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Max-Planck-Institut für Festkörperforschung, Stuttgart

Pressure Dependence of Elastic Constants and Optical Phonon Frequencies in Se and Te

A Study of the Homological Relationship
between the Vibrational Modes in These Materials

By

T. A. FJELDLY¹⁾ and W. RICHTER²⁾

The hydrostatic pressure coefficients for the elastic constants of Se and Te are shown to be large and positive in contrast to the negative mode Grüneisen parameters reported earlier for the optical vibrations. These results can be understood on the basis of the idea that the hydrostatic pressure promotes transfer of electrons from intrachain bonding orbitals to interchain bonding states. This strengthens the interchain "elastic" force constants while simultaneously weakening the intrachain "optic" force constants. The great similarity in the Se and Te lattices suggests that their vibrational spectra can be related by homology. Of the three lattice parameters describing each crystal, the intrachain bond angle is nearly identical and relatively pressure insensitive in the two lattices. Therefore, by a two-step transformation in which the c/a -ratio is first made equal by applying hydrostatic pressure, and secondly by properly scaling the mass and the unit cell, the two lattices can be made structurally identical. With this transformation and the available pressure data all zone centre phonons studied in the two materials could be related by a universal scaling factor for the "mode" force constants. Rough estimates for the higher-order pressure coefficients can also be made.

Es wird gezeigt, daß die hydrostatischen Druckkoeffizienten für die elastischen Konstanten von Se und Te groß und positiv sind, im Gegensatz zu den negativen Grüneisenparametern, die früher für die optischen Schwingungen beobachtet wurden. Diese Ergebnisse lassen sich auf der Grundlage der Vorstellung verstehen, daß der hydrostatische Druck den Transfer von Elektronen aus bindenden „Intrachain“-Orbitalen in bindende „Interchain“-Zustände fördert. Dies verstärkt die „elastischen“ Interchain-Kraftkonstanten, während sich gleichzeitig die „optischen“ Intrachain-Kraftkonstanten abschwächen. Die große Ähnlichkeit der Se- und Te-Gitter legt es nahe, daß sich ihre Schwingungsspektren durch Homologie verknüpfen lassen. Von den drei Gitterparametern, die jeden Kristall beschreiben, ist der Intrachain-Bindungswinkel nahezu identisch und relativ druckunempfindlich in beiden Gittern. Deshalb lassen sich die beiden Gitter strukturell identisch machen durch eine Zwei-Stufen-Transformation, bei der erstens das c/a -Verhältnis durch Anlegen des hydrostatischen Drucks gleich groß gemacht wird und zweitens Masse und Einheitszelle skaliert werden. Mit dieser Transformation und den bekannten Druckwerten können alle untersuchten Phononen des Zonenzentrums in den beiden Materialien durch einen universellen Eichfaktor für die „Moden“-Kraftkonstanten verknüpft werden. Es läßt sich auch eine Abschätzung für die Druckkoeffizienten höherer Ordnung durchführen.

¹⁾ Present address: Electronics Research Laboratory, The University of Trondheim, Trondheim, Norway.

²⁾ Present address: I. Physikalisches Institut der RWTH Aachen, 51 Aachen, FRG.

1. Introduction

We have measured the hydrostatic pressure dependence of elastic constants in Se and Te and found these to be large (up to 5%/kbar) and positive. An earlier report on the Raman frequencies in the same materials showed these to have negative mode Grüneisen parameters [1].

These results can be understood in terms of the nature of the bonding as described by von Hippel [2], Grosse [3], Gspan et al. [4], and Martin and Lucovsky [5, 6]. They discuss how both the progression towards heavier elements as well as the application of hydrostatic pressure promotes transfer of electrons from the intrachain bonding orbitals to bonding states between the chains.

It is often useful to think of the Se or Te lattice as composed of weakly interacting helical chains along the trigonal axis [2, 3]. This structure is an intermediate step in the progression from molecular sulfur to simple cubic metallic polonium; it is a distortion from simple cubic which satisfies the divalent nature of the group VIb atoms.

With hydrostatic pressure the relatively stiff chains in Se and Te deform little while the weak interchain forces result in a denser packing of the chains. This causes, for instance, the anomalous linear expansion of these crystals along the trigonal axis with hydrostatic pressure [7, 8]. The denser packing of the chains and the resulting transfer of valence charge from intra- to interchain orbitals cause the interchain force constants to stiffen rapidly at the expense of the intrachain force constants. This is what is reflected in the pressure behaviour of the long-wavelength acoustical and optical modes, which are dominated by the inter- and intrachain forces, respectively. The decrease in intrachain constants has been observed in previous experiments [1]. Here the interchain bonding is observed directly in the elastic constants under pressure.

A simple force constant expression can be derived for the elastic constant combination $C_{11} + C_{12}$, which corresponds to a radial deformation in the basal plane, in terms of the single force constant K_R between nearest neighbour atoms on different chains. Likewise, a simple expression can be obtained for C_{33} which reflects an axial deformation along the chains. The latter involves, in addition to K_R , also a force constant K_θ for the intrachain bond angle. For a more detailed discussion of this we refer to an earlier note on the subject [9].

The major part of this paper is devoted to a study of the homology between Se and Te, made possible by the pressure data now available. Earlier studies of homology between series of elements were done on the group IVb diamond type crystals, and it proved quite successful in relating the vibrational spectra of the diamond-silicon-germanium- α -tin series [10 to 12]. This was facilitated by the simple structure possessed by these lattices. Only a simple normalization, i.e., scaling of the mass, the force constant, and the lattice constant resulted in a universal set of dispersion curves for these elements. The direct result of such an exercise, besides demonstrating the large systematic similarities in a group of elements, is to find trends in the interatomic force constants for ultimate comparison with theory.

In the lower symmetry lattices complications arise as a consequence of additional degrees of freedom in the lattice parameters. Thus, in the Se-Te system, we have two degrees of freedom in addition to the simple scaling. Fortunately, one of these, the intrachain bond angle, is very close in Se and Te; and it does not seem to have either a significantly large or different pressure

dependence for the two lattices [13]. This, therefore, leaves only one extra degree of freedom, and we have arbitrarily chosen to consider the c/a -ratio, which is different in the two materials: we can produce $(c/a)_A$ of species A by pressurizing species B and vice-versa. Thus, we have a two-step transformation which consists of subjecting B to a pressure p_B until $(c/a)_B(p_B) = (c/a)_A(0)$, and then secondly executing the mass and unit cell scaling. When this transformation is performed on the lattice modes of species B, the comparison with species A gives valuable information about the corresponding force constants in the two materials. Our aim is, with the present data on zone centre phonons, to demonstrate the possible existence of a homological relationship between the two elements. Of course, the transformation can be carried out both ways, either $A \rightarrow B$ or $B \rightarrow A$, and we shall see that this leads to interesting conclusions about the reciprocity of the scaling of the force constants. In addition, a simplified approach allows us also to estimate magnitudes for higher order pressure coefficients for the lattice modes.

2. Experimental

The various sound velocities and their pressure dependence were measured with a standard ultrasonic pulse-echo overlap technique [14, 15]. The experimental set-up was built around a Matec 6000 rf pulse generator. The frequencies used were 20 to 30 MHz; and the quartz transducers were bonded to the samples with Nonaq stop-cock grease or solidified phenylsalicylate ("salol"). The latter proved a good and reliable bond that normally did not break when applying pressure. Moreover, in check runs with grease bonds, no observable distortions that could be attributed to the use of solid bonds were detected in the data.

The single crystal samples of Se and Te were prepared as plates ranging in thickness from 2.5 to 5 mm with faces perpendicular to the X -axis (only Te) and the Y - and Z -axis³) (both Se and Te). The samples were X-ray oriented to $\pm 1^\circ$. The surfaces were carefully lapped in a lapping jig with a light-weight (hollow) aluminium piston.

The hydrostatic pressure was achieved in a steel bomb furnished with a coaxial electrical feed-through. Silicone oil was used as the pressure transmitting fluid, and the system had a capability of 7 kbar. A standard manganin resistive cell served as the pressure gauge.

3. Results

The measured pressure dependence of effective elastic constants are shown in Fig. 1 and 2, not corrected for volume and length changes. These corrections have to be applied as the pulse-echo method measures only the transit time of a pulse through the sample. For a determination of velocities as a function of pressure one therefore needs the dependence of the sample length on pressure, which is determined through the linear compressibilities. To calculate the elastic constants one has in addition then to correct for the density changes, given by the volume compressibility. The compressibilities can be calculated from a complete set of zero pressure elastic constants [16]. The elastic constant C_{13} , which can only be determined by measurements with wave-vector directions between

³) The Z -direction corresponds to the trigonal axis; X is the twofold axis (in the basal plane) and Y is perpendicular to both X and Z (i.e., Y is also in the basal plane).

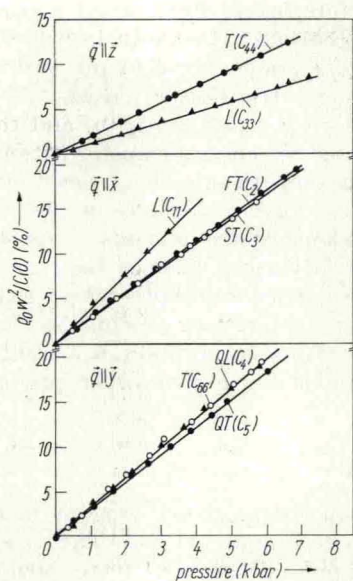


Fig. 1. Relative change in the effective elastic constants with hydrostatic pressure in Te; uncorrected for length and volume changes

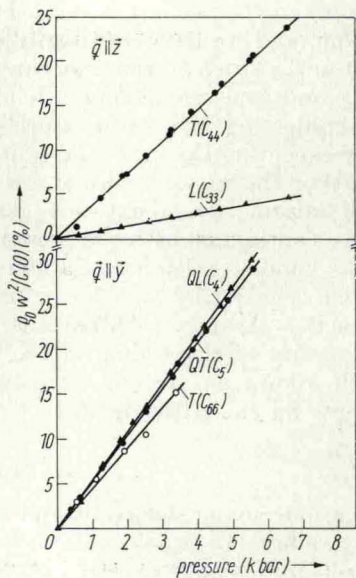


Fig. 2. Relative change in the effective elastic constants with hydrostatic pressure in Se; uncorrected for length and volume changes

the c -axis and the basal plane, was not measured here. We therefore took the compressibilities from the results of X-ray measurements under hydrostatic pressure, made by various authors. For Te the compressibilities quoted [7] are compatible with the value of C_{13} given by Malgrange et al. [17]. For Se large inconsistencies exist between the elastic constants [18, 19], linear compressibilities [8, 22], and volume compressibilities [20, 21]. This is probably due to the fact that none of these compressibility measurements has been performed on single crystalline material and in a true hydrostatic environment, conditions necessary for such an anisotropic and soft material like Se. Therefore the corrections performed on the Se data are somewhat uncertain. The corrected logarithmic pressure derivatives for the effective elastic constants are shown in Table 1. From the six independent hydrostatic pressure coefficients, we have information on five in both Se and Te; with three redundancies in the case of Te for checks on internal consistency. The sixth coefficient, involving the elastic constant C_{13} , was not determined here. We also obtained absolute values of the elastic constants, and these are compared with published data in Table 1. Our data on Te are in excellent agreement with those of Malgrange et al. [17]. Note that the effective "mode" elastic constants listed for the X - and Y -direction by Malgrange et al. were computed from their list of elastic constants using the expressions

$$C_{2,3} = \frac{1}{2} (C_{66} + C_{44}) \pm \left(\frac{1}{4} (C_{66} - C_{44})^2 + C_{14}^2 \right)^{1/2} \quad (1)$$

for the two mixed transverse modes in the X -direction and

$$C_{4,5} = \frac{1}{2} (C_{11} + C_{44}) \pm \left(\frac{1}{4} (C_{11} - C_{44})^2 + C_{14}^2 \right)^{1/2} \quad (2)$$

Table 1
Effective elastic constants and their logarithmic pressure derivatives for Se and Te

mode ^{a)}	C (10^{11} dyn/cm ²)					$\frac{1}{C} \frac{dC}{dp}$ ^{d)} (10^{-2} kbar ⁻¹)	
	Te		Se			Te	Se
	this work	ref. [17]	this work	ref. [19]	ref. [18]		
L(Z), C_{33}	7.05	7.22	8.20	8.02	7.41	1.79	2.1
T(Z), C_{44}	3.19	3.12	1.82	1.83	1.49	2.47	5.1
L(X), C_{11}	3.30	3.27	1.91 ^{b)}		1.87	3.78	5.2 ^{e)}
FT(X), C_2	3.66	3.72	2.12 ^{b)}		1.80	2.77	5.1 ^{e)}
ST(X), C_3	0.60	0.60	0.52 ^{b)}		0.24	2.74	3.7 ^{e)}
QL(Y), C_4	4.40	4.42	2.49		2.33	3.30	5.2
QT(Y), C_5	2.00	1.95	1.24		1.03	3.01	5.0
T(Y), C_{66}	1.25	1.21	0.82		0.55	3.30	4.2
$ C_{14} $	1.19 ^{b)}	1.24	0.62 ^{b)}		0.62		
C_{13}	2.31 ^{c)}	2.49	2.3 ^{c)}		2.60		

^{a)} Designations: L longitudinal, T transverse, FT fast transverse, ST slow transverse, QL quasi-longitudinal, QT quasi-transverse, (X), (Y), (Z) direction of phase velocity; C_2 to C_5 are defined in equations (1) and (2).

^{b)} Calculated from equations (1) and (2).

^{c)} Calculated from the volume compressibilities: Te: 0.52×10^{-11} cm²/dyn [7]; Se: 0.94×10^{-11} cm²/dyn [9].

^{d)} The linear compressibilities used are (in units of 10^{-3} kbar⁻¹): $-\frac{1}{a} \frac{da}{dp} = 2.8$ (Te), 5.7 (Se); $-\frac{1}{c} \frac{dc}{dp} = -0.4$ (Te), -2.0 (Se) [7 to 9]. Due to the relative large uncertainty

in the compressibilities of Se the pressure derivatives in this column can have an uncertainty of as much as 25% for C_{33} ; but typically less than 10% for the basal plane modes.

^{e)} Calculated from equations (3) to (5).

for the quasi-longitudinal (+) and quasi-transverse (-) modes in the Y-direction. (Note that the relationship given in reference [17] for C_2C_3 is obviously in error.) With the present elastic constants and the volume compressibility by Bridgeman [7] (0.52×10^{-11} cm²/dyn), we obtain a value for C_{13} as shown in Table 1.

For Se there exists in the literature a complete set of elastic constants by Mort [18], and measurement only along the trigonal axis (i.e., C_{33} and C_{44}) by Vedam et al. [19]. Our data for the latter are in very good agreement with those by Vedam et al. but Mort's values are lower by 10 to 20%. This is typical for his data when compared with the present ones, also for the X- and Y-direction. Our agreement with Vedam et al. for the Z-direction in Se, and the good agreement with Malgrange et al. for Te together with the fact that we performed all our measurements consistently, without variation in technique, lead us to believe that our data for the elastic constants in Se along with those of Vedam et al. are the more accurate. Using the present data, and a volume compressibility of 0.94×10^{-11} cm²/dyn (see [7] and the discussion in Section 4) we obtain an estimate for C_{13} (see Table 1) in Se.

Table 2

Consistency checks on the elastic constants and on their pressure derivatives in Te (see equations (3) to (5) in the main text). The elastic constants have the units (10^{11} dyn/cm²)

$C_2 + C_3$	= 4.26	$K_2 + K_3$	= 11.8
$C_{44} + C_{66}$	= 4.44	$K_{44} + K_{66}$	= 12.0
$C_4 + C_5$	= 6.40	$K_4 + K_5$	= 20.5
$C_{11} + C_{44}$	= 6.49	$K_{11} + K_{44}$	= 20.4
$[(C_2 - C_3)^2 - (C_4 - C_5)^2]^{1/2}$	= 1.90	$[(C_2 - C_3)(K_2 - K_3) - (C_4 - C_5)(K_4 - K_5)]^{1/2}$	= 2.4
$[(C_{44} - C_{66})^2 - (C_{44} - C_{11})^2]^{1/2}$	= 1.91	$[(C_{44} - C_{66})(K_{44} - K_{66}) - (C_{44} - C_{11})(K_{44} - K_{11})]^{1/2}$	= 2.6

The three redundancies in measurement of the absolute values and of the pressure coefficients for the elastic constants in Te allow us to perform three checks on internal consistency for both. Using the notation C_α and $K_\alpha = (d/dp)C_\alpha$ for the absolute values and the pressure coefficients of the elastic constants respectively, we have the following relationships:

$$C_{44} + C_{66} = C_2 + C_3, \quad K_{44} + K_{66} = K_2 + K_3, \quad (3)$$

$$C_{44} + C_{11} = C_4 + C_5, \quad K_{44} + K_{11} = K_4 + K_5, \quad (4)$$

$$\left. \begin{aligned} [(C_{44} - C_{66})^2 - (C_{44} - C_{11})^2]^{1/2} &= [(C_2 - C_3)^2 - (C_4 - C_5)^2]^{1/2} \\ [(C_{44} - C_{66})(K_{44} - K_{66}) - (C_{44} - C_{11})(K_{44} - K_{11})]^{1/2} &= \\ = [(C_2 - C_3)(K_2 - K_3) - (C_4 - C_5)(K_4 - K_5)]^{1/2}. \end{aligned} \right\} (5)$$

The two-digit subscripts reflect the conventional notation, while C_α ($\alpha = 2, \dots, 5$) are defined in (1) and (2). The square root signs in (5) are retained to preserve consistency with (3) and (4) in evaluating the errors.

Table 2 shows that the internal consistency in our measurements is quite satisfactory, with a maximum error of 4% in the elastic constants and in their pressure derivatives. This is also in agreement with the maximum uncertainty expected in our experiments. The larger relative discrepancy in the lower of (5) is merely due to the near cancellation of large numbers inside the square brackets. A similar uncertainty is also expected for the experimental data on Se. However, the lack of reliable values for the linear compressibilities introduces relatively large uncertainties in some of the logarithmic pressure derivatives of the elastic constants (see footnote in Table 1).

4. Atomic Force Constants and the Pressure Dependence of the Lattice Vibrations

As mentioned earlier, the qualitative features of the pressure dependence of the long-wavelength optical and acoustical vibrations finds a natural explanation in the ideas put forward, in particular by Martin and Lucovsky [5, 6]. The optical modes tend to soften and acoustical modes stiffen due to the weakening of the strong intrachain covalent bonds owing to transfer of electronic charge to the weak interchain bonds as the chains are packed closer together. This can be seen in the larger context of a progression from molecular sulfur to metallic

simple cubic polonium, where Te and Se are viewed as points in a continuous distortion from the simple cubic lattice. This distortion is described in terms of the ratio between the nearest distance between atoms on different chains R to the nearest neighbour distance r within a chain [2, 5, 6]. In this picture, it becomes quite clear that with the progression towards heavier atoms (i.e., with decreasing R/r), the interchain forces increase at the expense of the intrachain forces, for ultimately to become equivalent in the case of simple cubic polonium. However, the distortion parameter R/r also decreases in Se and Te with hydrostatic pressure, allowing the pressure data obtained here and earlier to find their natural explanation within this general picture. Quantitatively, these pressure data permit investigation of the changes in the various force constants with small reductions in the distortion. As an example, we have shown elsewhere [9] that the elastic constant combination $C_{11} + C_{12}$, which describes a radial distortion in the basal plane of the trigonal crystal can, to a good approximation, be related to the single force constant K_R between nearest neighbour atoms on different chains. The assumption made is that the nearest neighbour distance within the chain r is rigid, and that we have only central forces between the chains. This expression is

$$C_{11} + C_{12} = \frac{2\sqrt{3}}{c} \left(\frac{a}{R}\right)^2 \left(1 - \frac{3}{2}x\right)^2 K_R, \quad (6)$$

where x (0.2254 for Se and 0.2633 for Te) is the internal position parameter (xa is the chain radius). Using a simple power law expression $K_R \sim R^\alpha$ we find that owing to the rapid increase in $C_{11} + C_{12}$ with pressure, the power α must be about -14 for Se and -20 for Te!

With similar assumptions, but including an intrachain bond bending force constant K_θ we arrive at the following expression for C_{33} :

$$C_{33} = \sqrt{3} \left(\frac{1}{9xa}\right)^2 \frac{c^2}{a^2} \left[K_R \left(\frac{a}{R}\right)^2 + 2K_\theta \left(\sin \frac{\theta}{2}\right)^{-2} \right], \quad (7)$$

where θ (103.06° for Se and 103.23° for Te) is the intrachain bond angle. With the above result for K_R we find the values for the logarithmic derivatives $(a/K_\theta)(dK_\theta/da)$ to be very small for Se and about four for Te.

This demonstrates how the typical interchain force constant K_R increases drastically with pressure. The intrachain bond bending force constant K_θ clearly decreases in Te with pressure in agreement with the rough estimates given in [1]. For Se a good evaluation of this quantity was difficult owing to large inconsistencies between the elastic constants, linear compressibilities, and volume compressibilities [8, 18, 20 to 22]. Clearly accurate compressibility measurements on single crystalline samples in a true hydrostatic environment are needed for such an anisotropic material as Se. The compressibilities used are given in Table 1 (footnote d). The failure to demonstrate a definite decrease in K_θ with pressure for Se can partly be ascribed to the uncertainty in the compressibilities used; but, more likely, a more sophisticated force constant model is needed to express properly the elastic constant C_{33} . However, the experiments show that the elastic constant C_{33} , which contains the highest admixture of intrachain force constants, has the smallest increase with pressure of all the elastic constants measured (see Fig. 1 and 2 and Table 1), lending further evidence to the general ideas stated earlier.

5. Study of the Homology between Se and Te

We now consider the possibility of relating the vibrational spectra in Se and Te in a fashion similar to the one used by Kucher [10], Mostoller [11], and Nilson and Nelin [12] for the group IVb elements.

As mentioned earlier, only a simple scaling of mass, force constants, and lattice parameter suffices for the higher symmetry elements of the diamond type. It was further agreed that of the two extra parameters defining the trigonal Se (Te) lattice, only the difference in c/a -ratio was of significance, and that this could be controlled by hydrostatic pressure.

We shall now consider in detail how the transformations Se \rightarrow Te and Te \rightarrow Se are performed. The c/a -ratios in Se and Te are 1.14 and 1.33, respectively. The pressure dependence of c/a has been measured by Vereshagin et al. [8] for Se and by Jamieson and McWhan [23] for Te. Their results show that to perform the transformation Se \rightarrow Te, i.e., to make $(c/a)_{\text{Se}}(p_{\text{Se}}) = (c/a)_{\text{Te}}(0)$ we arrive at the positive pressure $p_{\text{Se}} \approx 40$ kbar. Likewise, for the transformation Te \rightarrow Se, we find the negative pressure $p_{\text{Te}} = -35$ kbar. To obtain these values the pressure dependence of c/a and a were fitted with parabolas. This was necessary in order to account for the nonlinearity in these quantities within the pressure range of interest. To make the fits we chose three representative points from each of the experimental data sets. These are shown in Table 3. Owing to the

Table 3

Data used to make parabolic fits to the dependence of c/a and a on pressure in Se and Te. The lowest row for each element (A) shows the pressure necessary to make $(c/a)_{\text{A}}(p_{\text{A}}) = (c/a)_{\text{B}}(0)$, where B is the other element

Se			Te		
p (kbar)	c/a	a (Å)	p (kbar)	c/a	a (Å)
0	1.135	4.366	0	1.33	4.474
7.5	1.172	4.217	22.5	1.40	4.276
15.0	1.209	4.114	35.8	1.423	4.218
40	1.33	3.824	-35	1.135	5.029

small pressure range of reference [8], which seems the most reliable for Se, the values obtained for Se are somewhat uncertain (± 5 kbar for p_{Se}).

The last step in the transformation is to scale the pressurized materials by the mass ratio, and by the single lattice constant a (or c).

We now apply this transformation to the lattice vibrations, and consider first the long-wavelength optical modes. Thus, for equivalent phonons in the two lattices A and B we arrive at the following relationship:

$$\omega_{\text{A}}^2(0) = \omega_{\text{B}}^2(p_{\text{B}}) S_{\text{B} \rightarrow \text{A}} \frac{M_{\text{B}}}{M_{\text{A}}}, \quad (8)$$

where

$$\omega_{\text{B}}^2(p_{\text{B}}) = \omega^2(0) + k_1^{\text{B}} p_{\text{B}} + k_2^{\text{B}} p_{\text{B}}^2 + \dots \quad (9)$$

Here p_B represents the pressure needed to fulfil the condition $(c/a)_B(p_B) = (c/a)_A(0)$ and is given above for Te and Se. M_B and M_A are the respective masses for the atoms A and B. $S_{B \rightarrow A}$ is the ratio of the equivalent zero-pressure force constant $K_A(0)$ in the material A and that of material B $K_B(p_B)$ under pressure p_B , i.e. $S_{B \rightarrow A} = K_A(0)/K_B(p_B)$. We note that the scaling of the unit cell does not enter into (8) for the optical modes due to their lack of dispersion at long wavelengths. The experimental Raman frequencies and their pressure coefficients are listed in Table 4. The long-wavelength acoustical modes are most conveniently discussed in terms of the ultrasonic velocities. As a conse-

Table 4

Raman modes: $\omega(0)$ frequencies under atmospheric pressure; k_1 first-order pressure coefficient of ω^2 (equation (9)); S_i mode force constant ratios obtained from the transformations Se \rightarrow Te and Te \rightarrow Se using first-order expansion in pressure (S_1) and second-order expansion (S_2). $k_2^{\text{Te}} = k_2^{\text{Se}} = k_2$ is the approximation used in the second-order expansion (see equation (9))
 $S_1 = K_{\text{Te}}(0)/K_{\text{Se}}(40)$ or $K_{\text{Te}}(-35)/K_{\text{Se}}(0)$

mode	$\omega(0)$ (cm ⁻¹)		k_1 (cm ⁻² /kbar)		$S_1 =$	$S_1 =$	$S_2 =$	$k_2 =$
	Te *)	Se *)	Te *)	Se *)	$S_{\text{Se} \rightarrow \text{Te}}$	$S_{\text{Te} \rightarrow \text{Se}}^{-1}$	$S_{\text{Se} \rightarrow \text{Te}} = S_{\text{Te} \rightarrow \text{Se}}^{-1}$	$k_2^{\text{Te}} = k_2^{\text{Se}}$ (cm ⁻² /kbar ²)
A ₁	121.0	238.6	-218	-305	0.53	0.63	0.57	-1.9
E''	141.4	235.8	-139	-90	0.62	0.72	0.66	-1.8
E'	92.8	148.6	-13	-21	0.66	0.66	0.66	-0.1

*) Values obtained from [1].

quence of the linear dispersion in these we obtain for the transformation B \rightarrow A

$$v_A^2(0) = v_B^2(p_B) S_{B \rightarrow A} \frac{M_B}{M_A} \left(\frac{l_A(0)}{l_B(p_B)} \right)^2, \quad (10)$$

where

$$v_B^2(p_B) = v_B^2(0) + k_1^B p_B + k_2^B p_B^2 + \dots; \quad (11)$$

$l(p)$ represents either of the lattice parameters a or c at the pressure shown in the parenthesis. The presence of $l(p)$ reflects the linear dispersion in the acoustical modes in the ultrasonic region. The experimental sound velocities v_0 and the pressure coefficients k_1 are listed in Table 5.

As mentioned, the transformation equations (8), (9) and (10), (11) can be carried out either as Se \rightarrow Te or Te \rightarrow Se. However, to claim a homological relationship between the vibrational modes in Se and Te for each of these transformations we must require that the force constant ratio $S_{B \rightarrow A}$ must be the same for all modes in the two species. Here we only consider zone centre modes; however, these involve a number of inter- and intrachain force constants, and should therefore serve as a good testing ground for the idea. We further expect some degree of reciprocity in the two transformations Se \rightarrow Te and Te \rightarrow Se in the sense that $S_{B \rightarrow A} = S_{A \rightarrow B}^{-1}$. For a simple representation of force constants by one-term power laws in the lattice parameter a and c , it can be shown (Appendix A) that this indeed seems to be the case. This point will, however, be further studied in the course of the discussion of the experimental data on the individual modes.

Table 5

Ultrasonic waves: v_0 sound velocities under atmospheric pressure; k_1 first-order pressure coefficients of v^2 (equation (11)); S_i ultrasonic force constant ratios obtained from the transformations Se \rightarrow Te and Te \rightarrow Se. The first-order pressure expansion (S_1) is only applicable for Se \rightarrow Te, and for the $q \parallel Z$ -direction for Te \rightarrow Se (see text). Again, the approximation $k_2^{\text{Se}} = k_2^{\text{Te}} = k_2$ is used in the second-order expansion (S_2)

mode *)	v_0 (10^5 cm/s)		k_1 (10^{10} cm ² /s ² kbar)		$S_1 =$	$S_1 =$	$S_2 =$	$k_2 =$
	Te	Se	Te	Se	$S_{\text{Se} \rightarrow \text{Te}}$	$S_{\text{Te} \rightarrow \text{Se}}^{-1}$	$S_{\text{Se} \rightarrow \text{Te}} = S_{\text{Te} \rightarrow \text{Se}}^{-1}$	$k_2^{\text{Te}} = k_2^{\text{Se}}$ (10^6 cm ² /s ² kbar ²)
L(Z)	3.36	4.14	0.143	0.194	0.54	0.44	0.52	8.7
T(Z)	2.26	1.95	0.100	0.157	0.61	0.51	0.61	2.0
L(X)	2.30	2.00 **)	0.172	0.169 **)	0.59		0.46	18.5
FT(X)	2.42	2.10 **)	0.132	0.182 **)	0.61		0.55	6.5
ST(X)	0.98	1.05 **)	0.021	0.030 **)	0.50		0.46	1.6
QL(Y)	2.66	2.28	0.197	0.221	0.61		0.51	16.5
QT(Y)	1.79	1.61	0.080	0.105	0.57		0.50	5.5
T(Y)	1.42	1.31	0.056	0.056	0.61		0.50	5.4

*) The symbols in this column are explained in Table 1.

***) These values are calculated from the results for the Z- and Y-directions.

It is clear from the magnitude of the pressures needed for the transformations that one cannot, in general, expect a simple linear behaviour in the squared lattice frequencies over such pressure ranges. This can be seen from the experimental information on the lattice parameters (and the c/a -ratio) versus pressure. As will be evident this poses certain problems, particularly in the discussion of the acoustical modes. However, with due consideration to this difficulty, we shall now proceed to evaluate our data within the framework of the ideas presented here.

6. Discussion

6.1 Discussion of the optical modes

The force constant ratio $S = S_{B \rightarrow A}$ of (8) is obtained from pressure expansion of $\omega^2(p)$ as shown in (9). Only the first-order expansion coefficient k_1 is known experimentally; and with this linear approximation we obtain the values for S_1 shown in Table 4 for the two independent transformations Se \rightarrow Te and Te \rightarrow Se. We have used the notation $S_1 = S_{\text{Se} \rightarrow \text{Te}}$ and $S_1 = S_{\text{Te} \rightarrow \text{Se}}^{-1}$ for the two transformations, respectively. We note that the agreement between the two values is in each case quite good. This shows (i) that for the optical modes the linear approximation is quite reasonable for ω^2 versus pressure, and (ii) that the reciprocity condition $S_{B \rightarrow A} = S_{A \rightarrow B}^{-1}$ is a quite reasonable one. The order of magnitude of the nonlinearity (i.e., k_2) in the pressure dependence of ω^2 can be estimated by making the rough approximation that $k_2^{\text{Te}} = k_2^{\text{Se}} = k_2$. Then, the two transformation relationships can be solved simultaneously for k_2 and S (now labelled $S_2 = S_{B \rightarrow A} = S_{A \rightarrow B}^{-1}$), giving the values shown also in Table 4. We note that S_2 is intermediate between the two independent estimates of S_1 . Further, we see that the coefficients k_2 are indeed small; predicting a very slight deviation from linearity in ω^2 over all pressure ranges of interest here. The sign

of k_2 , however, indicates that the second-order term tends to accelerate the softening in ω^2 with pressure.

We find that the magnitude of the force constant ratios S is quite similar for the three optical modes considered and in agreement with the requirement for a homological relationship to exist. The strong decrease of the force constants in progressing from Se to Te, reflected by the average value of $S = 0.63 \pm 0.05$ is also noteworthy.

From the fact that the optical phonons soften slightly when applying pressure, we already know $K_{\text{Se}}(40) < K_{\text{Se}}(0)$. The small value obtained for S therefore demonstrates the weakening of the intrachain forces with the progression from the lighter (Se) to heavier (Te) element.

6.2 Discussion of the acoustical modes

In calculating the force constant ratios for the long-wavelength acoustical modes we use the equations (10) and (11). Again, owing to the limited pressure range available in the present experiments we only have the linear part in the pressure expansion of v^2 . However, due to the remarkably large and positive pressure coefficients found here, the transformation Te \rightarrow Se cannot always be performed: a linear extrapolation to -35 kbar makes v^2 negative for at least one of the modes in Te. This is, of course, no problem for the transformation Se \rightarrow Te. The difficulty in Te \rightarrow Se most likely arises from omission of higher-order pressure effects, which seem to be of particular importance for the long-wavelength acoustical modes. These modes, and especially those with phase velocities in the basal plane, are dominated by the interchain force constants. As discussed previously, and demonstrated in the present experiments, these force constants stiffen very rapidly with pressure. A certain nonlinearity in the pressure behaviour of these modes should be expected from the foregoing discussion of the pressure dependence of the force constants (see Section 4 and also [9]). For the velocities corresponding to wave propagation in the Z-direction, for which the linear Te \rightarrow Se transformation could be performed, we find reasonable correspondence between the two first-order estimates of the force constant ratios S_1 (see Table 5), again indicating the reciprocity in S for the two transformations. Assuming that we always can use the condition $S = S_2 = S_{B \rightarrow A} = S_{A \rightarrow B}^{-1}$, we can again expand v^2 to second order in pressure with the approximation $k_2 = k_2^{\text{Te}} = k_2^{\text{Se}}$; and find simultaneous solutions for S_2 and k_2 . As for the optical modes, we expect S_2 to be a best average estimate of the force constant ratio S .

From the data in Table 5 we make the following observations: (i) The sign of the predicted second order pressure coefficient k_2 in v^2 is always positive, i.e., the stiffening of the acoustical modes is accelerated by the inclusion of the second-order pressure term. We recall that for the optical frequencies the softening was found to accelerate. These findings are consistent with the pressure dependence of the respective force constants as discussed in Section 4. (ii) The values of S_2 for all the acoustical modes considered are quite similar, about 0.52 ± 0.09 . This agrees quite well with the value range found for S_2 in the optical modes (Table 4). This is a particularly important result because it shows that the vibrational modes in Se(p_{Se}) and Te(0) or equivalently in Se(0) and Te(p_{Te}) can be related to each other by a single universal scaling factor! We recall that this is a necessary condition for a homological relationship to exist between the vibrations in the two species (via their respective pressure be-

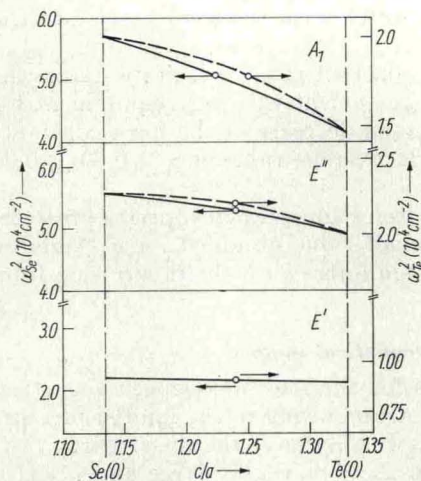


Fig. 3. Comparison of the c/a -dependence of ω^2 for the optical modes in Se and Te

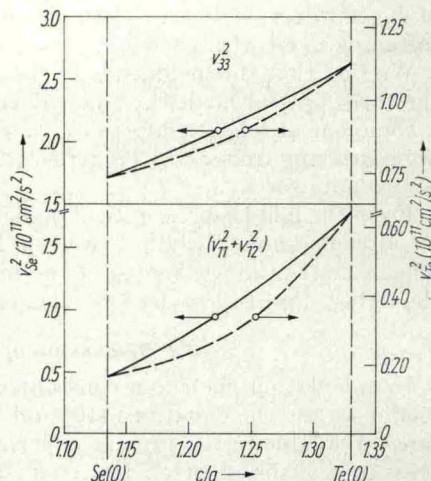


Fig. 4. Comparison of the c/a -dependence of v^2 for two acoustical modes in Se and Te

haviours). But again, although this study covers only a limited set of phonons at the zone centre, a wide range of atomic inter- and intrachain force constants are nonetheless involved. To complete the study, therefore, one needs information about the pressure behaviour of additional phonons, for instance, at the zone edge; an experimental undertaking that most probably will have to involve neutron spectroscopy.

In the diamond type materials the mode force constant ratio is given by [12]: $S_{B \rightarrow A} = a_B^3/a_A^3 = V_B/V_A$, where a and V are lattice constant and volume of the unit cell for materials A and B, respectively. Calculating now this volume ratio for $A = \text{Te}(0)$ and $B = \text{Se}(40)$ we obtain the value $S_{B \rightarrow A} = 0.624$. This number is quite close to the values listed for S in Tables 4 and 5. It demonstrates that the force constants in this case seem to be also mainly governed by a simple $1/V$ behaviour as was found in the diamond family [12].

Finally, in Fig. 3 and 4, we present a comparison of the c/a -dependence of some optical and acoustical modes in Se and Te, based on the various pressure dependences discussed earlier. For clarity the curves of ω^2 and v^2 have been scaled by the individual force constant ratios S ($= S_2$) as given in Tables 4 and 5. This makes the end points of the corresponding Se and Te curves coincide, per definition. For the optical modes the largest mismatch between the Se and Te curves is about 4% in the case of ω_{A1}^2 . The mismatch for the acoustical modes is 5% for v_{33}^2 , and as much as 20% for $v_{11}^2 + v_{12}^2$. The latter, corresponding to a radial compression in the basal plane, also has the most "anomalous" force constant ratio S (i.e. the largest deviation from the average value of S). This shows therefore that of the vibrational modes investigated, this particular mode has the poorest compliance with the scaling laws of the Se-Te homology.

7. Conclusion

We have presented a study of the pressure coefficients of various zone centre vibrational modes in Se and Te.

The experimental results show that the optical modes, which are dominated by the intrachain force constants, soften with hydrostatic pressure. In contrast, the long-wavelength acoustical phonons, which mainly probe the interchain force constants, stiffen rapidly. These observations are in general agreement with the ideas of Martin and Lucovsky [5, 6] and Gspan et al. [4] on the nature of the Se-Te system. They predict a transfer of valence charge from bonding orbitals within the chains to bonding states between the chains, both with increasing pressure and with progression towards heavier elements in the group VIb of the Periodic Table. We would like to note that a similar behaviour should be expected for the group Vb elements, where the lattices possess strong covalent bonding within layers and weaker interactions between layers. A study of these materials will be published elsewhere.

With the present pressure data we have studied the homology between Se and Te. We have demonstrated that equivalent optical and acoustical modes in the two materials can be related to each other by a simple transformation involving the mode pressure dependences. The ratio of effective force constants in the two materials with one subjected to a hydrostatic pressure such that their c/a -ratios are identical, has been shown to be approximately equal for most of the zone centre optical and acoustical modes. This indicates that a homological relationship indeed exists between trigonal Se and Te via their respective pressure dependences. We suggest that further experiments on the pressure dependence of zone edge and other phonons should be performed to complete this study.

It was also shown that a high degree of reciprocity exists between the force constants ratios obtained in the independent transformation Se \rightarrow Te and Te \rightarrow Se. This allowed us to predict rough estimates of second-order pressure coefficients (averages between Se and Te) for the zone centre modes considered.

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Appendix A

Assume that the force constant K for a specific mode can be written as a one-term power law in the lattice parameters a and c with exponents x and y :

Before transformation:

$$K_{\text{Te}}(0) = Ac_{\text{Te}}^x(0) a_{\text{Te}}^y(0),$$

$$K_{\text{Se}}(0) = Bc_{\text{Se}}^x(0) a_{\text{Se}}^y(0).$$

After transformation:

$$K_{\text{Te}}(p_{\text{Te}}) = Ac_{\text{Te}}^x(p_{\text{Te}}) a_{\text{Te}}^y(p_{\text{Te}}),$$

$$K_{\text{Se}}(p_{\text{Se}}) = Bc_{\text{Se}}^x(p_{\text{Se}}) a_{\text{Se}}^y(p_{\text{Se}}).$$

This gives the force constant ratios $S_{\text{Te} \rightarrow \text{Se}}$ and $S_{\text{Se} \rightarrow \text{Te}}$

$$S_{\text{Te} \rightarrow \text{Se}} = \frac{K_{\text{Te}}(0)}{K_{\text{Se}}(p_{\text{Se}})} = \frac{A}{B} \left(\frac{c_{\text{Te}}(0)}{c_{\text{Se}}(p_{\text{Se}})} \right)^x \left(\frac{a_{\text{Te}}(0)}{a_{\text{Se}}(p_{\text{Se}})} \right)^y = \frac{A}{B} \left(\frac{a_{\text{Te}}(0)}{a_{\text{Se}}(p_{\text{Se}})} \right)^{x+y},$$

$$S_{\text{Se} \rightarrow \text{Te}} = \frac{K_{\text{Se}}(0)}{K_{\text{Te}}(p_{\text{Te}})} = \frac{B}{A} \left(\frac{c_{\text{Se}}(0)}{c_{\text{Te}}(p_{\text{Te}})} \right)^x \left(\frac{a_{\text{Se}}(0)}{a_{\text{Te}}(p_{\text{Te}})} \right)^y = \frac{B}{A} \left(\frac{a_{\text{Se}}(0)}{a_{\text{Te}}(p_{\text{Te}})} \right)^{x+y}.$$

Note that the condition $(c/a)_B(p_B) = (c/a)_A(0)$ for the transformation has been used to derive the final expressions.

Finally, we arrive at the following condition, using the experimental (and extrapolated) values for the lattice parameter a with and without pressure:

$$S_{\text{Te} \rightarrow \text{Se}} S_{\text{Se} \rightarrow \text{Te}} = \left(\frac{a_{\text{Se}}(0) a_{\text{Te}}(0)}{a_{\text{Se}}(40) a_{\text{Te}}(-35)} \right)^{x+y} = (0.99)^{x+y}.$$

The value in the parenthesis is uncertain to a few per cent due to lack of experimental data. It can therefore be concluded that the reciprocity condition $S_{AB} = S_{BA}^{-1}$ appears to be fulfilled for this case.

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