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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

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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.

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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