibrations. The region of strong reflection (reststrahlen band) was located in the interval between the frequencies of longitudinal and transverse optical vibrations. In our case the reststrahlen band was bounded by the frequencies denoted by $\omega_\pm$ in Fig. 1. The meaning of these frequencies will be explained later.

We determined the frequencies of longitudinal and transverse optical phonons by comparing the experimental reflection spectra with those calculated using the expression for the permittivity $\varepsilon(\omega)$. Since it was not possible to prepare

TABLE I. Electrophysical parameters of $Pb_{0.8}Sn_{0.2}Te$ samples at $T = 77$ K.

Sample No.	Type of conduction	Carrier density, cm^{-3}	Carrier density allowing for Hall factor, cm^{-3}	m_s/m_0	$\hbar\omega_p$, meV
1	*n*	$1.5\cdot10^{16}$	$1.05\cdot10^{16}$	0.022	38
2	*n*	$3\cdot10^{17}$	$2.1\cdot10^{17}$	0.022	47
3	*p*	$4.2\cdot10^{17}$	$3.1\cdot10^{17}$	0.023	20
4	*n*	$6.1\cdot10^{17}$	$4.3\cdot10^{17}$	0.024	24
5	*p*	$1.3\cdot10^{18}$	$9.1\cdot10^{17}$	0.026	36
6	*p*	$8.4\cdot10^{18}$	$7.6\cdot10^{18}$	0.035	95
7	*p*	$1.1\cdot10^{19}$	$1.8\cdot10^{19}$	0.036	113
8	*p*	$2.0\cdot10^{19}$	$2.0\cdot10^{19}$	0.041	145

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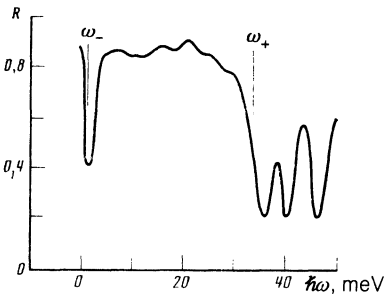

FIG. 1. Reflection spectrum of a $Pb_{0.8}Sn_{0.2}Te$ sample with a hole density 1.9×10^{18} cm^{-3}, recorded at $T=77$ K.

PbSnTe solid solutions with a free-carrier density less than 10^{16} cm^{-3}, it was necessary to allow for a contribution of free carriers to the permittivity which far from the fundamental absorption edge is described by

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

where ε_∞ is the high-frequency permittivity; ω_{LO} and ω_{TO} are, respectively, the frequencies of longitudinal and transverse opical modes; Γ is the phonon damping; $\omega_p^2=4\pi e^2N/m_s\varepsilon_\infty$ is the frequency of plasma oscillations of free carriers (N is the density of free carriers and m_s is their conductivity effective mass, calculated using the Kane model); τ is the mean free time of carriers.

The minima observed in the reflection spectra (Fig. 1) are due to the appearance of longitudinal oscillations in a crystal, representing coupled plasmon-phonon modes. The condition for the existence of these longitudinal oscillations is the vanishing of the dielectric function. The equation thus obtained are the plasmon-phonon mode frequecies ω_+ and ω_-. In the absence of damping ($\Gamma=1/\tau=0$), we obtain

$$\omega_\pm=\left\{\frac{1}{2}(\omega_{LO}^2+\omega_p^2)\pm\frac{1}{2}[(\omega_{LO}^2+\omega_p^2)^2-4\omega_{TO}^2\omega_p^2]^{1/2}\right\}^{1/2}. \qquad (2)$$

This equation describes the relationship between the plasmon-phonon frequencies $\omega_\pm$ and the frequencies of longitudinal and transverse optical phonons ω_{LO} and ω_{TO}. It follows from this equation that if $\omega_p\ll\omega_{LO}$, then the short-wavelength reflection minimum (ω_+) corresponds to the longitudinal optical frequency and, conversely, in the range $\omega_p\gg\omega_{LO}$ the long-wavelength minimum (ω_-) represents the transverse optical phonon frequency. The value of ω_p can be varied by selecting samples with different free-carrier densities. We used this approach to determine the transverse optical phonon frequency and its temperature dependence.

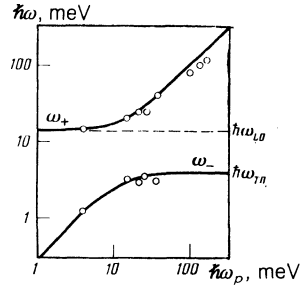

FIG. 2. Dependences of the energies corresponding to the frequencies of plasmon-phonon modes $\omega_\pm$ on $\hbar\omega_p$, obtained at room temperature for a sample with the parameters listed in Table I ($\hbar\omega_{LO}=14.8$ meV, $\hbar\omega_{TO}=4$ meV).

The continuous curves in Fig. 2 are the dependences of plasmon-phonon modes $\omega_\pm$ on ω_p calculated in accordance with Eq. (2), whereas the circles represent the values deduced from the reflection spectra of samples with different carrier densities. In the range of densities exceeding 10^{19} cm^{-3} there was no long-wavelength minimum because of the screening of the lattice vibrations by free carriers. The value of ω_+ obtained for the sample with the minimum carrier density of 1.5×10^{16} cm^{-3} was 14 meV and was independent of temperature. It agreed well with the value of ω_{LO} measured earlier.[10-12]

The experimental values of $\omega_\pm$ for samples with carrier densities less than 10^{18} cm^{-3} fitted the dependence obtained from Eq. (2).The plasma frequency was calculated for each of the samples allowing for the Hall factor of PbSnTe solid solutions, which was measured earlier.[13] The deviation of the experimental values of ω_+ from those calculated for higher carrier densities could be due to either a change in the effective carrier mass or due to the influence of the scattering of carriers by crystal imperfections. In view of the fact that this deviation was independent of temperature, preference should be given to the latter hypothesis (since the effective mass of holes in the solid solutions investigated decreased by a factor of 2 between room and liquid nitrogen temperatures even without allowance for the occupancy of the heavy valence band). It was found that the values of $\hbar/\tau$ deduced from the reflection spectra agreed well with the values of $\hbar/\tau_\sigma$ deduced from the conductivity. For example, in the case of a sample with a hole density 8.4×10^{18} cm^{-3}, it was found that $\hbar/\tau\approx62$ meV and $\hbar/\tau_\sigma\approx90$ meV.

As already mentioned, an increase in the density of free carriers (and, consequently, an increase in ω_p) caused the value of ω_- to approach ω_{TO}. It is clear from Fig. 2 that for a carrier density of $\approx10^{18}$ cm^{-3} ($\hbar\omega_p\approx30$ meV), the frequency ω_- became equal to ω_{TO}.

Figure 3 shows the experimental spectra of a sample with a hole density 1.3×10^{18} cm^{-3} recorded in the region of the long-wavelength reflection minimum at different temperatures. Cooling from room temperature to 200 K did not affect the frequency ω_{TO}. Further cooling shifted the minimum of ω_- toward longer wavelengths, which was due to softening of the transverse optical mode ω_{TO}. In the temperature range 10–45 K the frequency ω_- became less than the limiting value (10 cm^{-1}), which could be determined using the IFS-113V Fourier spectrometer. At temperatures below 10 K the long-wavelength plasmon-phonon mode appeared again.

The frequency ω_{TO} was deduced from the point of in-

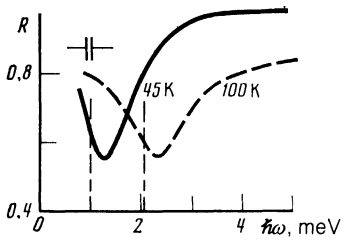

FIG. 3. Reflection spectra of a $Pb_{0.8}Sn_{0.2}Te$ sample with a hole density 1.9×10^{18} cm^{-3} recorded in the region of the long-wavelength plasmon-phonon mode at temperatures 100 K (continuous curve) and 45 K (dashed curve). The vertical dashed lines represent the positions of the reflection points.

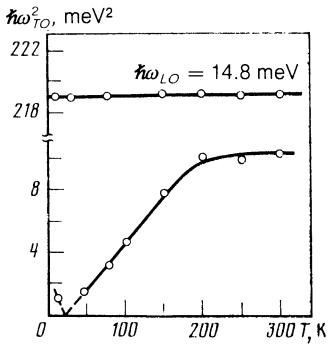

FIG. 4. Temperature dependences of $(\hbar\omega_{TO})^2$ and $(\hbar\omega_{LO})^2$ for $Pb_{0.8}Sn_{0.2}Te$ solid solution.

flection in the reflection spectrum. This method made it possible to allow for the shift of the frequencies $\omega_\pm$ due to carrier scattering.[14] The temperature dependences $\omega_{LO}^2(T)$ and $\omega_{TO}^2(T)$ are plotted in Fig. 4. The frequency ω_{LO} was independent of temperature and the experimental values of ω_{TO} fitted well a straight line corresponding to the Curie-Weiss law:

$$\omega_{TO}^2 = \text{const}(T - T_c). \tag{3}$$

As pointed out already, cooling below the phase transition temperature increased the frequency ω_{TO}.

Softening of the transverse optical mode indicated a structural modification of the crystal lattice the result of which was a phase transition at some critical temperature. The nature of the dependence $\omega_{TO}(T)$ and some of the experimental results[3,15] indicated that the phase transition observed in PbSnTe was of first order and that the frequency ω_{TO} vanished at the transition point. Consequently, it was necessary to extrapolate the dependence $\omega_{TO}(T)$ to zero in order to determine the critical temperature T_c. This gave $T_c = 20 \pm 2$ K.

We thus found that an investigation of the temperature dependences of the frequencies of longitudinal and transverse optical phonons in PbSnTe solid solutions made it possible to determine the temperature of the phase transition corresponding to modification of the crystal lattice from the cubic to the rhombohedral form.

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