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Soft-Phonon Couplings in the Pressure-Induced Phase Transition in SbSI

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The Raman spectra of the soft-phonon behavior in the ferroelectric transition in SbSI is studied by means of a new technique in which the phase transition is induced by hydrostatic pressure. The crystal temperature is maintained constant and the ferroelectric transition is created by a linear shift of the Curie temperature. Evidence is provided for the existence of two distinct mode couplings involving three phonons.

INTRODUCTION

Antimony sulfo-iodide is a crystal in which there coexist a large number of remarkable physical properties. SbSI is the first semiconductor found to be both photoconductive and also ferroelectric.[1,2] In addition, the crystal exhibits a strong electro-optical and electromechanical effect[3] and an unusually strong dependence of the band gap on the electric field,[4] as well as a very strong energy band-gap variation with temperature.[5] All these interesting properties superpose and vary substantially when the temperature changes, in particular around the Curie temperature T_C. In previous Raman-scattering investigations, it was reported that an optical $\Gamma_1(A_1)$ band shows a soft-mode behavior when T_C is approached from below.[6] It was also proposed that the band consists in fact of two optical modes which exhibit the level-repulsion characteristic for a system of coupled harmonic oscillators.[7,8] Infrared reflectivity measurements[9] show a temperature-dependent optical mode when T_C is approached from above. All these experiments were performed at various temperatures which modify simultaneously and appreciably the other fundamental properties of the crystal.

In this paper, we propose a different technique to study the phonon spectrum change during the phase transition in SbSI. Under hydrostatic pressure, the Curie temperature T_C is considerably lowered: $dT_C/dP \simeq -39$ to -50 °C/kbar, according to Refs. 5 and 10, and $dT_C/dP \simeq -37$ °C/kbar, according to Ref. 11. It is then expected that the ferroelectric transition may be induced by hydrostatic pressure at fixed temperature. The phonon behavior may therefore be studied at various T_C instead of T. This method presents the significant advantage of eliminating the influence of most of the other effects, since they are only slightly pressure dependent. Furthermore, with our experimental equipment an error of $\Delta P = 20$ bar on pressure is estimated; this corresponds to an error of about $\Delta T_C = 0.8$ °C on the Curie temperature. It is then possible to study the phase transition with more accuracy.

It is the purpose of this paper to present the Raman scattering of SbSI investigated at a set of fixed temperatures under hydrostatic pressure. Our attention is especially focused on the ferroelectric phase-transition region where substantial spectral change is expected. The results deduced from this experiment are somewhat different from those reported previously:

(i) Two mode couplings are actually observed.

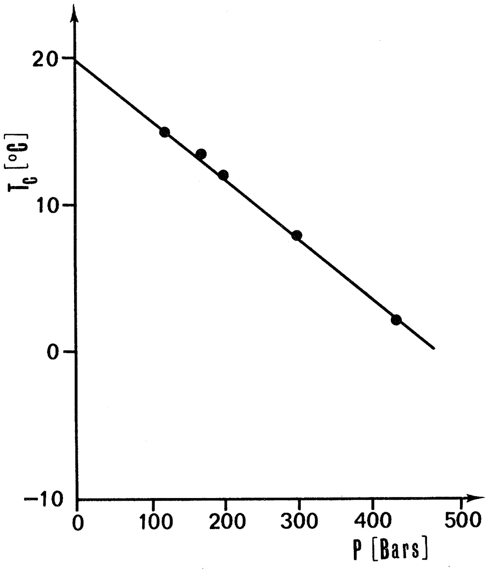

FIG. 1. Curie-temperature shift under hydrostatic pressure in SbSI.

In addition to the coupling of the soft mode with the mode at 30 cm^{-1} as reported in Ref. 7, another interaction between the mode at 48 cm^{-1} and the mode at 41 cm^{-1} is also found. These phonon-phonon interactions lower the slope of the $\log_{10}$-$\log_{10}$ plot of frequency vs $\Delta T = T_c - T$.

(ii) It appears that just before the ferroelectric transition, the frequency-vs-ΔT curve exhibits a flat structure covering an interval of a few degrees, indicating that in the crystal a certain degree of stability may set in.

EXPERIMENT

The spectra are excited by a 6764-Å krypton laser line with an output power of 10 mW. For this wavelength we are below the absorption band edge,[1,3] so that measurements are performed in transmission Raman spectroscopy. This condition is important for SbSI since the local heating is considerably diminished. The spectrometer and its detection technique, as well as the pressure generating system, are described elsewhere.[8,12] Furthermore, since the principal interest of this study is to investigate the behavior of the soft mode near the transition, only spectra in the Γ_1 polarization are followed with particular attention and presented. The incident light is then polarized perpendicularly to the scattering plane along the ferroelectric C axis. The scattered light is collected at a right angle to the incident direction and polarized along the same C axis so that the phonon wave vector is about 400 times larger than that of the polariton region, which is situated at about $k \simeq 1.25 \times 10^3$ cm^{-1}. Since it is seen from this experiment that all the Raman lines

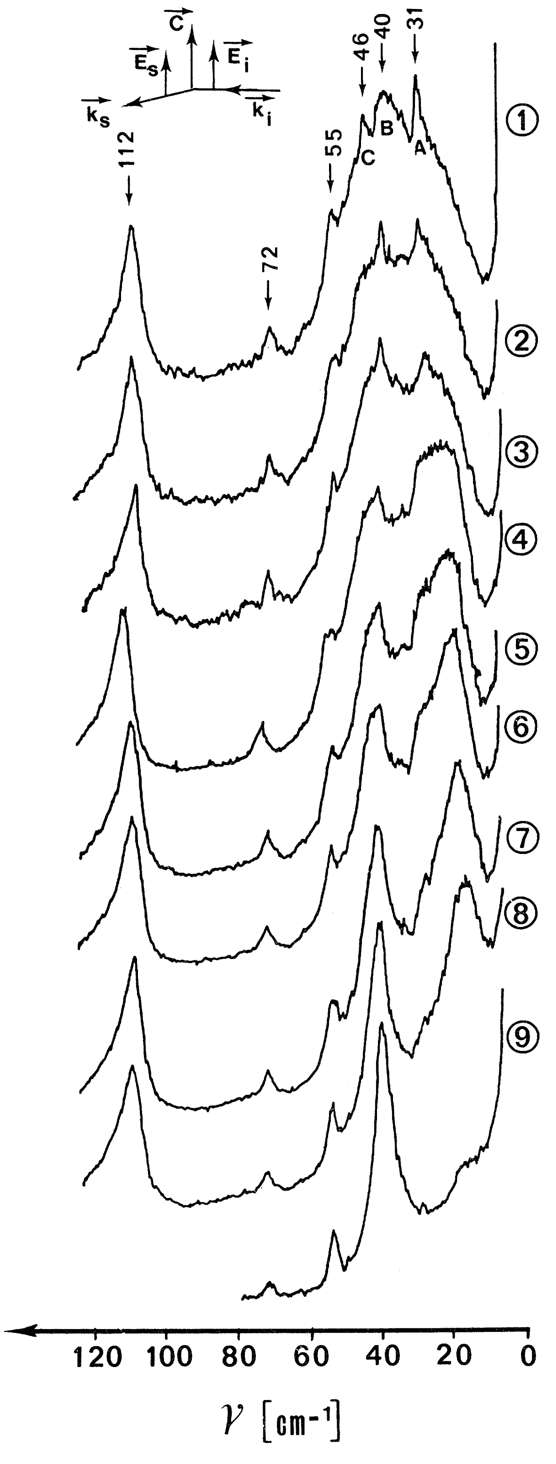

FIG. 2. Raman spectra of SbSI in the Γ_1 polarization performed with a slitwith of 1 cm^{-1}. The temperature is fixed at (3.0 ∓ 0.5) °C and the pressure varies from 1 to 400 bar. 1: $P = 1$ bar ($\Delta T = 17.1$ °C); 2: $P = 75$ bar ($\Delta T = 13.5$ °C); 3: $P = 100$ bar ($\Delta T = 12.5$ °C); 4: $P = 150$ bar ($\Delta T = 10.5$ °C); 5: $P = 200$ bar ($\Delta T = 8.5$ °C); 6: $P = 250$ bar ($\Delta T = 6.5$ °C); 7: $P = 300$ bar ($\Delta T = 3.4$ °C); 8: $P = 350$ bar ($\Delta T = 2.3$ °C); 9: $P = 400$ bar ($\Delta T = 0.5$ °C).

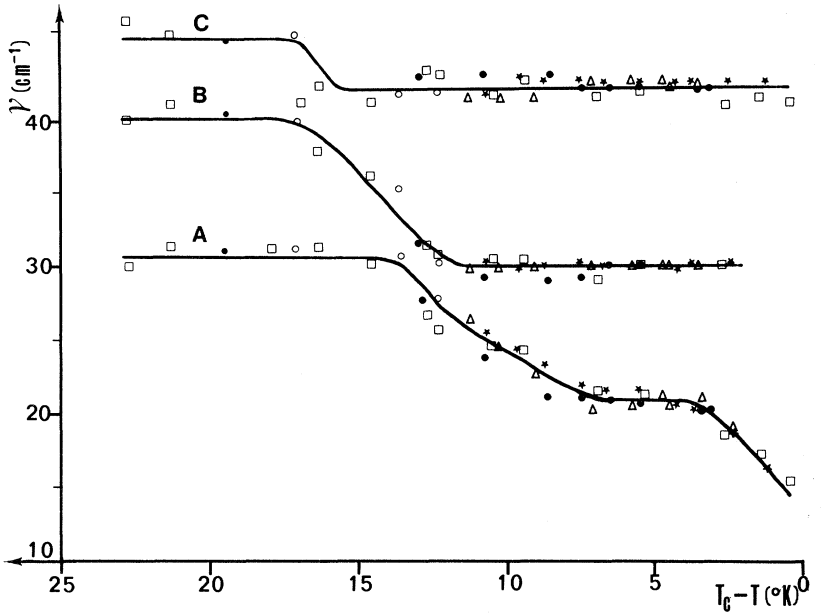

FIG. 3. Frequency shift of the three lowest-frequency optical modes as a function of $\Delta T = T_C - T$. The variation of ΔT is induced by hydrostatic pressure. The closed circles and the triangles represent data obtained at $T = 0$ °C and $T = 1.5$ °C, respectively; the stars and open circles represent data at $T = 3$ °C. For comparison, data obtained with $P = 200$ bar and represented by the squares are also given in the same curve.

with frequency $\nu > 50$ cm^{-1} are only slightly affected by hydrostatic pressure, they are not discussed here.

In order to measure the coefficient of pressure dependence of T_C under our experimental conditions, we determined T_C at various pressures by comparing the spectral change in the low-frequency region between the paraelectric and ferroelectric phases. Indeed, the last phase is characterized by the appearance of the soft mode, which is forbidden in the paraelectric phase.[8] Figure 1 represents the Curie-temperature shift in the pressure range used in this Raman study. It turns out that T_C follows a linear decrease with a coefficient $dT_C/dP = -40$ °C/kbar, which is in good agreement with that determined by dielectric constant measurements reported in Refs. 10 and 11.

Spectra in the Γ_1 polarization have been obtained for several fixed temperatures and studied in the pressure range extending from 1 to 500 bar, for which the transition is completely induced. In Fig. 2 we show one of the series of spectra obtained in the 0–120-cm^{-1} region. The temperature of the crystal is maintained at 3 °C. As shown in these spectra, the situation is more complicated than for the one-coupled-mode model. The over-all spectral change may be satisfactorily interpreted by means of a three-interacting-modes model in which the mode C, becoming soft, interacts first with the mode B (at 41 cm^{-1}) and then with the mode A (at 30 cm^{-1}). This interpretation is also supported by all the other series of spectra performed with $T = 0$ °C and $T = 1.5$ °C. The results are shown in Fig. 3, in which the frequency of the three lowest Γ_1 modes

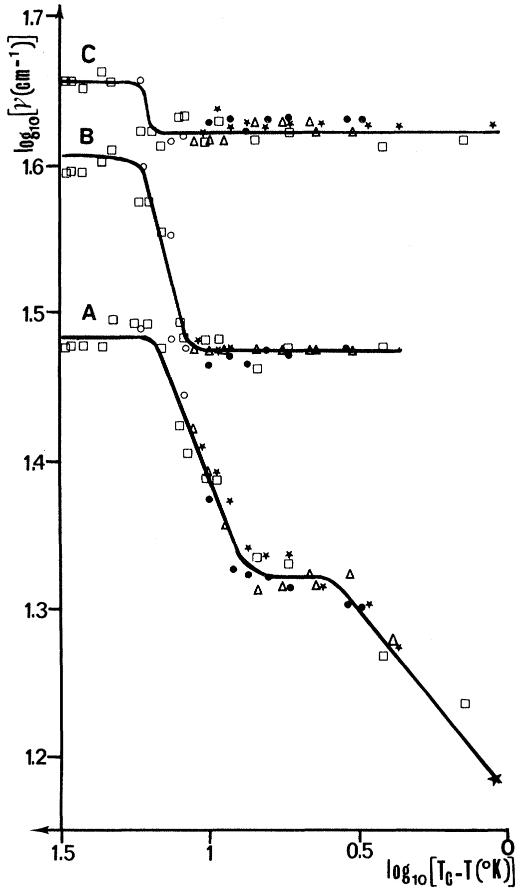

FIG. 4 Log$_{10}$-log$_{10}$ plot of the three lowest-frequency modes vs ΔT. The symbols representing experimental data have the same meaning as in Fig. 3.

is plotted vs the temperature-difference parameter $\Delta T = T_C - T$, where the correspondence between pressure and T_C has been made. In Fig. 4 the $\log_{10}$-$\log_{10}$ plot of these measurements is shown. It is evident from Figs. 3 and 4 that couplings between the mode C and the two lowest Γ_1 modes (B and A) are actually observed. The frequency of the mode C, which has initially a nearly constant value ($\omega_C = 45$ cm^{-1}) undergoes a strong decrease at $\Delta T \simeq 18$ °C. This decrease may be roughly described by the relation $\omega_C \simeq 2.3(T_C - T)$ cm^{-1}. ω_C approaches the frequency of the mode B (at 41 cm^{-1}) so closely that level repulsion sets in at $\Delta T \simeq 16$ °C. After this C-B mode coupling, ω_C maintains a practically constant value, whereas ω_B follows the approximate law $\omega_B \simeq 4.7(T_C - T)^{5/6}$ cm^{-1}. At $\Delta T \simeq 13$ °C, another anticrossing of frequencies between the modes B and A occurs; afterwards, ω_A begins to decrease following a $\omega_A \simeq 9.2\,(T_C - T)^{1/2}$ cm^{-1} law. Another observation is the existence of a region between $\Delta T \simeq 7$ °C and $\Delta T \simeq 3$ °C, where ω_A remains practically constant before it decreases again as T_C is approached. This indicates that in this region the crystal passes through a stable state. Finally, close to the transition ($\Delta T < 3$ °C), ω_A starts to decrease again with a law of the form $\omega_A \simeq 12.4\,(T_C - T)^{1/4}$ cm^{-1}.

DISCUSSION

In an earlier Raman investigation[7] in which the mode frequency was studied as a function of the crystal temperature, Harbeke, Steigmeier, and Wehner advanced the theory that there exists a coupling between the soft mode C and the mode A. They also mentioned that the soft mode C crosses the mode B without any interaction. We believe that there is no fundamental reason to distinguish mode B from mode A, since both modes belong to the same Γ_1 symmetry, which is also the symmetry of the soft mode. Hence, C-B mode coupling may occur as well as C-A coupling. In both cases we did observe a frequency difference between the flat region above and below the crossing point, which is also evidence of coupling. In our view, this discrepancy may be explained by the following arguments: The nonobservation of the C-B mode coupling in the previous investigation may be due to the relatively large instrumental slitwidth ($\simeq 3$ cm^{-1}) used in this experiment, so that the modes are not well resolved in the interacting region. Furthermore, our pressure-induced technique allows the study of the spectral changes with a precision better than $\Delta T = 1$ °C, whereas in the earlier experiment the spectra have been carried out with a temperature variation of at least a few degrees. Finally, it must be mentioned that an apparent transfer of intensity between the modes is also noted under our experimental conditions. Since there may exist an overlapping of this phenomenon and the Raman resonant effect, as noted in Ref. 7, more appropriate investigations are under way in order to distinguish between these two effects.

Although the phenomenon is reproducible for several different samples, the observation of the flat structure in the frequency-vs-ΔT plot in the 3 °C $< \Delta T <$ 7 °C region seems puzzling. It is not possible at the present stage to give an accurate interpretation of this phenomenon. Nevertheless, a model involving an eventual interaction between zone-center and zone-corner phonons as observed in $\mathrm{SrTiO_3}$[13] must be excluded since in the actual case there is no enlargement of the unit cell during the phase transition. On the other hand, the existence of another phase in which the crystal structure becomes stable just before the ferroelectric transition is improbable since no anomaly in x-ray,[14] specific-heat,[15] and dielectric-constant[2] measurements has been reported in this region. We believe that this temporary stable state in which the transition mechanism is somewhat "clamped" may result from a strong electron-phonon interaction, as expected in this semiconductor. It is also possible that this observation is closely related to some pressure effects. Further precise investigation of the electronic band structure under the same conditions and a good lattice-dynamics model, in which anharmonicity caused by electron-phonon interaction is taken into account, may prove a great help for the understanding of this phenomenon.

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