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Light scattering of InSb at high temperatures

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Raman scattering measurements in the small-gap semiconductor InSb show that the splitting between longitudinal and transverse long-wavelength optical phonons is drastically reduced and eventually disappears at temperatures approaching the melting point. These observations are attributed to screening of the long-range forces by free carriers, whose presence dominates as the fundamental energy gap diminishes near the melting point, and to contributions due to momentum nonconservation and lattice anharmonicity. Preliminary results on other III-V semiconductors are also discussed.

The effect of high temperature (T) on the frequency (ω) and damping constant (Γ) of the $q \simeq 0$ Raman-active optical phonons has been investigated extensively in recent years. Among the materials studied are Si (Ref. 1) and, to a lesser extent, III-V semiconducting compounds.[2-5] Softening of ω and increase of Γ as T is increased are common features in all these investigations, which in most of the cases have been described by the use of cubic and quartic anharmonicity terms in the lattice Hamiltonian.[6]

We report here the results of Raman measurements of $\omega(T)$ and $\Gamma(T)$ for the longitudinal (LO) and transverse (TO) $q \simeq 0$ optical phonons of InSb. This narrow-gap semiconductor exhibits a rather low melting point ($T_m = 800$ K) which enabled us to follow the lattice behavior as T approached T_m. According to our measurements (between 60 and 720 K) the frequencies $\omega_t(T)$ and $\omega_l(T)$ decrease linearly and nonlinearly, respectively, as T is increased, and indicate a definite merging at T_m. The widths $\Gamma_t(T)$ and $\Gamma_l(T)$ increase following a similar pattern. Previous experiments with the cubic materials GaSb, GaP, ZnSe, and GaAs (Refs. 2–5) were performed at temperature ranges far below T_m and did not reveal any such behavior.

The experimental system has been described elsewhere.[1] Pure InSb plates were polished and syton treated. We used the faces (100), (110), and (111) to observe scattering from LO and TO phonons separately or together. The samples were mechanically held on top of a resistance-heated ceramic plate. The temperature was measured with a Chromel-Alumel thermocouple, one contact of which was attached on the scattering face of the sample. The whole system was kept inside an evacuated Dewar. The low-temperature measurements were taken with a closed circulation He cryostat. Our data were obtained with the 514.5-nm line of an Ar^+ laser. The beam was focused on the sample with a cylindrical lens and its power did not exceed 200 mW. The spectral resolution was 2.5 cm^{-1}.

Figure 1 shows a typical set of Stokes spectra which were obtained from a (111) face. The two peaks in the low-frequency side of the spectra at 470 and 505 K are due to strong Raman scattering of Sb which starts shaping for $T \geq 470$ K. The fast softening of $\omega_l(T)$ made it necessary to use the (100) and (110) faces to obtain independent sets of data for $\omega_l(T)$ and $\omega_t(T)$, respectively, for the complete range of T. The results are shown in Figs. 2 and 3. Each data point for $\Gamma(T)$ has been corrected for instrumental broadening.[7] It was not possible to record spectra for $T > 720$ K because the surface of the samples deteriorated systematically between 730 and 750 K.

Particular attention was paid in analyzing the data of high temperatures. Since ω_l and ω_t become nearly equal at high T, we had to make sure that there was no contribution from forbidden TO in each LO spectrum at high T and vice versa. Such forbidden contributions appeared often, but not systematically, and their existence was checked by repeating the room-temperature spectra after each heating cycle. Figure 4 shows such a situation: as 405 K is reached from 300 K, the spectrum exhibits the expected LO phonon alone (a). After the sample is cooled down to 300 K, following heat treatment up to 700 K, the spectrum includes the TO phonon as well contrary to the selection rules (b). This type of forbidden contributions have also been observed in GaAs.[8] They are attributed to structural changes of the surface as a result of the temperature annealing.

The changes of ω_t and Γ_t with T can be described by two coefficients each C,D and A,B, respectively.[6,3,4] The C,D

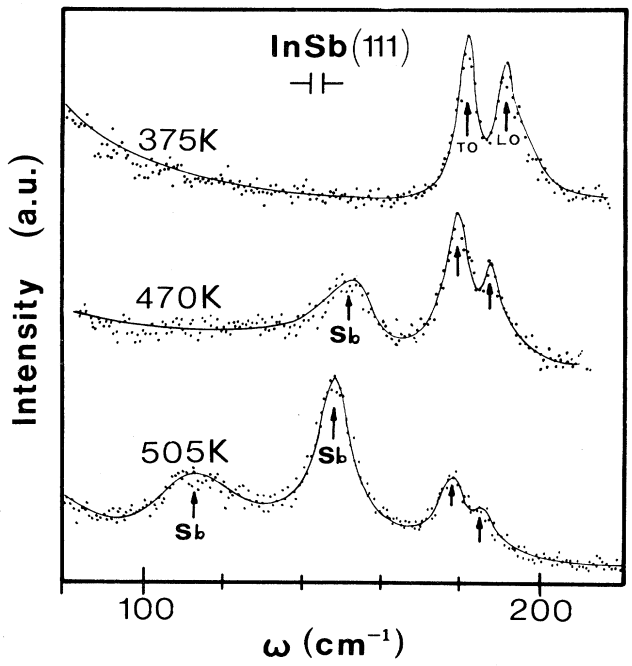

FIG. 1. Stokes-Raman spectra from a (111) face of InSb at different bulk temperatures. The peaks at ~ 114 and 150 cm^{-1} are due to scattering by Sb.

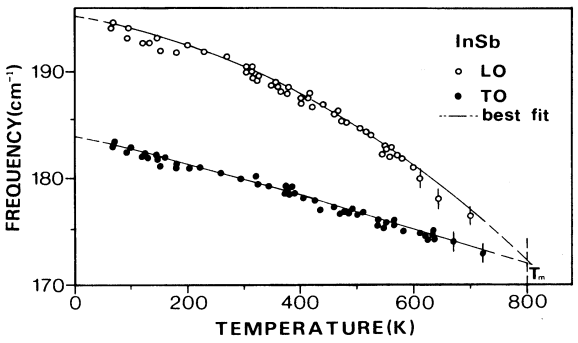

FIG. 2. Temperature dependence of ω_l and ω_t of InSb. Quenching of the LO-TO splitting at T_m is evident. Solid lines are best fits of theory (Refs. 3 and 4).

contributions to $\omega_t(T)$ represent collectively the optical-phonon decay to two and three acoustic phonons due to cubic and quartic anharmonic interactions.[4] The interpretation of the A and B contributions to $\Gamma_t(T)$ is analogous. The solid lines in Figs. 2 and 3 show the best fit of the theoretical expressions[6,3,4] to the data for the TO phonon, from which the following values are obtained in cm^{-1} units:

$$\omega_{0t}=183.2,\ C_t=-1.5,\ D_t\approx 0\ ,$$

$$A_t=1.7,\ B_t\approx 0,\ \Delta\Gamma_{0t}=0.1\ .$$

ω_{0t} is the value of $\omega_t(0)$ in the harmonic approximation, and $\Delta\Gamma_{0t}$ is a T-independent contribution due to crystal disorder. Using known values for the thermal expansion coefficient $\alpha(T)$ and the mode Grüneisen parameter γ_T (Refs. 9 and 10) we estimate that the volume contribution expressed as a percentage of the total frequency shift varies from 20% at 200 K to 25% at 720 K. Therefore, the TO frequency shift is largely due to anharmonicity and in fact to the cubic terms, judging from the overall linear appearance of $\omega_t(T)$ and $\Gamma_t(T)$. Furthermore, the *implicit fraction* η

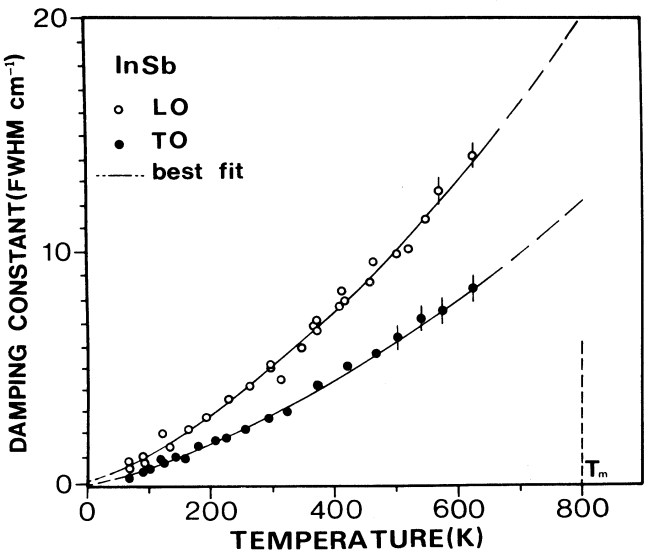

FIG. 3. Temperature dependence of the full width at half maximum of TO and LO phonons (corrected for instrumental broadening). Solid lines are best fits of theory (Refs. 3 and 4).

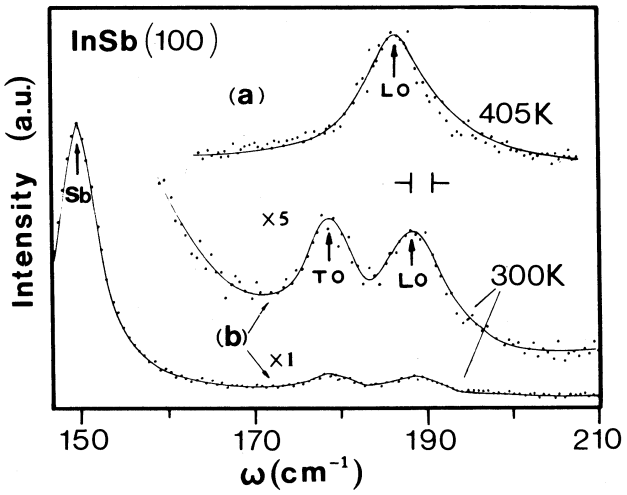

FIG. 4. Stokes-Raman sectrum from a (100) face of InSb: (a) beginning of heat treatment, (b) after heat treatment. Strong band at $\sim 150\ cm^{-1}$ is attributed to Sb.

defined as the ratio of the volume driven to the measured (total) T-driven rate of frequency shift,[11] takes the value of 0.075 in the range 300–700 K. Such small value for η is consistent with the considerable amount of covalent binding present in InSb.[11]

The most striking feature, however, in Fig. 2 is the accelerated softening of $\omega_l(T)$. The latter seems to approach $\omega_t(T)$ as $T\rightarrow T_m$, thus indicating an apparent quenching of the LO-TO splitting at T_m. At the same time, $\Gamma_l(T)$ shows a much faster increase than $\Gamma_t(T)$ (Fig. 3). It is reasonable to assume at first, that anharmonicity is again responsible for such effects. A similar fit of theory to the data would yield the values

$$\omega_{0l}=194.4,\ C_l=-0.7,\ D_l=0.2\ ,$$

$$A_l=2.4,\ B_l=-0.1,\ \Delta\Gamma_{0l}\approx 0$$

in cm^{-1} units, which imply exceedingly high quartic anharmonicity terms for the LO phonon. This is contrary to the trends of other III-V materials in which the quartic contributions for the LO phonon are found to be lesser than, or comparable in size to those for the TO phonon. Thus, we have to consider the possibility that other mechanisms may be present. Since, according to our measurements, the LO-TO splitting recovers completely its room-temperature value after the heat treatment, the mechanism sought cannot be related to whatever irreversible lattice changes that are responsible for the appearance of the forbidden TO scattering or scattering by Sb. On the other hand, it appears reasonable to assume that (i) The long-range Coulomb forces which are normally responsible for the LO-TO splitting are gradually reduced in the presence of thermally generated free carriers, and (ii) due to momentum nonconservation LO phonons other than those of $q\simeq 0$ participate in the scattering process.

It is known that the small direct gap of InSb exhibits large variation with temperature; i.e., $E_g=(0.235-0.000\,29T)$ eV.[12] At 750 K the gap is nearly closed and the material becomes practically a semimetal. In the range of 300–800 K the intrinsic carrier concentration changes from about 2×10^{16} to $2\times 10^{18}\ cm^{-3}$ with a corresponding change for the

high-temperature limit (Debye-Hückel form) of screening wave vector k_s from 0.3 to 1.8×10^6 cm^{-1}. (The Fermi-Thomas values are of the same order of magnitude, i.e., $0.5\text{–}1\times10^{-6}$ cm^{-1}.) The scattering wave vector, on the other hand, for 514.5 nm is $q_0=0.9\times10^6$ cm^{-1}, assuming momentum conservation. The penetration depth in the same range of temperatures is $\delta\geq200$ Å, while the width of the depletion layer changes from about 400 to 100 Å. These features indicate the following. (i) For the whole range of T used here the system is in the single-particle excitation regime.[13] (ii) At low temperatures the scattering is produced within the depletion layer where only free holes may interfere with lattice dynamics, the electrons being trapped by surface states. Because of their low concentration and large mass, the holes are expected to have an insignificant effect and the phonon frequency shifts are mainly dominated by anharmonicity. (iii) As T is increased, the number of bulk phonons participating in the scattering process increases. Their frequencies are influenced by anharmonicity and also by the screening action of the increasing free carriers.[14]

Momentum nonconservation is easily justified, especially at high temperatures, as due to impurities or lattice defects, gradual loss of long-range crystallinity, large phonon amplitudes, and, further, smearing of wave vectors due to absorption. For all those reasons one expects scattering by LO phonons with $q\geq q_0$. According to the phonon dispersion curves of InSb, the higher the q the lower the frequency of such phonons from near the center of the zone. Related phenomena arising from momentum nonconcervation in heavily doped p-GaAs have already been reported.[15]

From the above discussion it appears that the observed band shapes are due to scattering contributions from more than one type of LO phonons, such as screened and unscreened phonons with $q\geq q_0$ from the surface and bulk region. This explains qualitatively the fast decrease of $\omega_l(T)$ and also the sharp increase of the bandwidths $\Gamma_l(T)$. Similar scattering contributions for the TO phonons do not occur, since the effect of free carriers is considerably weaker[15] and, further, the dispersion curves of TO phonons are practically flat. Obviously a complete quantitative account of these observations poses an interesting and complicated problem. The multiple role of temperature should be recognized in determining the level of anharmonicity, carrier concentration, and momentum nonconservation.

It should be possible to test the role of the thermally excited carriers by studying the LO-TO splitting as a function of T in other materials, preferably of zincblende structure. If screening is an important mechanism, then quenching of the LO-TO splitting should occur at a temperature T_0, nearly equal to that temperature T_g for which E_g becomes zero (or even at $T_0<T_g$, to account for other mechanisms too). It is assumed of course that $T_g\leqslant T_m$ (or even $T_g\gtrsim T_m$). If $T_g>T_m$ there should be no quenching for $T\leqslant T_m$. The exact value of T_0 will be influenced by the level of anharmonicity and concentration-dependent energy gaps, the structure of the dispersion curves, and the impurity content of the material. It is coincidence that for InSb $T_g=810$ K $\gtrsim T_m=800$ K. Thus, considering all mechanisms the splitting should be practically zero at T_m, and this is what Fig. 2 shows. Preliminary measurements similar to those in Fig. 2, for InAs, GaSb, and InP gave the following information: for InAs, $T_m=1215$ K and $E_g(0\text{ K})=0.41$ eV.[12] We estimate $T_g=1170$ K $<T_m$, and observed $T_0\approx(1050\pm50)$ K $<T_g$. For GaSb, $T_m=1000$ K, $E_g(0\text{ K})=0.81$ eV, $T_g=2200$ K $>T_m$. The measurements indicate no quenching for $T<T_m$.[2] Finally for InP, $T_m=1330$ K, $E_g(0\text{ K})=1.423$ eV, $T_g=4900$ K $>T_m$. Again, the measurements indicate no quenching for $T<T_m$. According to these results, thermally excited free carriers appear to increasingly influence the long-range interatomic forces, at temperatures approaching the characteristic value of T_g. Obviously the effect should be enhanced in doped materials. A more complete account of this work is now in preparation.

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