

## Temperature and pressure dependence of phonon frequencies in GeS<sub>2</sub>, GeSe<sub>2</sub>, and SnGeS<sub>3</sub>

Z. M. Jakšić\*

Institute of Physics, P.O. Box 68, 11001 Belgrade, Yugoslavia

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The Raman spectra of  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub>, and SnGeS<sub>3</sub> crystals have been investigated as a function of temperature (18 to 300 K) at ambient pressure, and as a function of hydrostatic pressure, up to 4.9 GPa, at room temperature. Our aim was to separate the phonon–excitation–driven (“explicit”) and the thermal–expansion–driven (“implicit”) contribution to the total observed temperature coefficient ( $d\nu/dT$ ).  $\beta$ -GeS<sub>2</sub> exhibits a regular behavior: when its “external” modes are excited the coefficient is dominated by the implicit effect, while in the case of excited “internal” modes by the explicit effect. In the cases of  $\beta$ -GeSe<sub>2</sub> and SnGeS<sub>3</sub> a clear separation into external and internal modes was not possible, as in the case of  $\beta$ -GeS<sub>2</sub>. For  $\beta$ -GeSe<sub>2</sub> the explicit–implicit contributions to ( $d\nu/dT$ ) were determined for five “internal” modes. For most of the modes in SnGeS<sub>3</sub> “explicit” and “implicit” contributions to ( $d\nu/dT$ ) are of comparable magnitude.

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### 1 Introduction

In this paper, we report results of an extensive experimental investigation of the effect of pressure, and temperature, on Raman-active phonons in three inorganic molecular crystals:  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub>, and SnGeS<sub>3</sub>. The germanium disulfide and diselenide appear in three crystalline modifications [1–5], and in a disordered form, while SnGeS<sub>3</sub> appears in one crystalline modification only [6]. The crystal structures of  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub>, and SnGeS<sub>3</sub> are monoclinic (space group P2<sub>1</sub>/c). The basic building blocks of the crystal structure of  $\beta$ -GeS<sub>2</sub> (Se<sub>2</sub>), and SnGeS<sub>3</sub> are GeX<sub>4</sub> tetrahedra (X=S, Se), i.e. GeX<sub>4</sub> chains. Schematic illustrations of  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub>, and SnGeS<sub>3</sub> crystal structures represented by coordination tetrahedra are shown in Refs. [7, 8]. In the case of  $\beta$ -GeS<sub>2</sub> (Se<sub>2</sub>), the GeX<sub>4</sub> tetrahedra (X=S, Se) are mutually connected via corners forming (GeX<sub>4</sub>)<sub>∞</sub> chains along the *a*-axis, and via common edges connecting the chains along the *b*-axis and thus forming a layer. The unit cell of  $\beta$ -GeX<sub>2</sub> contains two such layers with eight molecular units each, within the identity period along the *c*-axis. In the case of SnGeS<sub>3</sub>, the GeS<sub>4</sub> tetrahedra are connected via corners, which form (GeS<sub>2</sub>S<sub>2/2</sub>)<sub>∞</sub> chains along the *c*-axis. The chains are mutually connected via Sn atoms. The unit cell of SnGeS<sub>3</sub> consists of two such chains with two corner-connected GeS<sub>4</sub> tetrahedra and four Sn atoms. The Sn atoms are surrounded by five S atoms, forming a deformed SnS<sub>5</sub> quadratic pyramid. The two layers comprising the SnGeS<sub>3</sub> unit cell are parallel to the *bc*-plane and normal to the *a*-axis of the crystal.

In general, molecular crystals have complex structure (several molecules per unit cell) and low symmetry. The central feature of molecular crystals is the coexistence of strong and weak bonding forces. In a molecular crystal the intramolecular bonding is strong, while the intermolecular bonding is weak. Rich

\* e-mail: jaksic@phy.bg.ac.yu, Tel: +381-11-611-466, Fax: +381-11-108-198

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first-order Raman spectra (72 modes in  $\beta$ -GeX<sub>2</sub> (X=S, Se), and 30 in SnGeS<sub>3</sub>) are a consequence of the existence of a hierarchy of force constants. In the Raman spectra of a typical molecular crystal, “internal” modes, which represent intramolecular vibrations, are often well separated from low frequency “external” modes arising from intermolecular vibrations. The pressure sensitivities of the intermolecular (external) and intramolecular (internal) modes differ. The frequencies of the external modes rapidly increase with pressure, while the pressure influence on the internal mode frequencies is much weaker. Thus pressure differentiates the strength of the bonds in a crystal [9, 10].

Layer crystals comprise a class of molecular crystals in which the molecular unit (individual layer) is macroscopically extended in two dimensions. In the layer crystals with more than one layer in the crystal unit cell, there are, so-called, rigid-layer modes (RL) [11]. These modes are “external” and appear at very low frequencies. The frequencies of the RL modes provide direct information about the strength of the interlayer forces in these crystals, since for such rigid-layer motions the restoring forces are provided entirely by layer–layer interactions. The layer crystal with two layers per unit cell has three RL modes in its Raman spectra.

The optical and vibrational properties of  $\beta$ -GeS<sub>2</sub> [12–14],  $\beta$ -GeSe<sub>2</sub> [15, 16], and SnGeS<sub>3</sub> [17] have been studied at room temperature and ambient pressure. These Raman and infrared studies have shown that the intralayer–interlayer bond-strength ratio in  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub>, and SnGeS<sub>3</sub> is about 120, 100, and 50 respectively. In Ref. [7, 8] the vibrational properties of  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub>, and SnGeS<sub>3</sub> were considered based on the vibrational properties of GeX<sub>4</sub> (X=S, Se) tetrahedra. The pressure influence on the optical properties of GeS<sub>2</sub> glasses and crystals was studied in Ref. [18]. More recently the pressure influence on the Raman scattering spectra of  $\beta$ -GeS<sub>2</sub> [19],  $\beta$ -GeSe<sub>2</sub> [20], and SnGeS<sub>3</sub> [21] has been studied. By measuring the Raman scattering spectra of  $\beta$ -GeS<sub>2</sub> for the pressure up to 15 GPa the RL modes were identified [19]. At the pressure of about 9 GPa a structural phase transition ( $\beta$ -GeS<sub>2</sub>  $\rightarrow$   $\gamma$ -GeS<sub>2</sub>) was observed. The pressure increase above 9 GPa produces a transformation into a fully disordered structure. The structural stability of  $\beta$ -GeSe<sub>2</sub> under pressure has been investigated at ambient pressure up to nearly 8 GPa [20]. This high-pressure Raman study has established that the layered structure of  $\beta$ -GeSe<sub>2</sub> undergoes transformations: first into a fully disordered structure, and then into a  $\alpha$ -GeSe<sub>2</sub> modification; further increase of the pressure leads to amorphisation. These phase transformations are reversible. The vibrational properties of SnGeS<sub>3</sub> have been studied by measuring the Raman scattering spectra under pressures below 19.5 GPa [21]. It was noted that the change in the intensity of high frequency modes was caused by inter-chain interaction changes caused by the pressure. However, a new crystalline modification was not identified.

The temperature dependence of Raman peaks has been seen to be more complicated in comparison to the dependence on pressure. Pressure alters only the equilibrium interatomic spacings inducing shifts of the phonon frequencies, but the influence of temperature on the phonon frequencies is manifold. The total observed frequency shift under temperature consists of two distinct contributions. The first so-called “explicit” contribution, which reflects the change of the vibrational amplitudes of atoms about their equilibrium positions, and the second part, known as the “implicit” contribution, reflects the change in the equilibrium interatomic spacings because of the thermal expansion. The explicit–implicit ratio in  $(d\nu/dT)$  is of great interest, since it is needed for the understanding of the effect of temperature on the phonon spectrum. An independent measurement of both, pressure and temperature dependence permits a separation of the “explicit” and “implicit” contributions in the total observed temperature coefficient. The temperature dependence of the phonon frequencies in molecular crystals has been analyzed [22] with an aim to evaluate the volume-driven contribution (“implicit”) to  $(d\nu/dT)$  against the “explicit” contribution arising from the effect of temperature on the vibrational amplitudes, when the volume of a crystal is held constant. The influence of temperature on the Raman spectra of  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub>, and SnGeS<sub>3</sub> has not been investigated yet.

In this paper, we report pressure and temperature effects on the Raman-active phonons in three molecular crystals:  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub>, and SnGeS<sub>3</sub>. The motivation was to separate the “explicit” and “implicit” contributions to  $(d\nu/dT)$ . The data for  $(d\nu/dT)$  have been analyzed using the standard procedure as

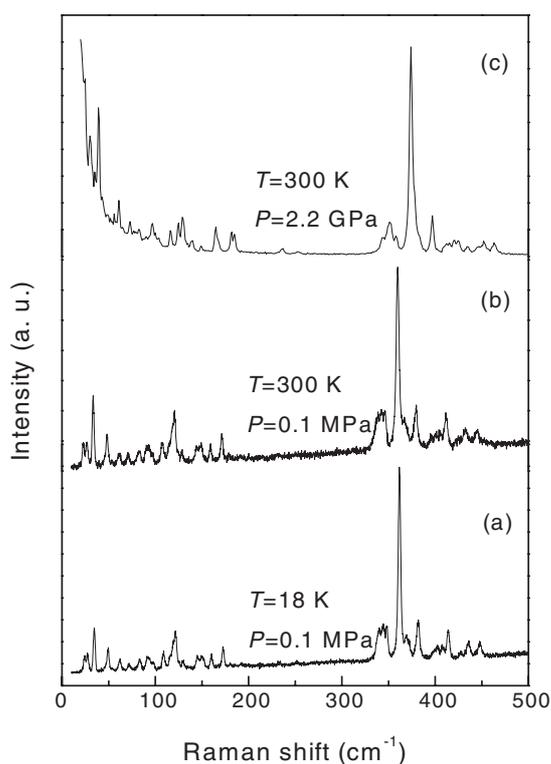
in [10, 22]. The explicit–implicit ratio in  $(d\nu/dT)$  has been analyzed by a comparison between the Raman scattering spectra at low temperatures with the same spectra at high pressures. The analysis of our data reveals that the layer structure is dominant in  $\beta$ -GeS<sub>2</sub>, less in  $\beta$ -GeSe<sub>2</sub>, and least in SnGeS<sub>3</sub>.

## 2 Experimental details

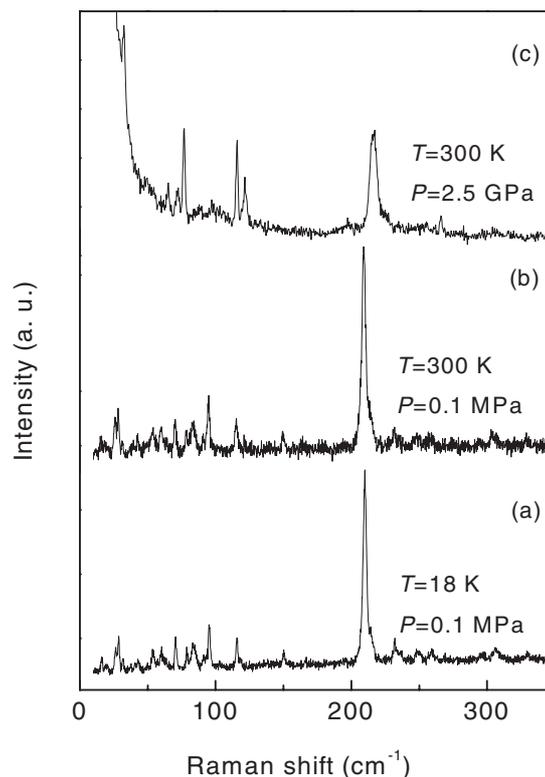
Single crystals of  $\beta$ -GeS<sub>2</sub> and  $\beta$ -GeSe<sub>2</sub> were grown using the standard Bridgman technique [12] while SnGeS<sub>3</sub> was obtained by the sublimation method [23]. All Raman scattering spectra were measured in a backscattering geometry using a 514.5 nm Ar laser line for excitation. The laser line was unpolarised and of different power (10 mW for  $\beta$ -GeS<sub>2</sub> and  $\beta$ -GeSe<sub>2</sub>, and 50 mW for SnGeS<sub>3</sub>). The Raman scattering radiation was spectrally analyzed by a monochromator (U 1000). A photo multiplier (RCA 31034-A) was used for detection. For hydrostatic pressure measurements we used the diamond anvil cell (NBS) design [24], with a methanol–ethanol mixture as a pressure transmitting medium. The pressures were determined using the ruby luminescence. Low temperatures (up to 10 K) were achieved by a helium optical cryostat.

## 3 Results and discussion

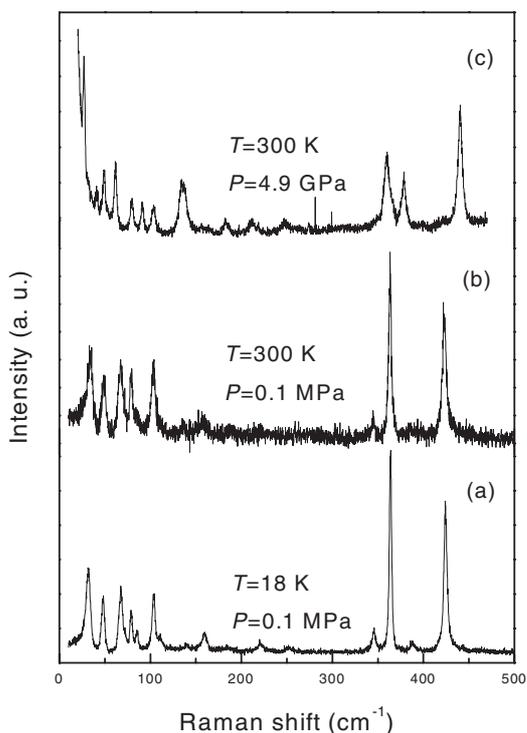
In Figs. 1–3, the room-temperature Raman spectra of  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub>, and SnGeS<sub>3</sub>, at two pressures together with those at 18 K and zero pressure are shown. The spectra marked with (a) were measured at



**Fig. 1** Nonpolarised Raman spectrum of crystalline GeS<sub>2</sub> at (a)  $P = 0.1$  MPa and  $T = 18$  K, (b)  $P = 0.1$  MPa and  $T = 300$  K and (c)  $P = 2.2$  GPa and  $T = 300$  K.



**Fig. 2** Nonpolarised Raman spectrum of crystalline GeSe<sub>2</sub> at (a)  $P = 0.1$  MPa and  $T = 18$  K, (b)  $P = 0.1$  MPa and  $T = 300$  K and (c)  $P = 2.5$  GPa and  $T = 300$  K.



**Fig. 3** Nonpolarised Raman spectrum of crystalline SnGeS<sub>3</sub> at a)  $P = 0.1$  MPa and  $T = 18$  K, b)  $P = 0.1$  MPa and  $T = 300$  K and c)  $P = 4.9$  GPa and  $T = 300$  K.

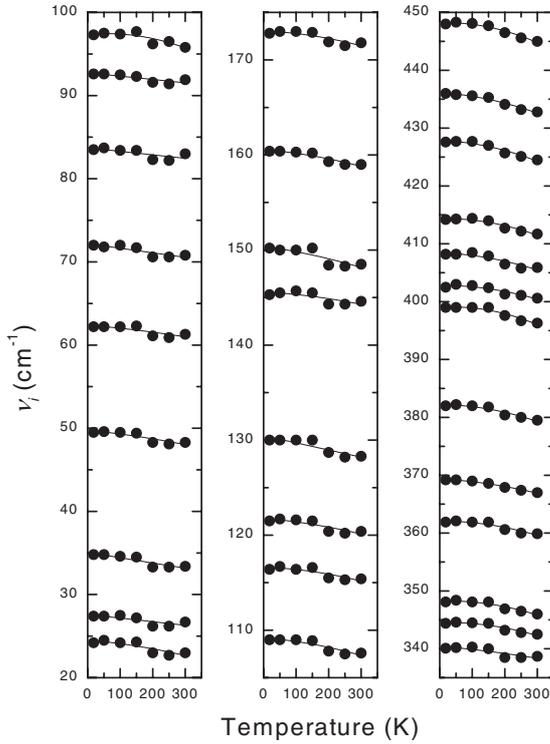
low temperature ( $T = 18$  K) and ambient pressure, the spectra marked with (b) were measured under normal conditions ( $T = 300$  K and  $P = 0.1$  MPa  $\approx 0$  Pa), while the spectra marked with (c) were measured at room temperature ( $T = 300$  K) and high pressure ( $P = 2.2$  GPa for GeS<sub>2</sub>,  $P = 2.5$  GPa for GeSe<sub>2</sub>, and  $P = 4.9$  GPa for SnGeS<sub>3</sub>). As seen from the Figs. 1–3, increasing the pressure causes an increase in all frequencies, while the temperature induced frequency shifts are smaller. Each spectrum is divided, by a well defined frequency-gap, into a low-(bond-bending) and high-(bond-stretching) frequency region. The mode frequencies of  $\beta$ -GeS<sub>2</sub> and SnGeS<sub>3</sub> are grouped into

two spectral regions: below  $200\text{ cm}^{-1}$  and between  $300\text{ cm}^{-1}$  and  $460\text{ cm}^{-1}$ , while the modes of  $\beta$ -GeSe<sub>2</sub> are grouped in a region below  $150\text{ cm}^{-1}$  and between  $200\text{ cm}^{-1}$  and  $350\text{ cm}^{-1}$ .

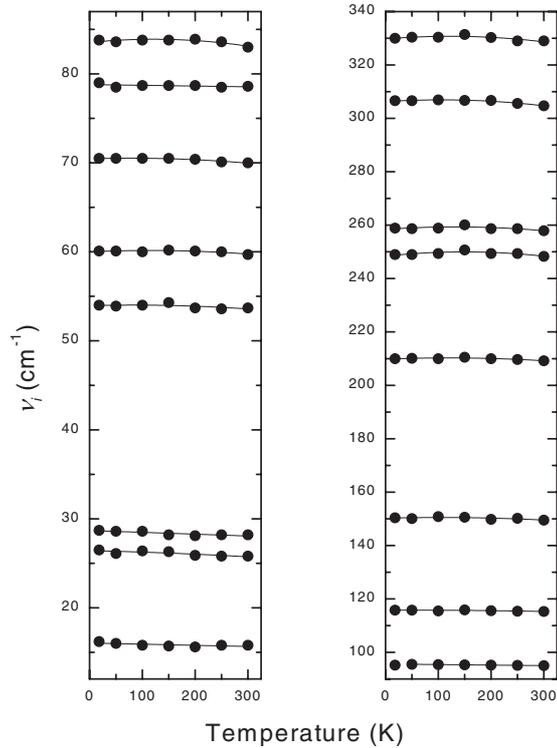
Temperature trajectories  $\nu_i(T)$  of the frequencies for all observed Raman modes in  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub>, and SnGeS<sub>3</sub> are shown in Figs. 4–6. In fact for  $\beta$ -GeS<sub>2</sub> the temperature dependences of the Raman frequencies are well behaved and very regular. All lines blue shift with decreasing temperature. All of the mode frequencies undergo very nearly the same fractional increase, about  $0.01\text{ cm}^{-1}/\text{K}$ , between 300 and 18 K. The temperature influence on the phonon frequencies in  $\beta$ -GeSe<sub>2</sub> and SnGeS<sub>3</sub> is notably weaker than on the modes in  $\beta$ -GeS<sub>2</sub>. For mode frequencies at 32 and 48  $\text{cm}^{-1}$  in SnGeS<sub>3</sub> the curves  $\nu_i(T)$  have positive slope, i.e. a temperature decrease induces a decrease in mode frequencies.

In Figs. 7–9 we present the pressure dependence of the Raman peaks for most of the observed modes in  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub> and SnGeS<sub>3</sub>, respectively. All pressure trajectories  $\nu_i(P)$  have positive slopes. It is evident from the Figs. 7 and 9 that there are large differences in the pressure sensitivity of the peaks in the Raman spectra for both  $\beta$ -GeSe<sub>2</sub> and SnGeS<sub>3</sub>.

In the Raman spectra of  $\beta$ -GeSe<sub>2</sub>, we detect only small number of “internal” modes which are slightly pressure sensitive (Fig. 8). The pressure dependences of the internal mode frequencies are nearly linear in the whole pressure range (0.0–0.8 GPa). The intensity of the “external” modes of  $\beta$ -GeSe<sub>2</sub>, which have a strong pressure sensitivity is low at the atmospheric pressure. These modes disappear from the Raman spectra by an increase in the pressure. Because of this we cannot follow the pressure dependence of these modes. Also, most from the many of the “internal” modes of  $\beta$ -GeSe<sub>2</sub> from the low frequency region appear in the Raman spectra only at zero pressure. Their pressure trajectories  $\nu_i(P)$  we can not follow also. At any pressure above 0.8 GPa many defects develop in the structure of  $\beta$ -GeSe<sub>2</sub>. The drastic structure changes of  $\beta$ -GeSe<sub>2</sub> induced by pressure can be detected from the Raman spectra (Fig. 2c). At the pressure of 2.5 GPa a high frequency mode at  $211\text{ cm}^{-1}$  (zero-pressure value) splits into a doublet, most of the modes disappear into the noise level and new lines appear in the Raman spectrum. Because of this the pressure variation  $\nu_i(P)$  of the Raman-active phonon frequencies of  $\beta$ -GeSe<sub>2</sub> have been followed up to 0.8 GPa.



**Fig. 4** Temperature dependences of Raman-active optical-phonon frequencies in crystalline GeS<sub>2</sub>.



**Fig. 5** Temperature dependences of Raman-active optical-phonon frequencies in crystalline GeSe<sub>2</sub>.

The experimental results for the rates of change of the frequencies with pressure for all three crystals have been given on Figs. 10–12 in the form of the fractional change per an increment of pressure,  $(d \ln \nu_i/dP) = (1/\nu_i)(d\nu_i/dP)$ . The Figs. 10–12 display the pressure-Raman data for the three crystals in a form which has a special significance with respect to the hierarchy of forces coexisting in a molecular solid. Each individual point in Figs. 10–12 corresponds to a Raman-active zone-center phonon which has been followed under pressure, with the horizontal coordinate set by the zero-pressure value of the frequency and the vertical coordinate provided by the initial ( $P=0$ ) logarithmic pressure derivative  $(1/\nu_i)(d\nu_i/dP)$ . The values of  $(d\nu_i/dP)$  at  $P=0$  are obtained from the Figs. 7–9 as the initial slope of  $\nu_i(P)$ . A log–log representation is used both for compactness and for reasons which will be immediately clear.

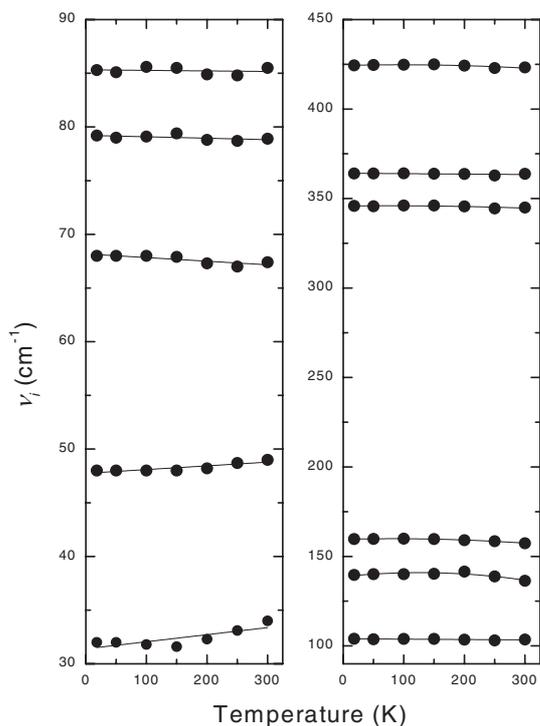
A convenient way of expressing the pressure effect on a given mode frequency is in terms of the mode Grüneisen parameter  $\gamma_i$  for phonon  $i$ ,

$$\gamma_i = -(\partial \ln \nu_i / \partial \ln V) = (1/\beta \nu_i) (\partial \nu_i / \partial P). \quad (1)$$

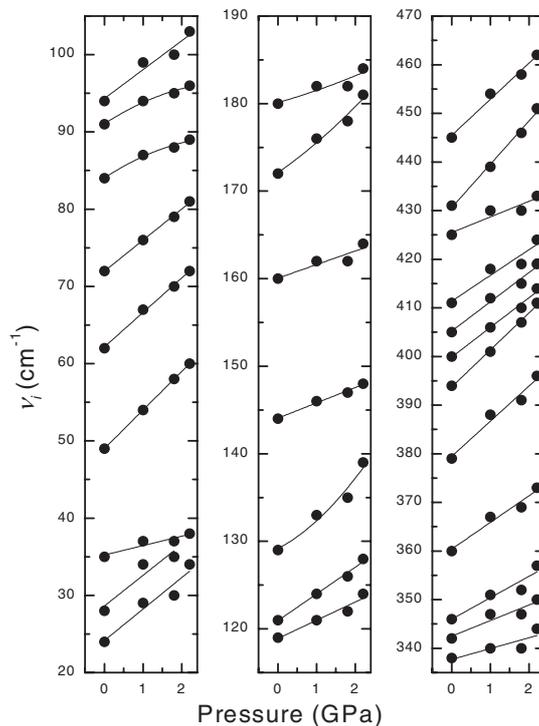
$V$  is the crystal volume,  $P$  the pressure, and  $\beta$  is the isothermal compressibility [9]. The Grüneisen parameter  $\gamma_i$  connects the volume dilation ( $\Delta V/V$ ) with the fractional change in a frequency under pressure  $P$  by

$$(\Delta \nu_i / \nu_i) = -\gamma_i (\Delta V / V) = \gamma_i \beta P. \quad (2)$$

In the Grüneisen approximation, all  $\gamma_i$  are assumed to be equal, i.e.  $\gamma_i = \gamma$  for each  $i$ . Grüneisen's approximation predicts that all mode frequencies uniformly change in Raman spectra when a crystal contracts under pressure. It has been reported [9, 10] that in the Raman scattering measurements under pres-



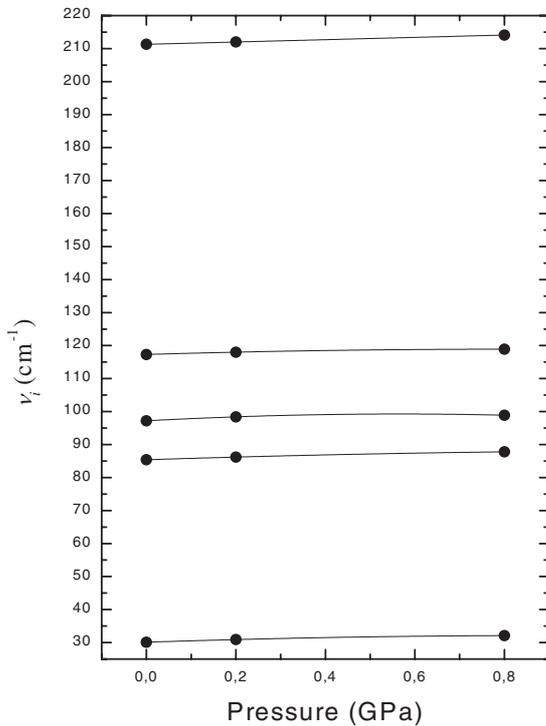
**Fig. 6** Temperature dependences of Raman-active optical-phonon frequencies in crystalline SnGeS<sub>3</sub>.



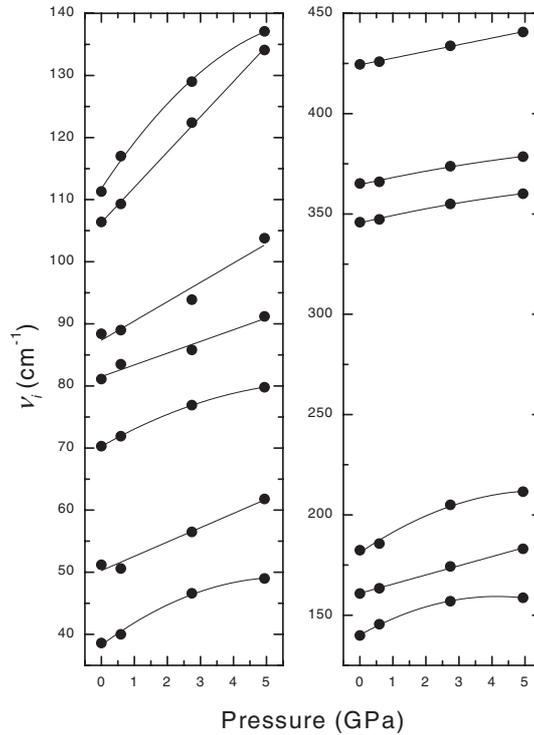
**Fig. 7** Pressure dependences of Raman-active optical-phonon frequencies in crystalline GeS<sub>2</sub>.

sure on three-dimensional crystals (in which exist one-type-bonding forces, covalent or ionic) the Grüneisen approximation is of reasonable validity. In the case of molecular crystals the Grüneisen approximation breaks down; while intermolecular modes are roughly in agreement with it, intramolecular modes are glaringly in disagreement. Experimental results of the influence of pressure on the Raman spectra of molecular crystals reveal that the compression-induced shifts of the phonon frequencies are strikingly inconsistent with the Grüneisen approximation [9, 10]. Far from being frequency independent, the mode-Grüneisen parameter  $\gamma_i$  varies strongly and systematically with the mode frequency  $\nu_i$  over the Raman spectrum. The frequency dependence of  $\gamma_i$  for molecular crystals can be described as  $\gamma_i(\nu_i) = \text{const}$  for “external” modes and  $\gamma_i(\nu_i) \sim \nu_i^{-2}$  for “internal” modes. The Grüneisen approximation works in the case of “external” modes, it breaks down drastically (by two orders of magnitude) for “internal” modes. An elementary vibrational model has been proposed for the prediction of the frequency dependence of the mode-Grüneisen parameter  $\gamma_i$  in molecular crystals [9]. According to this model, the frequency dependence of  $\gamma_i$  can be explained as a consequence of some disparate forces existing in molecular crystals.

Since  $(d \ln \nu_i / dP) = (1/\nu_i) (d\nu_i/dP) \sim \gamma_i$ , Figs. 10–12 show the frequency dependence of the Grüneisen parameters. The mode frequency dependence of  $\gamma_i$  in  $\beta$ -GeS<sub>2</sub> (Fig. 10) exhibits a vibrational scaling behavior consistent with the predictions of the elementary vibrational model for a molecular crystal [9]. The values of  $(1/\nu_i) (d\nu_i/dP) \sim \gamma_i$  are very large and remain constant for a few modes in  $\beta$ -GeS<sub>2</sub> at the lowest frequencies. For the “internal” modes which appear in the lower frequency (bond-bending mode) region, parameter  $\gamma_i(\nu_i)$  rapidly drops with increasing  $\nu_i$  as  $\gamma_i(\nu_i) \sim \nu_i^{-1.96}$ . The high frequency “internal” modes (bond-stretching modes) have low and frequency independent values of  $\gamma_i(\nu_i)$ . In Fig. 10, these modes are represented by a swarm of points. The horizontal line, labeled  $\gamma_i = \text{const}$ , is set at the mean value of  $(d \ln \nu_i / dP)$  in the external-mode regime. Within the confines of this low-frequency region, the Grüneisen approximation works well. As can be seen from Fig. 10 in the “exter-



**Fig. 8** Pressure dependences of Raman-active optical-phonon frequencies in crystalline GeSe<sub>2</sub>.



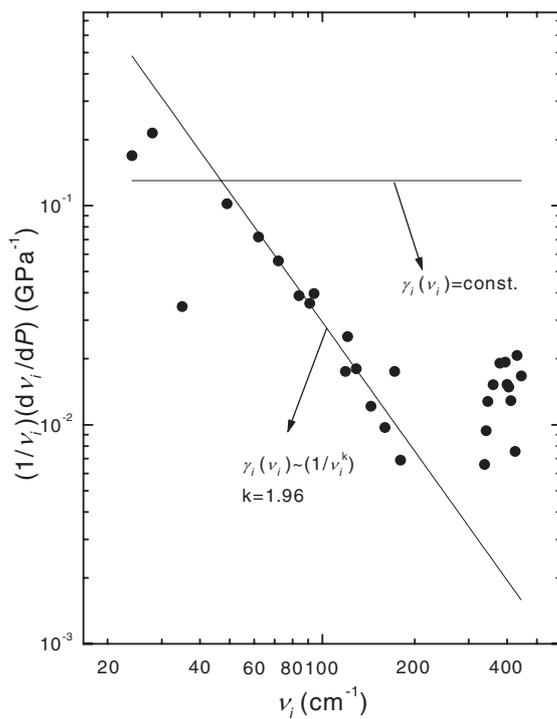
**Fig. 9** Pressure dependences of Raman-active optical-phonon frequencies in crystalline SnGeS<sub>3</sub>.

nal” mode regime there are four modes at 24, 28, 35 and 49 cm<sup>-1</sup>. In an earlier work [19] the modes of β-GeS<sub>2</sub> at 28 and 49 cm<sup>-1</sup> are identified as the RL modes and the mode at 35 cm<sup>-1</sup> as a low lying “internal” mode. Indeed, the values  $\gamma_i$  for the modes at 28 and 49 cm<sup>-1</sup> are near the horizontal line, while the  $\gamma_i$  for the mode at 35 cm<sup>-1</sup> is far away from the line. As discussed earlier [13], there are three RL modes. According to Fig. 10 a candidate for the third RL mode is the mode at 24 cm<sup>-1</sup>.

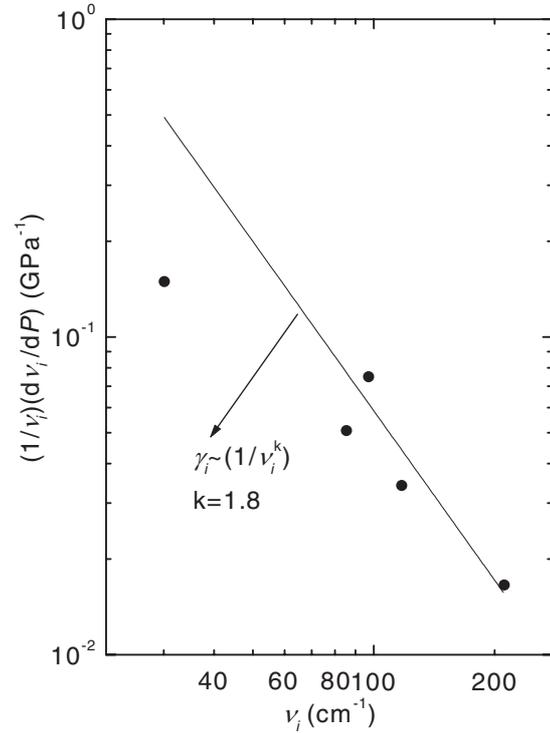
The frequency dependence of  $\gamma_i$  for five observed modes of β-GeSe<sub>2</sub> is shown in Fig. 11. This result is in accordance with the molecular character of this crystal. The “external” modes of β-GeSe<sub>2</sub> are not registered at atmospheric pressure. For the three highest frequency modes  $\gamma_i(\nu_i)$ 's drop with increasing  $\nu_i$  as  $\gamma_i(\nu_i) \sim \nu_i^{-1.8}$ .

In Fig. 12, we present a correlation between the mode-frequencies and the corresponding reduced pressure-slopes of SnGeS<sub>3</sub>. The modes are grouped in accordance with a general scheme proposed by Zallen [9, 10]. The modes with low (high) frequencies and high (low) reduced pressure-slopes, correspond to the “bond-bending + RL” (bond-stretching) group, respectively. Concerning the low-frequency modes, they all show comparable reduced pressure-slopes, with no distinct difference between the RL modes and the bond-bending vibrations, in accordance with the absence of any frequency gap between them. The three highest frequency modes show reduced pressure-slopes, smaller by one order of magnitude, in comparison to low-frequency ones. This fact justifies the assignment of those modes to the internal bond-stretching vibrations. We have estimated the power-low exponent for these modes to -1.7, i.e.  $\gamma_i(\nu_i) \sim \nu_i^{-1.7}$ . Unfortunately, it is not possible to separate “external” from “internal” modes as in β-GeS<sub>2</sub>.

Comparing the results shown in Figs. 10–12 we conclude that the layer molecular character is evident in β-GeS<sub>2</sub>, less in β-GeSe<sub>2</sub> and least in SnGeS<sub>3</sub>. Thus, the frequency dependences of  $\gamma_i$  are evidence of different intralayer–interlayer force constant ratios for these crystals [13, 15, 17]. This ratio is more than 100 in β-GeS<sub>2</sub>, about 100 in β-GeSe<sub>2</sub>, and about 50 in SnGeS<sub>3</sub>.



**Fig. 10** Correlation between the pressure-induced relative change and the mode frequency for crystalline GeS<sub>2</sub>. Estimated experimental error for the relative pressure shift range between 10% for modes below 170 cm<sup>-1</sup> and 20% for Raman modes above 300 cm<sup>-1</sup>.



**Fig. 11** Correlation between the pressure-induced relative change and the mode frequency for crystalline GeSe<sub>2</sub>. Estimated experimental error for the relative pressure shift is about 15% for all observed Raman modes.

The temperature dependence ( $d\nu/dT$ ) in crystals consists of the following two contributions, the first one (1) due to the effect of temperature on the vibrational excursion of atoms about their equilibrium positions (“explicit” term), and the second one (2) due to the volume change via thermal expansion (“implicit” term). These two contributions can be expressed by the following relation [22],

$$(d\nu/dT) \equiv (\partial\nu/\partial T)_p = (\partial\nu/\partial T)_v + (\partial\nu/\partial V)_T (\partial V/\partial T)_p = (\partial\nu/\partial T)_v - (\alpha/\beta) (\partial\nu/\partial P)_T, \quad (3)$$

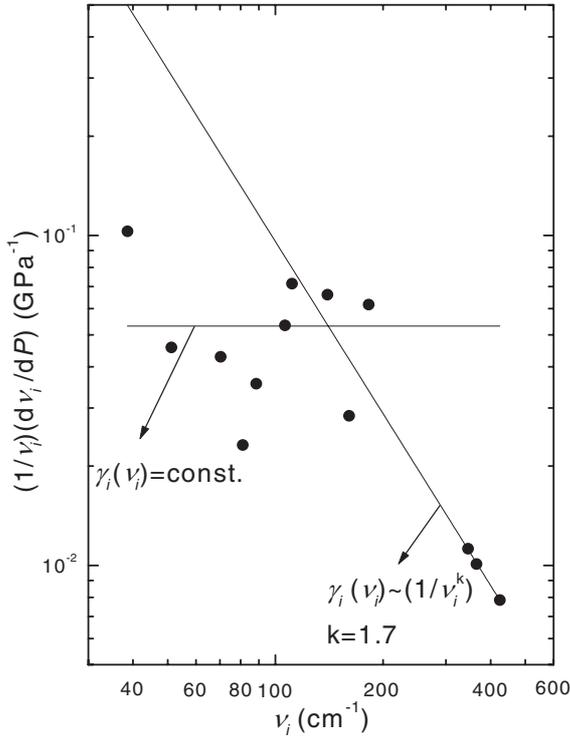
where  $\alpha = (1/V) (\partial V/\partial T)_p$  is the coefficient of volume thermal expansivity, and  $\beta = -(1/V) (\partial V/\partial P)_T$  is the compressibility.

The left side of Eq. (3) is the total observed temperature coefficient. The first term on the right side is the “explicit” contribution at constant volume; it reflects the effect of change in vibrational amplitudes, i.e. phonon occupation numbers, at fixed equilibrium positions. The second term, known as the “implicit” contribution, reflects the effect of change of the frequency which is a consequence of the thermal expansion of the crystal. The explicit–implicit ratio in ( $d\nu/dT$ ) is of great interest, since it is needed for the understanding of the effect of temperature on the phonon spectrum. The fraction of the total temperature coefficient, which can be attributed to the “explicit” contribution ( $(\partial\nu/\partial T)_v$ ) is denoted by  $\theta$  [10] i.e.

$$\theta = (\partial\nu/\partial T)_v (d\nu/dT)^{-1}. \quad (4)$$

The fraction of the total temperature coefficient, which can be attributed to the “implicit” contribution  $-(\alpha/\beta) (\partial\nu/\partial P)_T$ , is denoted by  $\eta$  [22] as

$$\eta = 1 - (\partial\nu/\partial T)_v (d\nu/dT)^{-1} = (dT/dP)_v (\beta/\alpha)^{-1}, \quad (5)$$



**Fig. 12** Correlation between the pressure-induced relative change and the mode frequency for crystalline SnGeS<sub>3</sub>. Estimated experimental error for the relative pressure shift range between 15% for modes below 200 cm<sup>-1</sup> and 20% for Raman modes above 300 cm<sup>-1</sup>.

where

$$(dT/dP)_v = - (d\nu/dP) (d\nu/dT)^{-1}. \quad (6)$$

Then, Eq. (3) becomes

$$1 = \theta + \eta. \quad (7)$$

From the measured values of  $\alpha$  and  $\beta$ ,  $\theta$  or  $\eta$  can be calculated using the Eq. (4) or (5).

An analysis of the explicit/implicit mix in  $(d\nu/dT)$  has already been accomplished for a few molecular crystals [10, 22]. An independent measurement of both, the pressure  $\nu(P)$  and temperature  $\nu(T)$  dependence of phonon frequencies permits a separation of  $(d\nu/dT)$  into the volume-derived and “explicitly” temperature derived terms. This analysis assumes  $(d\nu/dP) > 0$  and  $(d\nu/dT) < 0$ . This is the most typical behavior for mode frequencies in molecular crystals. The quantity  $(dT/dP)_v$ , defined as the negative of the ratio of the observed pressure and temperature coefficient is negative. This quantity has a simple interpretation as the increase in temperature  $dT$  which compensates a pressure increase  $dP$  in the sense of canceling the pressure effect on frequency and keeping it constant. The dimensionless parameter  $\eta$  has any value from 0 to  $+\infty$ . The most interesting values are  $\eta = 1$  and  $\eta = 0$ . For  $\eta = 1$ , when  $(dT/dP)_v = \beta/\alpha$ , the “explicit” contribution in the total observed temperature coefficient,  $(d\nu/dT)$ , is equal to zero, i.e.  $(d\nu/dT)$  is equal to a purely “implicit” contribution. For  $\eta = 0$  the temperature coefficient,  $(d\nu/dT)$ , is equal to a purely “explicit” contribution. For phonon frequencies with  $\eta \neq 0, 1$ , there are both “explicit” and “implicit” contributions. In the case of the phonon frequencies for which  $0 < \eta < 1$ , the “explicit” and “implicit” contributions in  $(d\nu/dT)$  have the same sign, while for the phonon frequencies with  $\eta > 1$  these contributions are of opposite sign. The third case is  $\eta = +\infty$ , when the values of the “explicit” and “implicit” contributions to  $(d\nu/dT)$  are similar in magnitude and of opposite sign. In this case the observed  $(d\nu/dT) = 0$ , i.e. the Raman spectrum is temperature independent.

**Table 1** Relative sensitivity to pressure and temperature, and separation of the explicit phonon contribution and implicit volume-driven contribution to the temperature coefficient, for phonon frequencies in crystalline  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub>, and SnGeS<sub>3</sub>.  $(dT/dP)_v$  is the ratio of the observed coefficients,  $-(dv/dP)/(dv/dT)$ , and  $\eta = 1 - (\partial v/\partial T)_v (dv/dT)^{-1}$  is the implicit and  $\theta = (\partial v/\partial T)_v (dv/dT)^{-1}$  is the explicit fraction of the total temperature dependence.

crystal	$\nu_i$ (cm <sup>-1</sup> )	$(dv_i/dP)_T$ (cm <sup>-1</sup> /GPa)	$-(dv_i/dT)_P$ $\times 10^{-3}$ (cm <sup>-1</sup> /K)	$-(dT/dP)_v$ $\times 10^3$ (K/GPa)	$\eta$	$\theta$
$\beta$ -GeS <sub>2</sub>	24	4.1	8.99	0.45	0.6	0.4
	28	6	4.34	1.38	1.7	-0.7
	35	1.2	6.03	0.20	0.2	0.8
	49	5	7.57	0.66	0.8	0.2
	62	4.5	6.18	0.72	0.9	0.1
	72	4	5.35	0.75	0.9	0.1
	84	3.3	4.20	0.78	0.9	0.1
	91	3.3	4.0	0.80	1	0
	94	3.7	14.20	0.26	0.3	0.7
	121	3	8	0.38	0.4	0.6
	129	2.3	7.5	0.31	0.3	0.7
	144	1.7	6.97	0.25	0.3	0.7
	160	1.5	8.9	0.17	0.2	0.8
	172	3.1	9.1	0.34	0.4	0.6
	338	2.2	9	0.25	0.3	0.7
	342	3.2	16	0.20	0.2	0.8
	346	4.4	17.5	0.25	0.3	0.7
	360	5.5	16.4	0.33	0.4	0.6
	379	7.2	18.9	0.38	0.4	0.6
	394	7.6	23.4	0.32	0.4	0.6
400	6.1	16.2	0.38	0.4	0.6	
405	6	17.7	0.34	0.4	0.6	
411	5.3	20.3	0.26	0.4	0.6	
425	3.2	22	0.14	0.1	0.9	
431	8.9	20.2	0.44	0.5	0.5	
445	7.4	24.7	0.3	0.4	0.6	
$\beta$ -GeSe <sub>2</sub>	30.1	4.5	2.1	2.18	2	-1
	85.4	4.3	8.6	0.5	0.5	0.5
	97.0	7.3	2	3.64	3.6	-2.6
	117.3	4	3.7	1.08	1	0
	211.3	3.5	11.5	0.30	0.3	0.7
SnGeS <sub>3</sub>	67.4	3.0	3.4	0.89	0.9	0.1
	78.9	1.9	1.3	1.41	1.4	-0.4
	85.5	3.1	0.5	5.93	6	-5
	103.7	5.7	2.1	2.75	3	-2
	136.4	9.3	48.3	0.19	0.2	0.8
	157.4	4.6	2.3	2	2	-1
	345	3.9	11.5	0.34	0.3	0.7
	363	3.7	2.4	1.53	1.5	-0.5
	423	3.3	18.2	0.18	0.2	0.8

Thus, parameter  $\eta$  has any value in the range  $0 \leq \eta \leq +\infty$ , and  $\theta$ , all the values from  $-\infty$  to  $+\infty$ . The most complete data on the explicit–implicit ratio in  $(d\nu/dT)$  exist for ionic crystals [25, 26]. For these crystals,  $\eta = 1$  for all phonon frequencies. Relatively few analyses separating the contributions to  $(d\nu/dT)$  have been carried out for covalently-network crystals. An analysis for ZnS indicates that the explicit and implicit effects are of comparable magnitude [27], while studies on the zincblende-structure copper halides yield a similar result but indicate a tendency for the explicit effect to be the larger one [28]. Analyses of the explicit–implicit contribution in  $(d\nu/dT)$  for molecular crystals show that the implicit effect dominates for external mode frequencies, while the explicit effect is dominant for internal mode frequencies [10, 22].

We have obtained the explicit–implicit ratio in  $(d\nu/dT)$  for  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub>, and SnGeS<sub>3</sub>. In Table 1 for all observed phonon frequencies  $\nu_i$  at standard conditions ( $P = 0$ ,  $T = 300$  K) the pressure coefficient  $(d\nu_i/dP)_T$  at  $P = 0$ , the temperature coefficient  $(d\nu_i/dT)_P$  at  $T = 300$  K, the experimental ratio  $-(d\nu/dP)(d\nu/dT)^{-1}$ , abbreviated as  $(dT/dP)_\nu$ , and both implicit  $\eta$  and explicit  $\theta$  fraction of the total temperature dependence are given. The value of  $(d\nu_i/dP)$  at  $P = 0$  and  $(d\nu_i/dT)$  at  $T = 300$  K is obtained as the initial slope of  $\nu_i(P)$  and  $\nu_i(T)$  respectively.

Unfortunately, parameters  $\alpha$  and  $\beta$  and their ratio  $(\beta/\alpha)$ , which are needed for the temperature analysis, are unknown for  $\beta$ -GeSe<sub>2</sub> and SnGeS<sub>3</sub> in the literature, while for  $\beta$ -GeS<sub>2</sub> only parameter  $\beta = 56 \times 10^{-3}$  GPa<sup>-1</sup> is known [18]. The value  $(\beta/\alpha)$  must be estimated. Using the observed behaviour of  $(dT/dP)_\nu$  we roughly estimated the ratio as  $(\beta/\alpha) = 800$  K/GPa for  $\beta$ -GeS<sub>2</sub>, and  $(\beta/\alpha) = 1000$  K/GPa for both  $\beta$ -GeSe<sub>2</sub> and SnGeS<sub>3</sub>, similar to As<sub>4</sub>S<sub>4</sub> [10].

The temperature dependence of the phonon frequencies in  $\beta$ -GeS<sub>2</sub> is quite regular: decreasing of temperature induces increasing of mode frequencies. For the modes at lower frequencies the “implicit” effect dominates in  $(d\nu/dT)$ ; when mode frequencies increase, the “explicit” contribution increases also and becomes dominant for modes at high frequencies. The temperature dependence of mode frequencies has been followed for most of the modes in  $\beta$ -GeSe<sub>2</sub>. As was mentioned previously, the pressure dependence of mode frequencies  $\nu(P)$  has been possible to follow only for five modes. Because of this the temperature analysis has been made only for these five internal modes of  $\beta$ -GeSe<sub>2</sub>. The three “internal” modes of  $\beta$ -GeSe<sub>2</sub> at low frequencies (30.1; 85.4; and 97 cm<sup>-1</sup>) have comparable values of the “explicit” and “implicit” contributions in  $(d\nu/dT)$ . Only for the mode at 85.4 cm<sup>-1</sup> the “explicit” and “implicit” contribution have the same sign, others two have opposite sign. For the mode at 117 cm<sup>-1</sup> the contribution in  $(d\nu/dT)$  is purely “implicit”. The “explicit” contribution is dominated by the highest frequency internal mode of  $\beta$ -GeSe<sub>2</sub>. The temperature analysis was performed only for a few internal modes of  $\beta$ -GeSe<sub>2</sub>. These results confirm the molecular character of this crystal. A similar situation exists for the explicit–implicit ratio in  $(d\nu/dT)$  for SnGeS<sub>3</sub>. The “implicit” contribution is dominant for most of the modes at lower frequencies, but the “explicit” contribution is important also. For two internal modes at 345 and 423 cm<sup>-1</sup> the “explicit” contribution is dominant, while for the third mode at 363 cm<sup>-1</sup> the “explicit” contribution is large and negative. The comparable values of the explicit and implicit contributions in  $(d\nu/dT)$  observed for most of the modes in SnGeS<sub>3</sub> suggest that the covalent bonding is dominant. Similar but of opposite sign values for the explicit–implicit contribution in  $(d\nu/dT)$  correspond to the situation when there is no net effect of temperature on phonon frequencies in SnGeS<sub>3</sub>.

The temperature analyses, i.e. the found explicit–implicit ratio in  $(d\nu/dT)$  show that the molecular character is most evident in  $\beta$ -GeS<sub>2</sub>, less in  $\beta$ -GeSe<sub>2</sub> and least in SnGeS<sub>3</sub>, and confirm that different ratios of the intramolecular/intermolecular force constants exist in those crystals [13, 15, 17]. As it is well-known the intramolecular to intermolecular force-constant ratio in SnGeS<sub>3</sub> is a half of the one in  $\beta$ -GeSe<sub>2</sub> and less than a half of the one in  $\beta$ -GeS<sub>2</sub>.

#### 4 Concluding remarks

We have studied the influence of both temperature and pressure on the Raman spectra of  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub>, and SnGeS<sub>3</sub> crystals. The pressure dependence of the Raman peaks has been analyzed in terms

of the Grüneisen parameter  $\gamma$ . The frequency dependence of the Grüneisen parameter  $\gamma(\nu_i)$  has been determined for all three crystals. Then  $\gamma(\nu_i)$  has been used to separate the “external” modes from the “internal” modes in  $\beta$ -GeS<sub>2</sub>. In the case of  $\beta$ -GeS<sub>2</sub>, all three RL modes have been identified. The correlation between the pressure-induced relative change (i.e. the mode-Grüneisen parameter) and mode frequency for  $\beta$ -GeS<sub>2</sub> is in accordance with previous findings on molecular crystals;  $\gamma(\nu_i)$  is very large and remains constant for the external modes but rapidly drops as  $\gamma(\nu_i) \sim \nu_i^{-1.96}$  in the internal mode region. The frequency dependence of  $\gamma(\nu_i)$  for  $\beta$ -GeSe<sub>2</sub> and SnGeS<sub>3</sub> has not allowed us to separate “external” and “internal” modes.

The influence of temperature has also been studied for all three crystals. The fractional increase of frequency is almost the same for all modes in  $\beta$ -GeS<sub>2</sub> (0.01 cm<sup>-1</sup>/K), for temperatures between 300 K and 18 K. The temperature influence on phonon frequencies in  $\beta$ -GeSe<sub>2</sub> is less pronounced than in  $\beta$ -GeS<sub>2</sub> while in SnGeS<sub>3</sub> is just noticeable. The knowledge of both, pressure and temperature, dependences of phonon frequencies has allowed us to separate the “explicit” phonon-excitation contribution and the “implicit” volume-driven contribution to the observed temperature coefficient ( $d\nu/dT$ ) for all of three crystals. The “explicit” and “implicit” contributions to ( $d\nu/dT$ ) are given in Table 1. In the case of  $\beta$ -GeS<sub>2</sub> the obtained results for the ratio between the “explicit” and “implicit” contributions to ( $d\nu/dT$ ) are in good agreement with the results for molecular crystals [10, 22]. The “implicit” contribution is dominant for the “external” modes. The “explicit” contributions increase with increasing frequency and become dominant for the high frequency “internal” modes. The case of  $\beta$ -GeSe<sub>2</sub> crystal is similar. As mentioned previously the temperature analysis was performed only for a few internal modes of  $\beta$ -GeSe<sub>2</sub>. In the case of SnGeS<sub>3</sub> for lower phonon frequencies the “implicit” contribution is dominant, but for these modes there is an important “explicit” contribution with opposite sign. For two high frequency “internal” modes the “explicit” contribution is dominant. The third high frequency mode has an important negative “explicit” contribution. The temperature dependence of the phonon frequencies in SnGeS<sub>3</sub> has shown that for most of the modes the “explicit” and “implicit” contributions have comparable magnitudes and opposite signs, consequently the temperature influence on phonon frequencies is indiscernible. This assignment of the explicit and implicit contributions in ( $d\nu/dT$ ) for SnGeS<sub>3</sub> suggests that the covalently bonding-force is dominant in this crystal.

In conclusion the results presented on both, the pressure and the temperature influence on phonon frequencies of  $\beta$ -GeS<sub>2</sub>,  $\beta$ -GeSe<sub>2</sub>, and SnGeS<sub>3</sub> confirm the layer character of these crystals.

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