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**Comments and Addenda**


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**Pressure dependence of the Raman spectra of the IV-VI layer compounds GeS and GeSe**

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The effect of hydrostatic pressure on the Raman-active  $A_g$  and  $B_{3g}$  modes in the IV-VI orthorhombic layer compounds GeS and GeSe is reported. The pressure coefficients and corresponding mode Grüneisen parameters of the rigid-layer modes are found to be an order of magnitude larger than those of the rocksalt-type modes. This behavior is consistent with the weaker interlayer forces of these materials as compared to intralayer forces.

### I. INTRODUCTION

Considerable information about the lattice dynamics of the layer compounds, GeS, GeSe, SnS, and SnSe has been obtained recently by means of Raman and infrared spectroscopy.<sup>1</sup> We report here the effect of hydrostatic pressure on the Raman modes of GeS and GeSe. Investigations of the effect of hydrostatic pressure on lattice vibrations have proved to be very useful. For example the mode-Grüneisen parameter, which describes the fractional change in the frequency of a crystal mode produced by a pressure-induced decrease in volume, enters into the theories of thermal expansion and the equation of state of solids.<sup>2</sup> The mode-Grüneisen parameters of three-dimensional solids are nearly independent of the phonon frequency and exhibit values close to unity for group-IV and III-V semiconductors<sup>3-6</sup> (the TA phonons do, however, often exhibit anomalous negative Grüneisen parameters). In contrast, two-dimensional solids, in which the interlayer forces are small compared to the intralayer forces, exhibit a strong departure from the Grüneisen approximation.<sup>7</sup> In these materials the mode-Grüneisen parameters of the "rigid-layer modes" are anomalously larger than those of the internal modes of strongly bonded atoms in a layer. This effect can be understood as produced by the strong anisotropy of the interlayer and intralayer bonds which results in a large stiffening of the weak interlayer bonds under the application of hydrostatic pressure.

The purpose of this paper is to discuss the effect of pressure on the Raman spectra of germanium sulphide and germanium selenide which have been shown to be in some sense intermediate cases between the two-dimensional (layer type) and three-dimensional crystals.<sup>1,8,9</sup> We have observed striking differences in the pressure coefficients of various Raman-active phonons. These results are discussed in the context of the quasi-two-dimensionality of these materials.

### II. EXPERIMENT

The Raman spectra of GeS and GeSe have been reported earlier.<sup>1,9</sup> These materials crystallize in an orthorhombic structure and have eight atoms per unit cell forming double-layer planes normal to the longest axis. Of the 21 optical phonons, 12 are Raman active. There are four modes of  $A_g$  and two modes of  $B_{3g}$  symmetry which can be observed by backscattering on a layer plane for parallel and crossed polarizations, respectively. The vibrational description of these modes and their frequencies are listed in Table I. We have investigated the pressure dependence of these modes at room temperature. Freshly cleaved samples were mounted in a hydrostatic pressure bomb with sapphire windows of the type described elsewhere.<sup>3</sup> The 6471-Å line of Kr<sup>+</sup> laser was used to excite the spectrum. A Jarrel-Ash monochromator equipped with holographic gratings, and a cooled ITT FW-130 photomultiplier with photon counting electronics, were used. The positions of the

TABLE I. Frequencies (in  $\text{cm}^{-1}$ ), pressure coefficients (in  $10^{-6} \text{ bar}^{-1}$ ), and description of the Raman-active  $A_g$  and  $B_{3g}$  modes in GeS.

Description	Symmetry	$\omega_i$ ( $\text{cm}^{-1}$ )	$\frac{1}{\omega_i} \frac{d\omega_i}{dP}$ ( $10^{-6} \text{ bar}^{-1}$ )
Rigid-layer shear mode along $\vec{a}$	$A_g$	$48 \pm 1$	$8.0 \pm 1$
Rigid-layer shear mode along $\vec{b}$	$B_{3g}$	$55 \pm 1$	$7.0 \pm 1$
Layer-waving mode	$A_g$	$111 \pm 1$	$1.2 \pm 0.2$
Rocksalt-type mode along $\vec{a}$	$B_{3g}$	$212 \pm 1$	$1.0 \pm 0.2$
Layer-breathing mode	$A_g$	$238 \pm 1$	$2.7 \pm 0.2$
Rocksalt-type mode along $\vec{b}$	$A_g$	$269 \pm 1$	$0.7 \pm 0.2$

Raman peaks were accurately measured with respect to the emission lines of a neon calibration lamp. Both the  $A_g$  and  $B_{3g}$  spectra were measured in a single run with unpolarized scattered radiation. This presented no problem since the  $A_g$  and  $B_{3g}$  modes do not overlap and can be identified by their positions as reported in Ref. 1. Figure 1

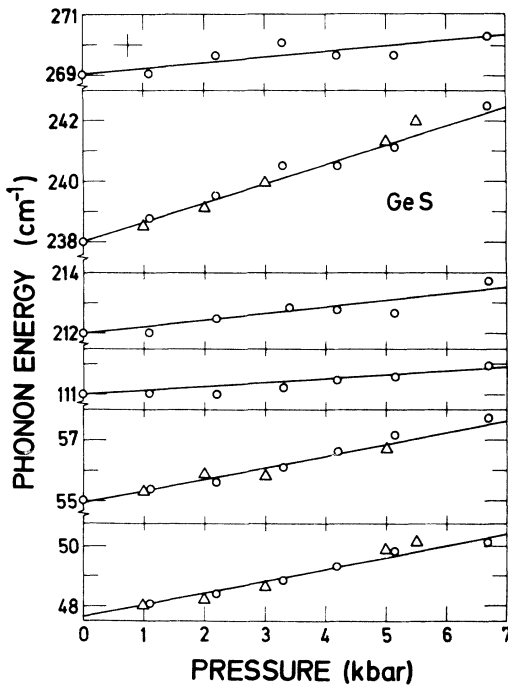


FIG. 1. Hydrostatic pressure dependence of the  $A_g$  (at 48, 111, 238, and 269  $\text{cm}^{-1}$ ) and  $B_{3g}$  (at 55 and 212  $\text{cm}^{-1}$ ) phonon modes of GeS at room temperature. The solid lines are a linear least-square fits to the data points.

shows the pressure dependence of the Raman-active modes. The circles and triangles were obtained in two separate runs. The solid lines are a linear least-squares fit to the datapoints. The pressure coefficients of the modes obtained from these data are included in Table I.

### III. DISCUSSION

The mode-Grüneisen parameter  $\gamma_i$  for a phonon of frequency  $\omega_i$  is defined in terms of the crystal volume  $V$ , the pressure  $P$  and the compressibility  $K$  as follows:

$$\gamma_i = -\frac{V}{\omega_i} \frac{d\omega_i}{dV} = -\frac{d \ln \omega_i}{d \ln V} = \frac{1}{K} \frac{d \ln \omega_i}{dP}. \quad (1)$$

In the Grüneisen approximation  $\gamma_i$  is assumed to be independent of mode frequency. In layer-type materials consisting of bonds of widely different strengths, however, such an approximation is not valid.<sup>7</sup> The disparity between the pressure coefficients for different modes in Table I illustrates this fact. If we suppose the force constants  $k_i$  and the bond lengths  $r_i$  describing a layer-type material can be grouped into interlayer and intralayer types, the fractional change in crystal volume under pressure can be written

$$\Delta V/V = 2\Delta r_0/r_0 + \Delta r_1/r_1. \quad (2)$$

Here  $r_0$  and  $r_1$  are the intralayer and interlayer bond lengths, respectively. The fractional changes in the interlayer and intralayer force constants  $k_1$  and  $k_0$  can be expressed via Eqs. (1) and (2) as

$$\Delta k_0/k_0 = -2\gamma_0(2\Delta r_0/r_0 + \Delta r_1/r_1) \quad (3)$$

and

$$\Delta k_1/k_1 = -2\gamma_1(2\Delta r_0/r_0 + \Delta r_1/r_1). \quad (4)$$

We assume that the force constants scale with the appropriate bond lengths according to the relationship

$$\Delta k_0/k_0 = -2n \Delta r_0/r_0, \quad (5)$$

$$\Delta k_1/k_1 = -2n \Delta r_1/r_1. \quad (6)$$

Available data<sup>6,7</sup> suggest that  $n$  lies between 3 and 4 for most materials. Solving Eqs. (3)–(6) we obtain

$$\gamma_0 = n(k_1/k_0)(1 - 2k_1/k_0),$$

and

$$\gamma_1 = n(1 - 2k_1/k_0)$$

under the assumption  $k_1 \ll k_0$  which is valid for layer-type materials. These results indicate the Grüneisen parameters  $\gamma_1$ , associated with the rigid-layer modes can be related to  $\gamma_0$ , associated with the rocksalt-type modes, by

$$\gamma_1 = (k_0/k_1)\gamma_0. \quad (7)$$

Unfortunately, compressibility data for GeS and GeSe are not available. Thus we are not able to determine accurately the  $\gamma_1$  from our data. However, an analysis based on the previous discussion enables us to make realistic estimates. The ratio ( $k_0/k_1$ ) has been estimated previously<sup>1,8,9</sup> based on the Davydov splittings of the rocksalt-type modes and the frequencies of the rigid-layer modes; it ranges from 10 to 30. The ratios of the mode-Grüneisen parameters  $\gamma_1/\gamma_0$  should have similar values according to Eq. (7). A glance at the values of pressure coefficients for the rigid-layer modes and the rocksalt-type modes in Table I suggest the ratios  $\gamma_1/\gamma_0$  to be  $\sim 10$ . Considering the simplicity of the model which assumes only one parameter  $\gamma$  for all the interlayer or intralayer modes, this agreement is reasonable. The inadequacy of this model is demonstrated by the larger pressure coefficient of a layer-breathing mode at 238  $\text{cm}^{-1}$  which is an intermediate case between interlayer and intralayer.

The compressibilities  $K$  of the IV-VI compounds PbS, PbTe, and SnTe have been reported.<sup>10-12</sup> By plotting these values against the corresponding unit cell volumes, we find that  $K$  varies nearly linearly with the volume of the unit cell. The value of  $K$  of GeS estimated by extrapolating this linear relation is  $(1.5) \times 10^{-6} \text{ bar}^{-1}$ . The fractional

change in the lattice constant  $c$  normal to the layers determined by x-ray diffraction as a function of pressure<sup>13</sup> sets a lower limit of  $\sim 1$  for  $K$ . A value for  $n$  between<sup>7</sup> 3 and 4 yields a value of  $K$  between 1.5 and 2 for GeS. The  $\gamma_0$  and  $\gamma_1$  estimated from Eqs. (3)–(6) and the measured values of pressure coefficients (Table I) are  $\sim 0.5$  and  $\sim 5 \times 10^{-6} \text{ bar}^{-1}$ , respectively.

The Raman spectra of the  $A_g$  and  $B_{3g}$  modes of GeSe show a pressure dependence similar to that of GeS. The rigid-layer mode at 39  $\text{cm}^{-1}$  and the rocksalt-type modes at 151 and 188  $\text{cm}^{-1}$  have pressure coefficients of  $7.0 \pm 1$  and  $1 \pm 0.5$ , respectively (units of  $10^{-6} \text{ bar}^{-1}$ ). The layer-breathing mode at 174  $\text{cm}^{-1}$  exhibits a pressure coefficient of  $(2.9 \pm 0.2) \times 10^{-6} \text{ bar}^{-1}$ . The ratio of pressure coefficients for the rigid-layer modes and the rocksalt-type modes yields for ( $\gamma_1/\gamma_0$ ) a value of 10. This falls in the range of force-constant ratios reported in Ref. 1. The values of  $\gamma_0$  and  $\gamma_1$  for GeSe estimated by using the compressibility obtained with the extrapolation described above are very similar to the corresponding values for GeS.

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