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Temperature dependence of the first-order Raman scattering in GaS layered crystals

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Abstract

The temperature dependence (15–293 K) of the six Raman-active mode frequencies and linewidths in gallium sulfide has been measured in the frequency range from 15 to 380 cm⁻¹. We observed softening and broadening of the optical phonon lines with increasing temperature. Comparison between the experimental data and theories of the shift and broadening of the interlayer and intralayer phonon lines during the heating of the crystal showed that the experimental dependencies can be explained by the contributions from thermal expansion and lattice anharmonicity. The pure-temperature contribution (phonon–phonon coupling) is due to three- and four-phonon processes. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

A^{III}B^{VI}-type semiconducting compounds, GaS, GaSe, and InSe, crystallize with a layer structure. These layer compounds are characterized by highly anisotropic bonding forces. The high anisotropy arises from the fact that layer–layer interaction is considerably weaker than the bonding force within a layer. In GaS, the van der Waals force contributes predominantly to the interlayer interaction, while the bonding force within a layer is primarily covalent. Because of the extremely weak interlayer interaction, a GaS crystal can be easily cleaved along the layers. In GaS, the layers consist of four sheets of atoms stacked along the *c*-axis in the sequence S–Ga–Ga–S, and there are two layers in the unit cell.

The lattice vibrations of the GaS crystal have been studied by many authors using Raman scattering [1–3], infrared reflectivity and absorption [3,4], inelastic neutron scattering [5], and Brillouin scattering measurements [6]. The room temperature Raman scattering spectra of a GaS crystal are

measured under pressure up to 20 GPa using a diamond anvil cell, and the pressure coefficients for all the Raman-active modes are obtained [7].

The purpose of this paper is to present the results of the temperature dependence of the optical phonon frequencies and linewidths, full-width at half-maximum (FWHM), of GaS in the 15–293 K temperature range. We report softening of the optical phonon frequencies and broadening of the linewidths with increasing temperature as observed in some other semiconductors. The analysis of our results indicates that the purely anharmonic contribution to the phonon frequency shift and linewidth broadening are due to interactions with phonons of other branches.

2. Experimental

Gallium sulfide polycrystals were synthesized from high-purity elements (at least 99.999%) taken in stoichiometric proportions. Single crystals of GaS were grown by the modified Bridgman method. The analysis of X-ray diffraction data showed that they crystallize in a hexagonal unit cell with parameters: *a* = 0.359 and *c* = 1.549 nm. Crystals suitable for measurements were obtained by easy cleavage perpendicular to the optical *c*-axis. As-grown GaS is an

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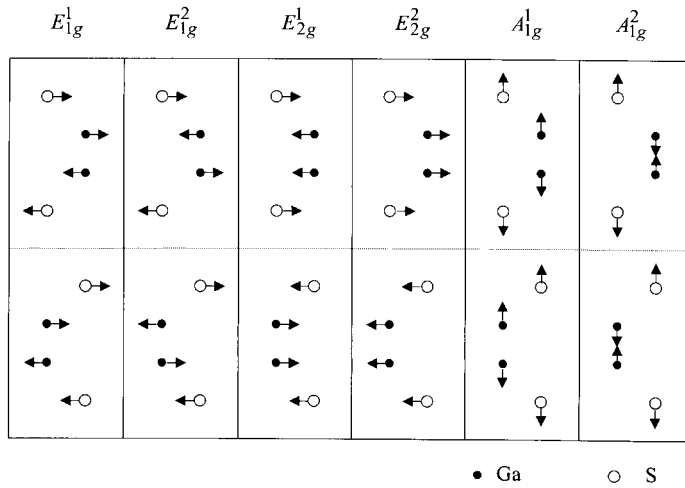


Fig. 1. Atomic displacement vectors for interlayer and intralayer Raman-active optical modes of the GaS crystal.

n-type semiconductor having an indirect band gap with energies of 2.591 and 2.597 eV at 77 and 4.2 K, respectively [8].

Unpolarized Raman scattering measurements in GaS layered crystals were performed in the back-scattering geometry in the frequency range from 15 to 380 cm^{-1} . The 514.5-nm ($h\nu = 2.41$ eV) line of an argon laser was used as the exciting light source. 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 determined within accuracy of 0.1 cm^{-1} . A “CTI-Cryogenics M-22” closed-cycle helium cryostat was used to cool the crystals from room temperature down to 15 K. The temperature was controlled within an accuracy of 0.5 K. In order to avoid sample heating effects we have chosen a cylindrical lens to focus the incident beam on the sample. The laser power was kept below 100 mW. No changes in the spectra were observed when the applied power was reduced by a factor of two.

To achieve high resolution we reduced the slit widths in the spectrometer down to 25 μm . The measured phonon

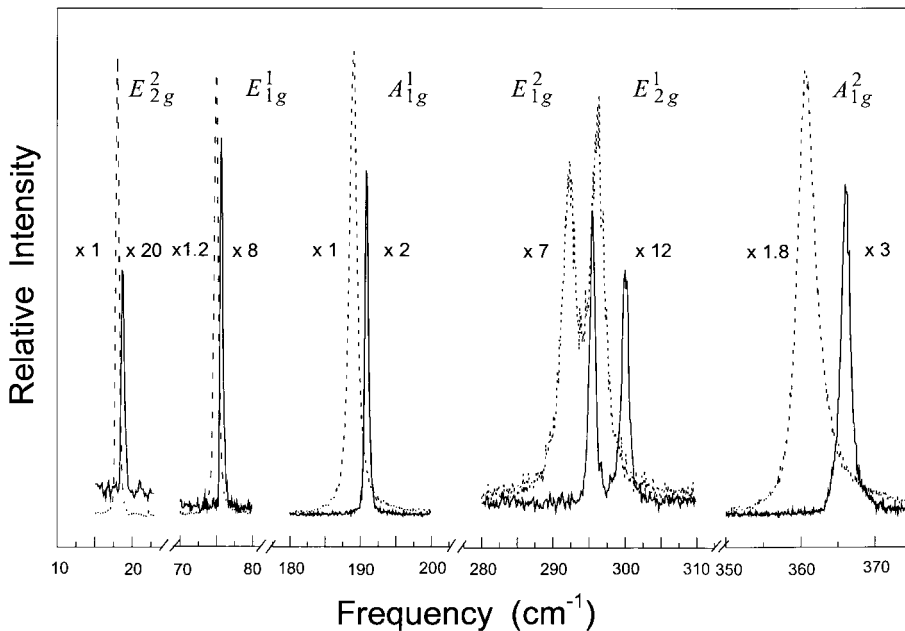


Fig. 2. Comparison of the extended individual parts of Raman spectra of the GaS crystal at $T = 15$ K (solid curves) and $T = 293$ K (dashed curves).

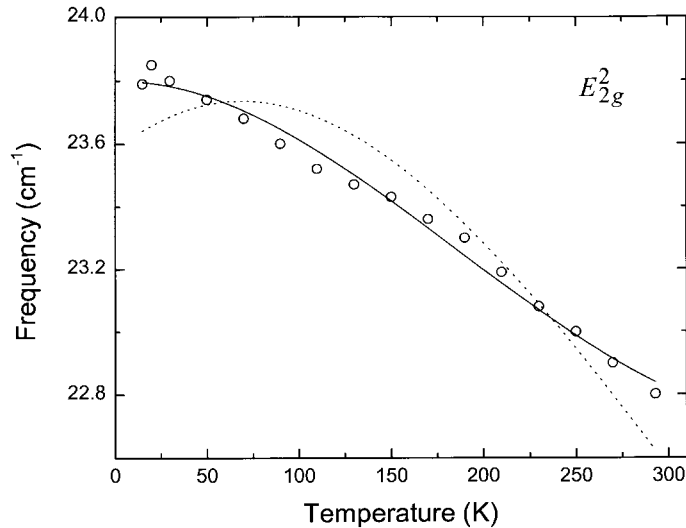


Fig. 3. Temperature dependence of the E_{2g}^2 interlayer mode frequency in the GaS crystal (open circles). The solid curve gives the theoretical fit using both three- and four-phonon processes. The dashed curve gives the theoretical fit using only three-phonon processes.

lines of the GaS crystals are so narrow that even with the reduced slits one has to correct for finite instrumental resolution. The width of the response function of the spectrometer was determined by measuring the linewidth of the laser line with the same slit apertures as in the Raman experiment. With the slit widths of $25 \mu\text{m}$ we could obtain the instrumental resolution of 0.39 cm^{-1} . The observed peak is the convolution of the Lorentzian shape of the actual phonons with the response function of the spectrometer, which is considered to be a Gaussian. The convolution product of a Gaussian times Lorentzian curve is the so-called Voigt profile. To make the deconvolution, at first, we fit a Voigt profile to our experimental peaks, and then calculate the Lorentzian linewidth using the fitted width of the Voigt profile and the experimentally determined width of the spectrometer response function.

3. Results and discussion

GaS has the hexagonal structure and belongs to the space group D_{6h}^4 . There are 24 normal modes of vibration at the center of the Brillouin zone and these can be described by the irreducible representations of the D_{6h} point group [1]

$$\Gamma \equiv 2A_{1g} + 2A_{2u} + 2B_{1u} \\ + 2B_{2g} + 2E_{1g} + 2E_{1u} + 2E_{2g} + 2E_{2u}.$$

Thus, there are six non-degenerate Raman-active modes ($2A_{1g} + 2E_{1g} + 2E_{2g}$) and two infrared-active modes ($E_{1u} + A_{2u}$).

The symmetry coordinates found by the Melvin projection operators method [9] were used to obtain the displacement vectors of atoms in all phonon modes. Fig. 1 shows the

atomic displacement vectors for interlayer and intralayer optical modes of GaS. As seen from this figure, in these modes all the gallium and sulfur atoms move either perpendicular or parallel to the layers.

Fig. 2 presents the Raman spectra of the GaS crystal at 15 and 293 K. The phonon spectra of GaS have been reported previously at room temperature from Raman and infrared measurements [1,4]. The present assignment of the observed modes is in excellent agreement with that of Ref. [1]. We have measured and analyzed the interlayer and intralayer optical modes with room temperature frequency values $74.7 (E_{1g}^1)$, $291.8 (E_{2g}^2)$, $295.8 (E_{2g}^1)$, $22.8 (E_{2g}^2)$, $189.0 (A_{1g}^1)$, and $360.9 (A_{1g}^2) \text{ cm}^{-1}$. As seen from Fig. 1, in the E_{1g}^1 , E_{1g}^2 , E_{2g}^1 , and E_{2g}^2 shear modes the atoms vibrate in the direction of bending bonds, whereas the A_{1g}^1 and A_{1g}^2 compressional modes correspond to the stretching vibrations of the atoms. The interlayer shear mode E_{2g}^2 in which entire layers vibrate rigidly out of phase with their neighbors relates only to the weak layer–layer interaction. The low value of this mode frequency ($\nu = 22.8 \text{ cm}^{-1}$) gives information about the strength of the layer–layer interaction in GaS. Polian et al. [7] previously observed that all mode frequencies of the GaS crystal increase with pressure. It was reported that there is a large difference between the mode Grüneisen parameter (γ) of the interlayer shear mode E_{2g}^2 (22.7) and the γ values of the intralayer shear (E_{1g}^1 (1.0), E_{1g}^2 (2.3), and E_{2g}^1 (2.3)) and compressional (A_{1g}^1 (2.6) and A_{1g}^2 (1.6)) modes which represents the difference in the interlayer and intralayer restoring forces.

The total frequency shifts of the GaS Raman modes in the temperature range 15–293 K were found to be $1.0 (E_{1g}^1)$, $3.5 (E_{1g}^2)$, $4.1 (E_{2g}^1)$, $1.0 (E_{2g}^2)$, $1.9 (A_{1g}^1)$ and $5.1 (A_{1g}^2) \text{ cm}^{-1}$ (Fig. 2). The experimental results (open circles) for the line positions $\nu(T)$ of the interlayer E_{2g}^2 mode and one of

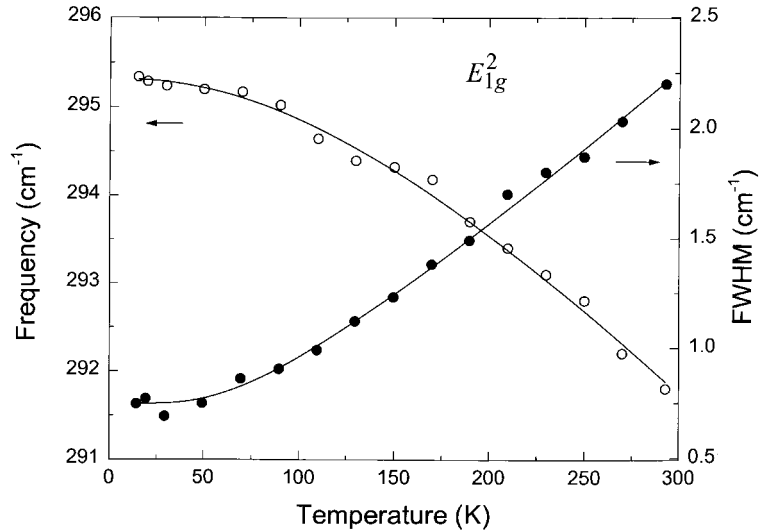


Fig. 4. Temperature dependencies of the E_{1g}^2 intralayer mode frequency (open circles) and linewidth (solid circles) in the GaS crystal. The solid curves give the theoretical fits using three-phonon processes.

the intralayer modes (E_{1g}^2) are shown in Figs. 3 and 4, respectively. The phonon frequency shift with temperature can be described by the expression [10–12]:

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

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 [12]:

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

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

The purely anharmonic contribution to the frequency shift can be modeled as [10,12]:

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

where the first term corresponds to the coupling of the

Table 1

Parameters for fitting the temperature dependencies of Raman frequencies and linewidths of the GaS crystal

Modes	ν_0 (cm ⁻¹)	A (cm ⁻¹)	B (cm ⁻¹)	C (cm ⁻¹)
E_{1g}^1	75.8	-0.070	0	-
E_{1g}^2	295.6	-0.262	0	0.748
E_{2g}^1	300.3	-0.563	0	0.974
E_{2g}^2	23.8	-0.005	0.001	-
A_{1g}^1	191.1	-0.246	0	0.289
A_{1g}^2	367.7	-1.904	0	1.369

optical phonon to two identical phonons (three-phonon processes) and the second term corresponds to the coupling of the optical phonon 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 [7] and $\alpha(T)$ [13], the frequency shift for the interlayer mode was fitted (solid curve in Fig. 3) by means of Eqs. (1)–(3) with ν_0 , A and B as adjustable parameters. A least-squares fit using the full expression of Eq. (3), i.e. both cubic and quartic terms, leads to a good agreement with the experimental data for the interlayer E_{2g}^2 mode (Fig. 3). The fitting parameters are presented in Table 1. Since one would expect the contribution of four-phonon processes to be small compared to that of three-phonon processes, the ratio B/A should be small. The actual value of this ratio is 0.2, so this expectation is fulfilled.

If we try to fit the experimental data with three-phonon processes only, by omitting the term in Eq. (3) with factor B , we obtain the dashed curve in Fig. 3 with adjustable parameters $\nu_{01} = 23.6$ cm⁻¹ and $A_1 = 0.037$ cm⁻¹. As seen from Fig. 3, the agreement between the calculated values and the experimental points do not represent the data well. Consequently, we deduce that the contribution of four-phonon processes to the frequency shift $\Delta_2(T)$ is important for the interlayer E_{2g}^2 mode.

Eqs. (1)–(3) have been also used to fit the temperature dependencies of intralayer mode frequencies by suitably choosing the parameters ν_0 and A with fixed parameter $B = 0$, i.e. taking into account only three-phonon processes. For all intralayer modes the agreement between the theoretical and experimental dependencies was found to be good. Fig. 4 shows this agreement for one representative (E_{1g}^2) of the intralayer modes. The resulting parameters for all the

intralayer modes are shown in Table 1. These results indicate that the pure-temperature dependence of the frequencies $\Delta_2(T)$ is dominated by the three-phonon processes. The four-phonon coupling processes (quartic interaction) are not effective for the intralayer modes.

The fact that for the intralayer modes to describe the experimental results it is sufficient to include only three-phonon processes, whereas for the interlayer mode four-phonon processes have also to be included, may be associated with difference in sets of atomic displacements for these modes. Indeed, as seen from Fig. 1, in the intralayer E_{1g}^1 , E_{1g}^2 , E_{2g}^1 , A_{1g}^1 and A_{1g}^2 modes the restoring forces are due to the strong intralayer gallium–gallium ($C_{Ga-Ga}^s = 15.3$, $C_{Ga-Ga}^c = 110$ N/m [2]) and/or gallium–sulfur ($C_{Ga-S}^s = 111$, $C_{Ga-S}^c = 130$ N/m), and weak interlayer sulfur–sulfur ($C_{S-S}^s = 1.5$, $C_{S-S}^c = 9.5$ N/m) bonds, whereas in the interlayer E_{2g}^2 mode only the weak interlayer sulfur–sulfur bonds are involved in restoring forces. Here C^c and C^s are the compressional and shear force constants, respectively, associated to the relative displacements of the atom planes.

The linewidth of the GaS phonons was studied systematically as a function of temperature in the range of 15–293 K. The measured linewidths of the interlayer mode E_{2g}^2 (0.43 cm⁻¹) and the low-frequency intralayer mode E_{1g}^1 (0.47 cm⁻¹) at low temperatures became comparable to that of the instrument. Therefore we have not analyzed the temperature dependence of the linewidth of these two modes. The corrected linewidth of the intralayer Raman modes at room temperature were found to be 2.2 (E_{1g}^1), 2.1 (E_{2g}^1), 1.1 (A_{1g}^1), and 2.9 (A_{1g}^2) cm⁻¹. The linewidth of all the optical modes are found to increase with temperature. The temperature dependence of the E_{1g}^2 mode linewidth (solid circles) is shown in Fig. 4. The broadening of the phonon lines is due to anharmonicity of the lattice vibrations. The presence of anharmonic forces in a crystal lead to interactions between the harmonic normal modes of the crystal and these interactions produce a temperature dependent lifetime of the normal modes.

The temperature dependence of the phonon linewidth can be described as follows [10,14]:

$$\Gamma = C \left[1 + \frac{2}{e^x - 1} \right] + D \left[1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right], \quad (4)$$

where C is the broadening of the phonon line due to the cubic anharmonicity at absolute zero (the decrease in phonon lifetime τ due to the decay of the optical phonon into two identical phonons) and D is the broadening of the phonon line due to fourth-order anharmonicity at absolute zero (the decrease of τ due to the decay of an optical phonon into three identical phonons).

The temperature dependencies of the intralayer mode linewidths were fitted using Eq. (4). For all modes a good agreement between the theoretical and experimental data was observed. As a representative example, the solid curve of Fig. 4 shows a least-squares fit of Eq. (4) for one (E_{1g}^2) of the intralayer modes. There was no difference

between the fits with and without the second term of Eq. (4), and hence the value of D for all the modes is taken to be zero. The values of C for all the modes that were used are given in Table 1. Therefore, based on this very simple model, it appears that the cubic anharmonicity accounts well for the temperature dependence of the linewidth of the optical phonons studied, and there is no necessity to take into account the four-phonon coupling.

4. Conclusions

The analysis of the temperature dependence of the optical modes in GaS crystals shows that the Raman frequency shift and broadening of linewidths are 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 softening and broadening of the phonon lines were determined. We have shown that the term corresponding to quartic processes should be included in the frequency shift expression $\Delta_2(T)$ only for the interlayer E_{2g}^2 mode, having a very low value of frequency (22.8 cm⁻¹) and anomalously high value of mode Grüneisen parameter (22.7).

Note of the Editors: We would like to bring to the attention of the readers the recent paper by A. Debernardi, *Solid State Communications*, Vol. 113 (1) (1999), and references therein.

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