



PERGAMON

Solid State Communications 110 (1999) 231–236

solid
state
communications

Temperature dependence of the Raman-active phonon frequencies in indium sulfide

N.M. Gasanly^{a,1,*}, H. Özkan^a, A. Aydinli^b, İ. Yilmaz^a

^aPhysics Department, Middle East Technical University, 06531 Ankara, Turkey

^bPhysics Department, Bilkent University, 06533 Ankara, Turkey

Received 1 August 1998; received in revised form 5 November 1998; accepted 1 December 1998 by F. Yndurain

Abstract

The temperature dependence of the Raman-active mode frequencies in indium sulfide was measured in the range from 10 to 300 K. The analysis of the temperature dependence of the A_g intralayer optical modes show that Raman frequency shift results from the change of harmonic frequency with volume expansion and anharmonic coupling to phonons of other branches. The pure-temperature contribution (phonon–phonon coupling) is due to three- and four-phonon processes. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: A. Semiconductors; D. Optical properties; E. Inelastic light scattering

1. Introduction

The layer-type semiconductors, $A^{III}B^{VI}$, where A is Ga, In; B is S, Se, have attracted particular interest in recent years due to high degree of anisotropy in their physical properties. In indium sulfide, the In atoms have a tetrahedral coordination (three S atoms and one In atom), the two S atoms and one In atom being in one layer, whereas the third S atom is in the neighboring layer. Therefore, the crystal structure of InS can be considered as a three-dimensional network which is slightly different from a layered structure of its counterparts (GaS, GaSe, InSe).

A room temperature pressure-induced structural phase transition in InS crystal was predicted on the basis of Raman scattering studies at various hydrostatic pressures up to 1.2 GPa [1]. Six of the nine

modes of the Brillouin zone center, observed in the Raman spectra show a decrease in frequency as pressure increases. They proposed that the initial orthorhombic phase of InS transforms into the calomel type (Hg_2Cl_2) structure under pressures of $P = 7 \pm 1$ GPa. Subsequent measurements of the electrical resistance [2], Raman spectra, optical properties and lattice parameters [3,4] show certain anomalies between 2.5 and 5 GPa. In a previous article [5], we have reported the variation of the Raman frequencies and the lattice parameters of InS as a function of pressure up to 30 and 16 GPa, respectively. Anomalies in the pressure dependence of the Raman frequencies and rather rapid decrease of the lattice parameter b toward a with pressure clearly indicated a phase transition at 5.0 ± 0.3 GPa. The continuous structural changes of the orthorhombic low-pressure modification as well as the high-pressure monoclinic structure were investigated.

The influence of anharmonic interactions on the lattice vibrations can be experimentally studied by

* Corresponding author.

¹ On leave from Physics Department, Baku State University, Baku, Azerbaijan.

measuring changes of phonon frequencies with temperature and pressure. A large number of articles devoted to the study of the temperature dependence of the frequency shift and the linewidth of the first-order Raman scattering in semiconductors may be found in the literature [6–10]. They showed that the Raman shifts can be successfully modeled by including the effects of thermal expansion and the phonon–phonon coupling.

The purpose of this article is to present the results of the temperature dependence of the optical phonon frequencies of InS in the 10–300 K temperature range. We report softening of the optical phonon frequencies at the Brillouin zone center with increase in temperature as observed in some other semiconductors. The analysis of our results indicates that the purely anharmonic contribution to the phonon frequency shifts is due to interactions with phonons of other branches.

2. Experimental

InS polycrystals were synthesized from particular high-purity elements (at least 99.999%) taken in stoichiometric proportions. Single crystals of InS were grown by the modified Bridgman method. The analysis of X-ray diffraction data showed that they crystallize in an orthorhombic unit cell with parameters: $a = 0.394$, $b = 0.444$ and $c = 1.065$ nm. Due to the fact that one of its three In–S bonds extends into the neighboring layers, InS crystal has no distinct cleavage plane. Crystals suitable for measurements were obtained by hard cleavage perpendicular to the OX-axis (optical c -axis). As-grown InS is a n -type semiconductor having an indirect band gap with an energy of 1.90 and 2.11 eV at 300 and 10 K, respectively [11].

Unpolarized Raman scattering measurements were performed in the back-scattering geometry in the frequency range from 20 to 350 cm^{-1} . The 632.8 nm ($h\nu = 1.96$ eV) line of a He–Ne laser and the 617.5 nm ($h\nu = 2.01$ eV) line of dye laser were used as exciting light sources. The scattered light was analyzed using a U-1000 ‘‘Jobin Yvon’’ double grating spectrometer and a cooled GaAs photomultiplier supplied with the necessary photon counting electronics. The Raman line positions were

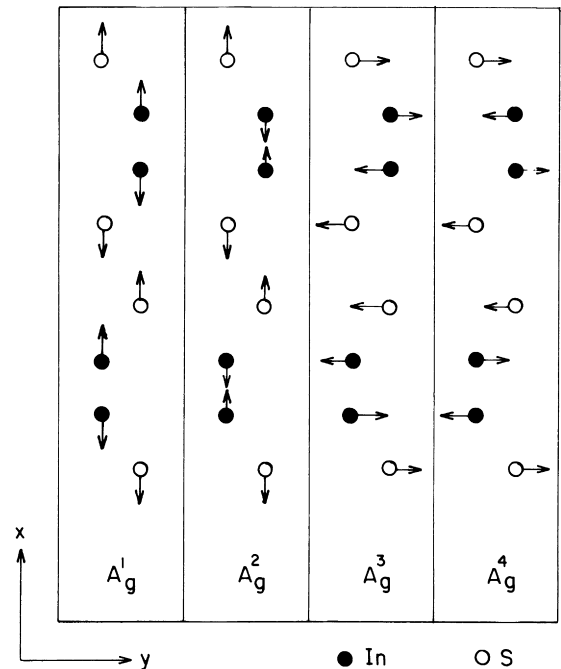


Fig. 1. Atomic displacement vectors for A_g intralayer optical modes of InS.

determined within an accuracy of 0.2 cm^{-1} . A ‘‘CT1-Cryogenics M-22’’ close-cycle helium cryostat was used to cool the crystals from room temperature down to 10 K. The temperature was controlled within an accuracy of ± 1 K. In order to avoid sample heating effects, we chose a cylindrical lens to focus the incident beam on the sample. The laser power was kept below 30 mW. No changes in the spectra were observed when the applied power was reduced by a factor of two.

3. Results and discussion

InS has the orthorhombic structure composed of four molecules in a primitive unit cell and belongs to the space group Pmnn. According to the group theory, there should be 24 fundamental phonon modes

$$\Gamma \equiv 4A_g + 2A_u + 4B_{1g} + 2B_{1u} + 2B_{2g} \\ + 4B_{2u} + 2B_{3g} + 4B_{3u}.$$

Thus, there are 12 Raman active modes in InS,

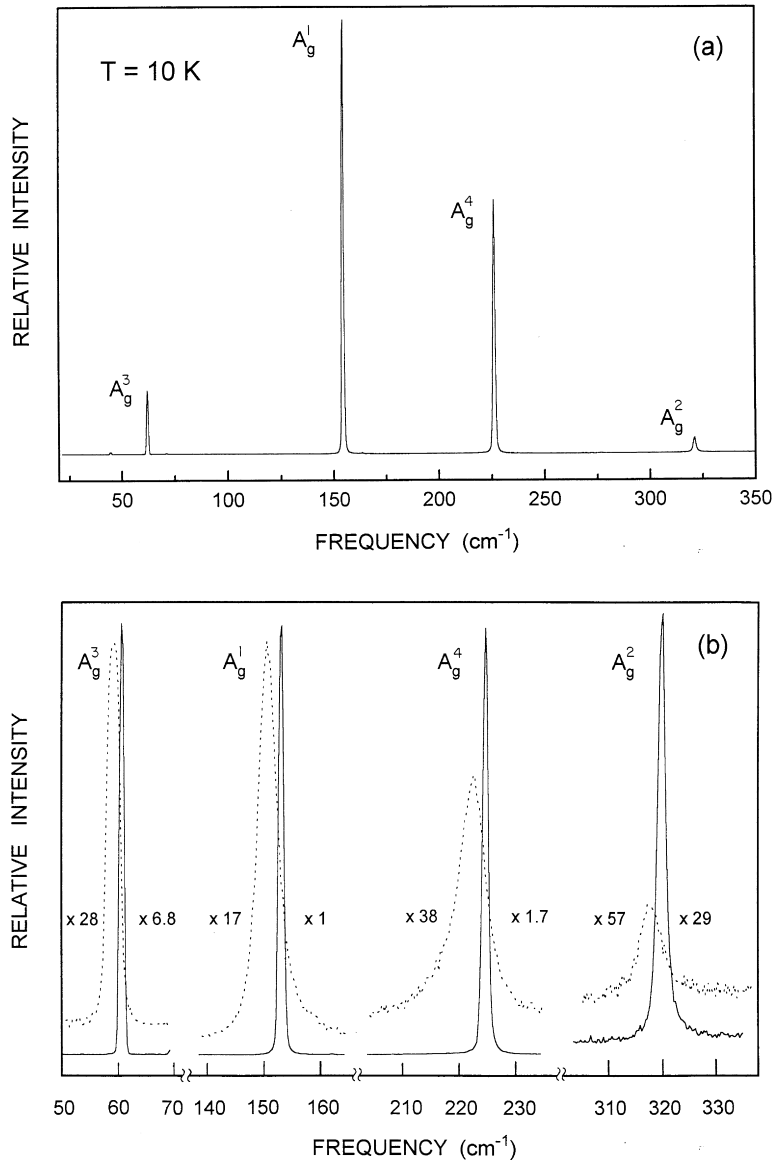


Fig. 2. (a) Raman spectrum of InS at $T = 10$ K; (b) extended parts of Raman spectra of InS at $T = 10$ K (solid curves) and $T = 300$ K (dashed curves).

given by $4A_g + 4B_{1g} + 2B_{2g} + 2B_{3g}$. The symmetry coordinates found by Melvin projection operators method [12] were used to obtain the displacement vectors of atoms in all phonon modes. Fig. 1 shows the atomic displacement vectors for A_g intralayer optical modes of InS. As seen from this figure at each A_g mode all the indium and sulfur atoms move either perpendicular or parallel to the layers.

Fig. 2 presents the Raman spectra of InS at 10 and 300 K. The phonon spectra of InS have been reported previously at room temperature from Raman and infrared measurements [5,13,14]. The present assignment of the observed modes is in excellent agreement with that of Ref. [5]. We have measured and analyzed only the most intensive, at employed geometry, A_g intralayer optical modes with room temperature

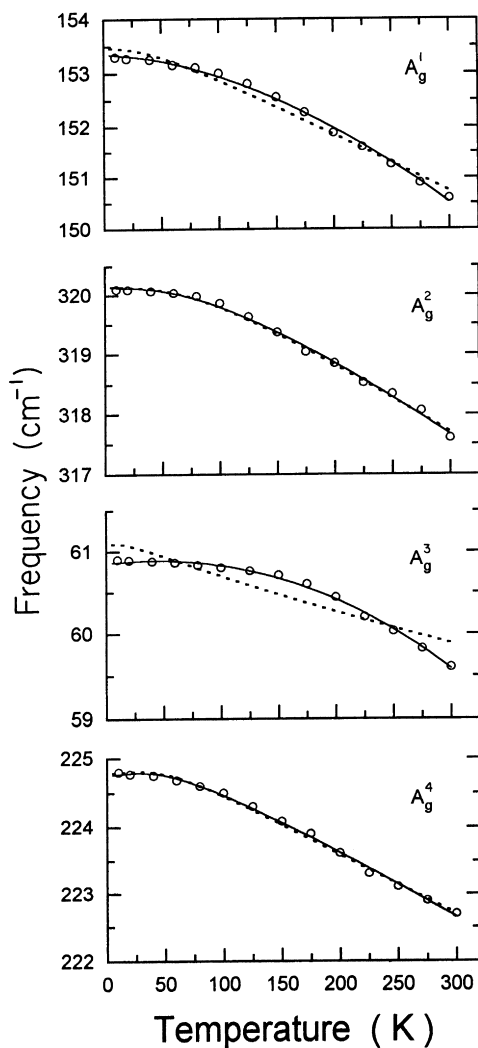


Fig. 3. Temperature dependencies of the Raman frequencies in InS (open circles). The solid curves give the theoretical fits using both three- and four-phonon processes. The dashed curves give the theoretical fits using only three-phonon processes.

frequency values 59.5 (A_g^3), 150.6 (A_g^1), 222.7 (A_g^4), and 317.6 (A_g^2) cm^{-1} . As seen from Fig. 1, in the A_g^1 and A_g^2 modes the atoms vibrate in the direction of stretching bonds, whereas the A_g^3 and A_g^4 modes correspond to the bending vibrations of the atoms. It was previously observed that the frequencies of A_g^1 and A_g^2 modes increase and those of A_g^3 and A_g^4 modes decrease with pressure [1]. It was reported that the Grüneisen parameters of the first two modes are positive ($\gamma_1 = 0.7$, $\gamma_2 = 0.2$) and those of the last two are negative ($\gamma_3 = -1.5$, $\gamma_4 = -0.4$). Thus, negative Grüneisen parameters were observed for modes at which the atoms move perpendicular to the OX-axis of the crystal.

The frequency shifts of A_g modes investigated in the temperature range 10–300 K were found to be 2.7 (A_g^1), 2.5 (A_g^2), 1.2 (A_g^3), and 2.1 cm^{-1} (A_g^4). The experimental results (open circles) for the line positions $\nu(T)$ of different A_g modes are shown in Fig. 3. The phonon frequency shift with temperature can be described by the following expression [7]

$$\nu(T) = \nu_0 + \Delta_1(T) + \Delta_2(T), \quad (1)$$

where $\nu_0 + \Delta_2(0)$ is the Raman shift as T approaches 0 K, $\Delta_1(T)$ represents the volume dependence of the frequency due to the thermal expansion of the crystals and $\Delta_2(T)$ specifies the contribution of anharmonic coupling to phonons of other branches.

$\Delta_1(T)$ can be written as [7]:

$$\Delta_1(T) = \nu_0 \left[\exp\left(-3\gamma \int_0^T \alpha(T') dT'\right) - 1 \right], \quad (2)$$

where $\alpha(T)$ is the coefficient of linear thermal expansion.

The purely anharmonic contribution to the frequency

Table 1

Parameters for fitting the temperature dependence of Raman frequencies of InS crystal

| Modes | ν_0 (cm^{-1}) | A (cm^{-1}) | B (cm^{-1}) | B/A | ν_{01} (cm^{-1}) | A_1 (cm^{-1}) |
|---------|------------------------------|--------------------------|--------------------------|--------|---------------------------------|----------------------------|
| A_g^1 | 153.4 | -0.022 | -0.038 | 1.727 | 153.9 | -0.419 |
| A_g^2 | 321.0 | -0.818 | -0.034 | 0.042 | 321.3 | -1.129 |
| A_g^3 | 60.9 | 0.011 | -0.007 | -0.636 | 61.2 | -0.153 |
| A_g^4 | 225.6 | -0.836 | -0.022 | 0.026 | 225.8 | -1.007 |

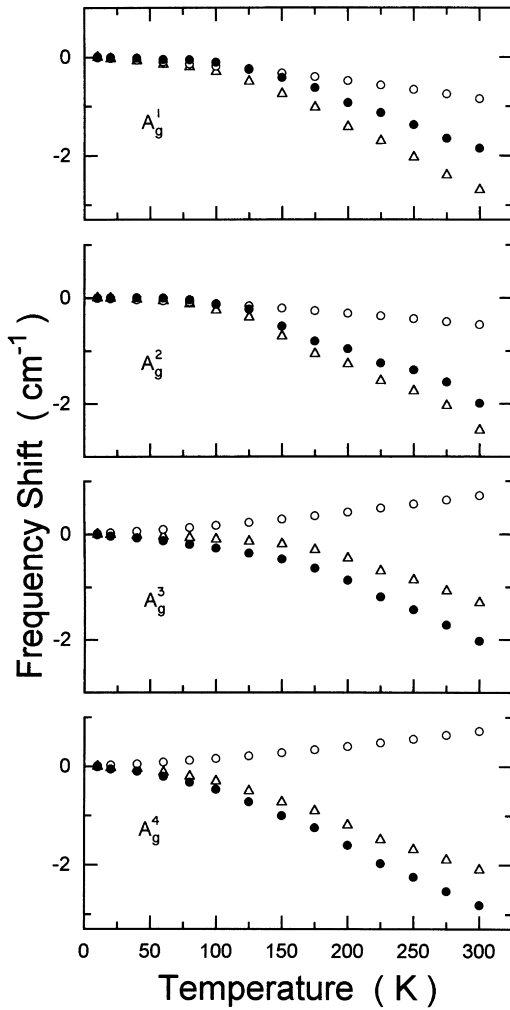


Fig. 4. Experimental Raman frequency shifts as a function of temperature (triangles). Open and solid circles are the thermal-expansion and the purely anharmonic contributions to the line shifts, respectively.

shift can be modeled as [6]:

$$\Delta_2(T) = A \left[1 + \frac{2}{e^x - 1} \right] + B \left[1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right], \quad (3)$$

where the first term corresponds to the coupling of the optical phonon to two identical phonons (three-phonon processes) and the second term corresponds to the coupling to three identical phonons

(four-phonon processes). Here, $x = hc\nu_0/2k_B T$ and $y = hc\nu_0/3k_B T$.

Using the experimental values of γ [1] and $\alpha(T)$ [15], the frequency shifts for A_g modes were fitted (solid curves in Fig. 3) by means of Eqs. (1), (2) and (3) with ν_0 , A and B as adjustable parameters. The agreement between the experimental points and the solid curves is seen to be good for all A_g modes. The fitting parameters are presented in Table 1. The absolute values of B/A for A_g^2 and A_g^4 modes are very low, 0.042 and 0.026, respectively. This indicates that pure-temperature dependence of the frequencies $\Delta_2(T)$ is dominated by the three-phonon processes. The four-phonon coupling processes (quartic interaction) are less effective. This result is consistent with the previous experiments in Si and Ge [6,7], ZnSe and ZnTe [8], CuGaS₂ [9] and AgGaS₂ [10] compounds. By contrast, relatively higher absolute values for B/A were found for A_g^1 and A_g^3 modes, 1.727 and 0.636, respectively (Table 1). Consequently, we deduce that the contribution of four-phonon processes to the frequency shift $\Delta_2(T)$ is important for these modes.

If we try to fit the experimental data with three-phonon processes only, by omitting the term in Eq. (3) with the factor B , we obtain the dashed curves in Fig. 3 with adjustable parameters ν_{01} and A_1 , also given in Table 1. The agreement between calculated curves and the experimental points is quite good for A_g^2 and A_g^4 modes, but for A_g^1 and A_g^3 modes the curves do not represent the data well, especially for the latter mode. This further demonstrates that the four-phonon processes are important for the A_g^1 and A_g^3 modes.

We have stated before that to describe the results obtained for A_g^2 and A_g^4 modes, having high absolute values of adjustable parameter A , mainly three-phonon processes is sufficient, whereas for A_g^1 and A_g^3 modes with lower values of A (almost 50 times) both three- and four-phonon processes should be included. These features may be related to the differences in sets of atomic displacements for these pairs of modes. Indeed, as seen from Fig. 1, in the A_g^2 and A_g^4 modes the restoring forces are due to the In–In and In–S bonds, whereas in the A_g^1 and A_g^3 modes primarily the In–In bonds are involved.

We have also calculated the thermal-expansion contribution to the line shift [$\Delta_1(T)$] for A_g modes by using the experimental values of γ and $\alpha(T)$ and obtained the value of the adjusted parameter ν_0 . The

variations of $\Delta_1(T)$ are given in Fig. 4 for all A_g modes, together with the experimental frequency shifts. The pure-temperature effect on the frequency shift [$\Delta_2(T)$], obtained from the difference between the experimental results and the thermal expansion contribution $\Delta_1(T)$ are also plotted in Fig. 4 (solid circles). An interesting feature of these plots is that for A_g^3 and A_g^4 modes, having negative Grüneisen parameters, the pure-temperature contribution $\Delta_2(T)$ dominates the pure-volume contribution $\Delta_1(T)$ for the entire temperature range studied. But for A_g^1 and A_g^2 modes, having positive Grüneisen parameters, $\Delta_2(T)$ prevails $\Delta_1(T)$ only at relatively high-temperature ranges 150–300 K and 100–300 K, respectively.

The analysis of the temperature dependence of the A_g symmetrical optical modes in InS crystal shows that the Raman frequency shift is well described by considering the thermal-expansion and pure-temperature (phonon–phonon coupling) contributions. The cubic (three-phonon) and quartic (four-phonon) anharmonicities responsible for the pure-temperature contributions to the A_g mode frequency shift were determined. We have shown that the term corresponding to quartic processes should be included in the frequency shift expression $\Delta_2(T)$ for A_g^1 and A_g^3 modes.

References

- [1] F.E. Faradzhev, N.M. Gasanly, A.S. Ragimov, A.F. Goncharov, S.I. Subbotin, *Solid State Commun.* 39 (1981) 587.
- [2] K. Takarabe, K. Wakamura, E. Ito, *Solid State Commun.* 46 (1983) 215.
- [3] K. Takarabe, *Phys. Status Solidi (b)* 143 (1987) K67.
- [4] K. Takarabe, *Phys. Status Solidi (b)* 145 (1988) 219.
- [5] U. Schwarz, A.F. Goncharov, K. Syassen, N.M. Gasanly, *Proc. Joint XV AIRAPT and XXXIII EHPRG Int. Conf.*, Singapore, 1996, p. 427.
- [6] M. Balkanski, R.F. Wallis, E. Haro, *Phys. Rev. B* 28 (1983) 1928.
- [7] J. Menendez, M. Cardona, *Phys. Rev. B* 29 (1984) 2051.
- [8] J.L. Lacombe, J.C. Irwin, *Solid State Commun.* 8 (1970) 1427.
- [9] J. Gonzalez, E. Moya, J.C. Chervin, *Phys. Rev. B* 54 (1996) 4707.
- [10] J. Gonzalez, Y. Guinet, J. Lefebvre, *Cryst. Res. Technol.* 31 (1996) 453.
- [11] T. Nishino, Y. Hamakawa, *Japan. J. Appl. Phys.* 16 (1977) 1291.
- [12] M.A. Melvin, *Rev. Mod. Phys.* 28 (1956) 18.
- [13] F.E. Faradzhev, N.M. Gasanly, B.N. Mavrin, N.N. Melnik, *Phys. Status Solidi (b)* 85 (1978) 381.
- [14] N.M. Gasanly, F.E. Faradzhev, A.S. Ragimov, V.M. Burlakov, A.F. Goncharov, E.A. Vinogradov, *Solid State Commun.* 42 (1982) 843.
- [15] N.G. Aliev, I.G. Kerimov, M.M. Kurbanov, *Termodinamicheskie svoistva metallicheskih splavov (in Russian)*, 1975, p. 315.