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Temperature induced phonon behaviour in germanium selenide thin films probed by Raman spectroscopy

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Abstract

Here we report a detailed study of temperature-dependent phonon properties of exfoliated germanium selenide thin films (several tens of nanometers thick) probed by Raman spectroscopy in the 70–350 K temperature range. The temperature-dependent behavior of the positions and widths of the Raman modes was nonlinear. We concluded that the observed effects arise from anharmonic phonon–phonon interactions and are explained by the phenomenon of optical phonon decay into acoustic phonons. At temperatures above 200 K, the position of the Raman modes tended to be linearly dependent, and the first order temperature coefficients χ were -0.0277 , -0.0197 and $-0.031 \text{ cm}^{-1} \text{ K}^{-1}$ for B_{3g} , $A_{g(1)}$ and $A_{g(2)}$ modes, respectively.

Keywords: Raman spectroscopy, germanium selenide, phonon properties, temperature

(Some figures may appear in colour only in the online journal)

1. Introduction

2D layered crystals are at the frontier of research on novel materials and their applications in electronic and optoelectronics devices [1]. Most studies in this area concern transition metal dichalcogenides such as molybdenum or tungsten disulfide and diselenide, which present unique electronic and optical properties [2]. However, another group of layered semiconductors based on IV–VI compounds have recently attracted the attention of researchers. Germanium selenide, the member of this group, crystallized in layered orthorhombic structure (figure 1(a)), present a narrow-band-gap in the range of 0.5–1.5 eV [3]. GeSe as other IV–VI materials is good candidate for photovoltaic [4] and photodetection devices as well as resistive switching memory devices [5]. The near infra-red photodetectors based on GeSe nanosheets was demonstrated [6] with parameters comparable to devices based on other 2D materials. Additionally, unlike conventional narrow-band-gap semiconductors such as lead, cadmium or

mercury compounds, GeSe and other IV–VI materials consist of earth abundant, less toxic elements such as Ge, Se, Sn, and S. Germanium selenide can also be used in thermoelectric devices, where high Seebeck coefficients (S) and electric conductivity (σ) and low thermal conductivity (κ) are simultaneously required. Theoretical studies predicts that GeSe is a high efficient thermoelectric material [7], with thermal properties similar to other IV–VI materials such as SnSe for which a very large power factor ($ZT = 2.62$) and low thermal conductivity ($0.4\text{--}0.7 \text{ W m}^{-1} \text{ K}^{-1}$ at $T = 300 \text{ K}$) was recently found [8]. These facts makes investigation of the thermal and phonon properties of germanium selenide particularly important.

As a result of growing interest in layered 2D semiconductors, Raman spectroscopy was used to investigate optical, electrical and thermal properties [9–13] of these materials. There are reports about room temperature [14] and temperature dependent [15] Raman scattering in bulk germanium selenide single crystals. However, in those early works, no detailed analysis of temperature dependence of Raman modes of GeSe thin films was performed.

Here we present a detailed analysis of the effect of temperature on the phonon properties of exfoliated germanium selenide thin films. In addition to other works, we report the

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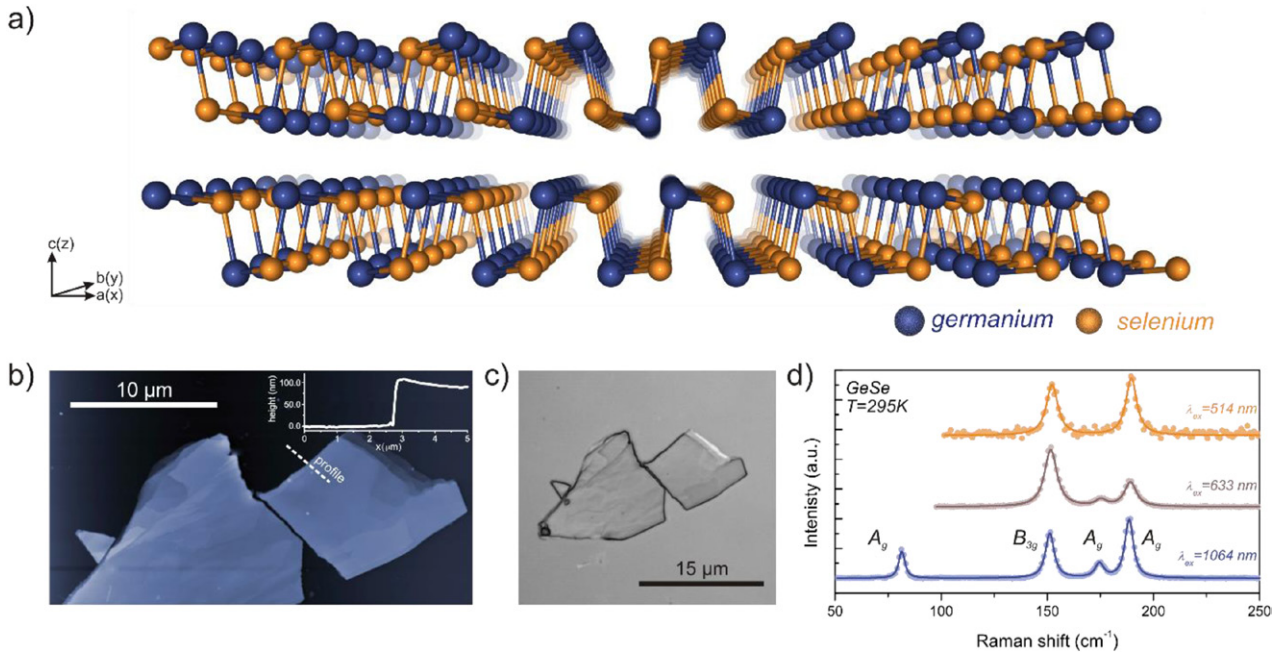


Figure 1. (a) Crystal structure of germanium diselenide, (b) AFM image of an investigated GeSe flake (the inset shows height profile of the flake), (c) confocal optical microscopy image of the same flake, and (d) room temperature Raman spectra of GeSe taken with $\lambda_{\text{ex}} = 514$, 633 and 1064 nm.

temperature dependence of not only Raman mode positions but also their widths. At low temperatures, we found a non-linear temperature dependence of the positions and widths of all visible Raman modes. The observed nonlinear behavior results from anharmonic phonon–phonon interactions and was explained by the phenomenon of optical phonon decay into two or three acoustic phonons. At higher temperatures, the positions of Raman modes tend to exhibit linear dependence, and first order coefficients (χ) were extracted. The obtained results are useful for investigations of phonon-related thermal properties of germanium selenide and other IV–VI layered materials.

2. Experiment

Germanium selenide thin flakes were fabricated using a conventional mechanical exfoliation technique from bulk single crystals (2D semiconductors) on an SiO_2 (285 nm)/Si substrate [16]. Optical confocal microscopy (monochromatic light, $\lambda = 405$ nm) and atomic force microscopy (AFM) images are depicted in figures 1(b) and (c). The thicknesses of investigated thin films were obtained from AFM measurements in semi-contact mode and were about several tens of nanometers. Raman measurements were performed with a Renishaw inVia Raman Microscope in the backscattering geometry using a krypton 633 nm (1.96 eV) laser line and a $50\times$ objective. In addition, room temperature Raman spectra of GeSe were collected using a 514 nm (2.41 eV) Ar laser line and a 1064 nm (1.16 eV) Nd:YAG laser. The determination of mode positions and widths had a resolution of approximately 0.5 cm^{-1} . The laser power, calibrated on the sample, was kept low (0.2 mW) to avoid unintentional additional heating of the sample. Temperature-dependent measurements were carried out in

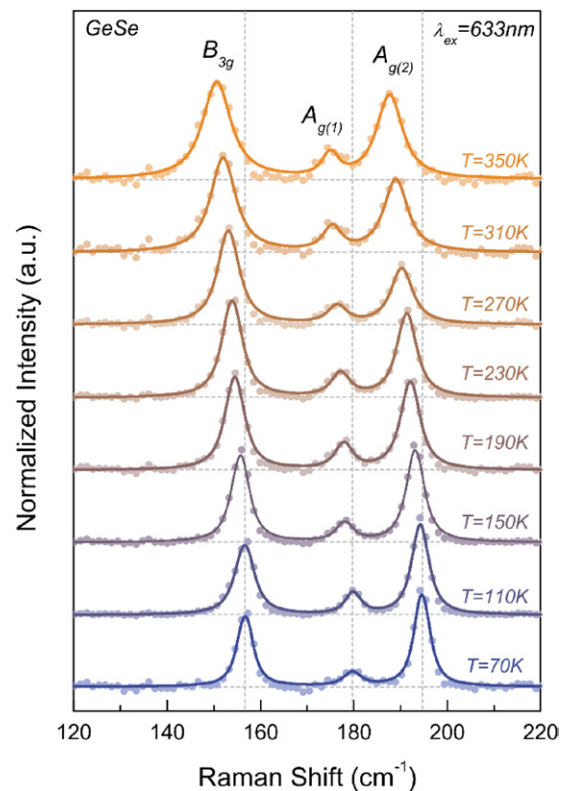


Figure 2. Selected Raman spectra of GeSe thin flakes measured at temperatures ranging between 70 K and 350 K ($\lambda_{\text{ex}} = 633$ nm).

an optical cryostat with temperatures in the 70–350 K range with 20 K steps. The measurements for each temperature were performed several times to minimize any statistical variation. Obtained Raman spectra were fitted using the Levenberg–Marquardt algorithm with a Lorentzian shape function.

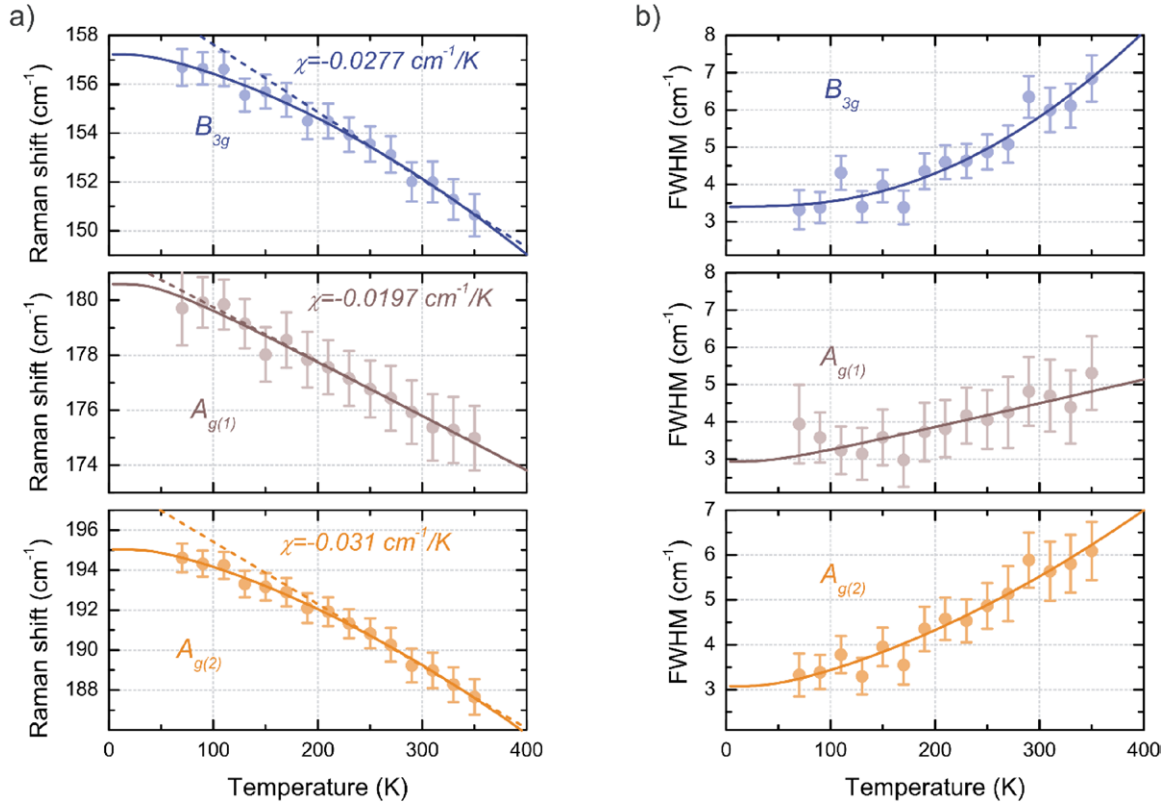


Figure 3. Temperature dependence of (a) positions and (b) FWHMs of GeSe B_{3g} , $A_{g(1)}$, and $A_{g(2)}$ Raman modes.

3. Results and discussion

Germanium selenide is a IV–VI layered semiconductor, and like its isomorphs GeS, SnS, and SnSe, it crystallizes at room temperature into stable, orthorhombic structures ($Pnma$). The unit cell of GeSe consists of eight atoms with unit cell parameters as follows: $a = 4.38 \text{ \AA}$, $b = 3.82 \text{ \AA}$, $c = 10.79 \text{ \AA}$ [14] (figure 1(a)). Germanium selenide belongs to the $Pnma$ space group (D_2^{16} point group), and group theory predicts 21 optical modes. Among them, 12 are Raman active ($4A_g + 2B_{1g} + 4B_{2g} + 2B_{3g}$), 7 are IR active ($3B_{1u} + 1B_{2u} + 3B_{3u}$) and 2 are inactive ($2A_u$) [14, 15]. Figure 1(d) shows Raman spectra of GeSe flake (100 nm thick, figures 1(b) and (c)) taken with different excitation wavelengths, $\lambda_{\text{ex}} = 514$, 633 and 1064 nm, and with circular polarization. Four, three, and two Raman modes were observed for $\lambda_{\text{ex}} = 1064$ nm, $\lambda_{\text{ex}} = 633$ nm and $\lambda_{\text{ex}} = 514$ nm, respectively. The two Raman peaks located at 152 cm^{-1} and 189 cm^{-1} were observed with all wavelengths. An additional peak shows up at 176 cm^{-1} in spectra with $\lambda_{\text{ex}} = 633$ and 1064 nm. In the spectrum obtained with wavelength $\lambda_{\text{ex}} = 1064$ nm, besides the modes mentioned above, a peak at $\sim 81 \text{ cm}^{-1}$ was observed. We have assigned the observed modes to the following symmetries: A_g (~ 81 , 176 and 189 cm^{-1}) and B_{3g} ($\sim 152 \text{ cm}^{-1}$) [15]. For convenience, A_g modes are labelled as $A_{g(1)}$ (176 cm^{-1}) and $A_{g(2)}$ (189 cm^{-1}).

Figure 2 shows the evolution of selected Raman spectra over the temperature range of 70–350 K. All observed GeSe Raman modes downshifted and broadened with increasing temperature. Moreover, the nonlinear temperature dependence of mode position can also be seen. The temperature dependent

Raman studies were also performed on few different flakes with different thickness (ranging from 50 to 200 nm) and similar non-linear temperature dependence of Raman spectra was observed. The detailed calculated Raman mode positions and FWHMs (Full Width at Half Maximum) are depicted in figure 3.

The origin of the temperature dependence of the Raman spectra could arise from anharmonic phonon–phonon interactions as well as thermal expansion [17, 18]. However, the thermal expansion coefficient α , which describes the volume change upon temperature change, determined experimentally and by *ab initio* calculations, is low in GeSe ($\alpha \approx 5 \times 10^{-5} \text{ K}^{-1}$) [19]. Thus, we attributed the observed changes in the Raman spectra to anharmonic effects.

To describe the temperature dependence of Raman mode position, we applied the approach developed by Balkanski *et al* [20] based on the extended Klemens–Hart–Aggarwal–Lax model [21, 22]. In this model, the temperature dependence of Raman mode position results from the cubic and quartic anharmonicity of lattice potential, which leads to optical phonon decay into two (three phonon process) or three (four phonon process) acoustic phonons. Balkanski *et al* proposed the following formula to describe temperature dependence of Raman mode position [19]:

$$\omega(T) = \omega_0 + A \left[1 + \frac{2}{e^x - 1} \right] + B \left[1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right] \quad (1)$$

where $x = \hbar\omega_0/2k_B T$, $y = \hbar\omega_0/3k_B T$, $\hbar\omega_0$ is the energy of optical phonon extrapolated to $T = 0 \text{ K}$, \hbar is the Planck

Table 1. Calculated parameters from fit of equations (1)–(3) to temperature dependence of the positions and widths of GeSe Raman modes.

| GeSe mode | ω_0 (cm ⁻¹) | A (cm ⁻¹) | B (cm ⁻¹) | Γ_0 (cm ⁻¹) | C (cm ⁻¹) | D (cm ⁻¹) | χ (cm ⁻¹ K ⁻¹) ^a |
|------------|--------------------------------|-------------------------|-------------------------|--------------------------------|-------------------------|-------------------------|---|
| B_{3g} | 157.8 | -0.53 | -0.06 | 3.57 | -0.24 | 0.07 | -0.0277 |
| $A_{g(1)}$ | 181.9 | -1.31 | — | 2.51 | 0.42 | — | -0.0197 |
| $A_{g(2)}$ | 196.03 | -0.9 | -0.09 | 2.67 | 0.36 | 0.04 | -0.031 |

^a Calculated for 230–350 K temperature range.

constant divided by 2π , k_B is the Boltzmann constant, and A and B are anharmonic constants. This approach was also used to describe the temperature dependence of Raman mode position of various 2D and layered materials including molybdenum disulfide monolayers [23], rhenium and tin diselenides [24], tungsten ditelluride [25]. The fit of equation (1) to experimental data is shown in figure 3(a). The theoretical curve fits very well to experimental data, thus confirming that phonon decay is the main factor responsible for temperature dependence of GeSe Raman spectra. The main decay channel for the $A_{g(1)}$ mode involved three phonons, whereas for $A_{g(2)}$ and B_{3g} modes, the contribution of a four phonon process was apparent. The fit parameters are presented in table 1. As the probability of the four phonon process is much lower than the three phonon process, the A constant is greater than the B anharmonic constant, and the B/A ratio is small.

Equation (1) tends to linear dependence at high temperatures, and temperature dependence of mode position can be described by following equation:

$$\omega(T) = \omega_0 + \chi T \quad (2)$$

where χ is the first order temperature coefficient. By using equation (2) to fit the experimental data from 230 K to 350 K, we obtained the following values of χ : -0.0277, -0.0197 and -0.031 cm⁻¹ K⁻¹ for B_{3g} , $A_{g(1)}$ and $A_{g(2)}$ GeSe Raman modes, respectively.

The FWHM associated with the phonon lifetime of Raman modes increased with increasing temperature (figure 3(b)) and, similar to the peak position, also revealed a nonlinear temperature dependence that is described according to following equation:

$$\Gamma(T) = \Gamma_0 + C \left[1 + \frac{2}{e^x - 1} \right] + D \left[1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right] \quad (3)$$

where Γ_0 is the peak broadening due to lattice disorder [26], ω_0 is previously determined from the temperature dependence of Raman shift phonon frequency at $T = 0$ K and C and D are anharmonic constants. The FWHM theoretical curve also matched very well to the experimental data. Moreover, the phonon decay processes responsible for the nonlinear behavior of mode width are consistent with the analysis carried out for mode position. The $A_{g(1)}$ mode width broadened with increasing temperature and resulted from optical phonon decay into two acoustic phonons, whereas for B_{3g} and $A_{g(2)}$ modes, the main optical decay channel involved two and three acoustic phonons. This further confirms that anharmonic phonon–phonon interactions were responsible for the temperature dependence of GeSe Raman spectra.

4. Conclusion

In conclusion, we have performed temperature-dependent Raman studies of exfoliated germanium selenide thin films and determined their phonon properties in the temperature range of 70–350 K. The nonlinearity of temperature dependence of both Raman mode position and width was explained by the phenomenon of optical phonon decay into two or three acoustic phonons. The first order temperature coefficients were extracted and are $\chi = -0.0277, -0.0197$ and -0.031 cm⁻¹ K⁻¹ for B_{3g} , $A_{g(1)}$ and $A_{g(2)}$ modes, respectively. The results obtained in this work bring better understanding of phonon properties of germanium selenide thin films and could be further used to study thermal properties like thermal conductivity or thermal boundary resistance on foreign substrates with, for example, the use of Raman spectroscopy-based optothermal methods [10, 27, 28].

Acknowledgments

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