High-pressure Mössbauer study of SnSe

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SnSe is a member of the IV-VI family of binary compounds which have orthorhombic structure and are layered, exhibiting properties that place SnSe intermediate between two- and three-dimensional crystals. Mössbauer measurements have been made on SnSe under hydrostatic pressure in the range 0.001 to 55 kbar. The results are interpreted with respect to interlayer and intralayer bonding. Two ranges of response to the pressure were found: (1) a lower-pressure range (below 30 kbar), in which measurable changes in isomer shift and quadrupole splitting were found, and (2) a higher-pressure range (between 30 and 55 kbar), where no further changes were found. The lower-pressure range is interpreted as a range in which the interlayer bonds are changed.

I. INTRODUCTION

The IV-VI binary compounds of the type $A^{IV}B^{VI}$ are divided into two main groups according to their crystal structure. SnTe, PbS, PbSe, and PbTe belong to the O_h^5 ($Fm3m$) space group with NaCl-type lattices;[1] GeS, GeSe, SnS, and SnSe belong to the D_{2h}^{16} ($Pcmn$) space group with orthorhombic structure.[1] This orthorhombic subgroup of IV-VI compounds consists of structures intermediate between three-dimensional and two-dimensional materials, constructed of two-dimensional layers weakly bonded to each other to produce a three-dimensional material.[2] Raman and infrared studies show that for SnSe the intralayer force constants are up to 21 times larger than the interlayer force constants.[3] Pressure coefficients of these force constants for GeS and GeSe, determined with use of Raman spectroscopy, also reinforce the layerlike structure of these materials.[4] This paper, by the use of Mössbauer spectroscopy and hydrostatic high-pressure techniques, examines the bonding of the Sn atoms in SnSe.

SnSe is an orthorhombic crystal with eight atoms per unit cell and lattice parameters $a = 4.46$ Å, $b = 4.19$ Å, and $c = 11.57$ Å.[5] The Sn and Se atoms form double layers made up of two planes of zigzag Sn–Se chains perpendicular to the longest axis. Each atom has the coordination environment of a heavily distorted octahedron and the lattice can be thought of as a deformed NaCl type.[1] Each atom forms six dominant heteropolar bonds, the strongest of which are in three bonds to nearest neighbors in the same double layer. Three weaker bonds are to further neighbors, two of which are in the same double layer, one to an atom in the next layer.[1] Table I gives the lengths of these six bonds for SnSe and related compounds. Also included is a quantity Δ which is a measure of the deviation from an ideal NaCl-type structure ($\Delta=0$). Δ is the difference between the average of the three shortest and the average of the three longest bond lengths.[1]

Mössbauer spectroscopy probes the changes in the electron density at the Sn nucleus (isomer shift), changes in the symmetry of the electrons at the Sn nucleus (quad-rupole splitting), and changes in the rigidity of the Sn nucleus in the lattice (recoilless fraction). For materials that are intermediate between three and two dimensions, there is an anisotropy in the strength of the bonds between atoms. High-pressure techniques alter this anisotropy and, in conjunction with such a technique as Mössbauer spectroscopy that probes the material on a fine scale, the bonds can be characterized.

The Sn atoms in SnSe occupy one type of symmetry site, a distorted octahedron. Therefore, a single Mössbauer line was measured. The line is quadrupole split due to the interaction of the nuclear quadrupole moment with the electric-field gradient at the nucleus created by the unequal population of the $5p$ orbitals and the nonuniform crystal field. Application of pressure will result in more change in the bond lengths of the weaker bonds than in those of the stronger bonds. A change in bond lengths will result in changes in the isomer shift, quadrupole splitting, and recoilless fraction. In this paper we interpret the changes in the quantities measured in SnSe by looking at the interlayer and intralayer bonding.

II. EXPERIMENT

Our SnSe sample was prepared in the following manner. Appropriate amounts of isotopically enriched (84.5% ^{119}Sn) tin of purity $\geq 99.95\%$ and selenium of the same purity to total 0.008 g were mixed in a quartz tube 25 mm in length, 4 mm o.d., and 3mm i.d. The tube was sealed under a vacuum of 5×10^{-5} torr and the sample heated to a temperature of 1000 °C in a furnace that allowed for periodic manual mixing. After $2\frac{1}{2}$h at 1000 °C, the sample was quenched in water.

An x-ray-diffraction measurement made with a Philips Model 12215/0 x-ray generator using a Debye-Scherrer camera (diam $= 5.73$ cm) and the $K\alpha$ line ($\lambda = 0.154$ nm) of Cu showed the SnSe occurring in a single phase.

The equipment used in the Mössbauer measurements has been described previously.[6] Ca ^{119}SnO$_3$ ($E_\gamma = 23.8$ keV) and ^{57}Fe ($E_\gamma = 14.4$ keV) sources were mounted on opposite ends of the same drive rod so that simultaneous

TABLE I. Bond lengths of the six heteropolar bonds in SnSe and related compounds (in Å) (Ref. 1). The Sn—Se bond marked with an asterisk is the bond between double layers. See the text for the definition of Δ (Ref. 1).

SnSe	SnS	GeS	GeSe
Sn(1)Se 2.77	Sn(1)S 2.62	Ge(1)S 2.47	Ge(1)Se 2.56
(2)Se 2.82	(2)S 2.68	(2)S 2.64	(2)Se 2.59
(2)Se 3.35	(2)S 3.27	(1)S 2.91	(2)Se 3.32
(1)Se 3.47*	(1)S 3.39	(2)S 3.00	(1)Se 3.37
$\Delta = 0.59$	$\Delta = 0.65$	$\Delta = 0.39$	$\Delta = 0.77$

measurements of the six-line spectrum of α-iron could be made to provide accurate velocity calibration. The spectra were analyzed using a least-squares Lorentz curve-fitting program.

The pressure measurements were made using two diamond-anvil cells of the National Bureau of Standards design. The sample chamber was created by a hole, 0.25–0.50 mm in diameter, cut in a 0.1-mm-thick gasket of W or a $W_{10}Ta_{90}$ alloy, centered between the diamonds ($\frac{1}{4}$ carat to $\frac{1}{3}$ carat). The pressure was hydrostatic, transmitted by a 16:3:1 mixture of methanol + ethanol + water. This mixture remains hydrostatic to 145 kbar at room temperature.[7] Each measurement was made at room temperature and took from 5 to 7 d to complete.

The pressure was measured in the cell by using ruby fluorescence. Three ruby chips were loaded into the cell along with the SnSe. Under pressure the ruby fluorescence lines shift to longer wavelengths according to the relationship $P = 2.76\Delta\lambda$, where the pressure P is measured in kbar and the wavelength shift $\Delta\lambda$ is measured in Å. This linear relationship holds for pressures up to 200 kbar.[8]

III. RESULTS AND DISCUSSION

A typical Mössbauer spectrum of SnSe is shown in Fig. 1. The line is split due to quadrupole interactions and the two halves of the doublet are labeled A and B for clarity. Figure 2 shows the change with pressure of the isomer shift of the centroid of this doublet. The change in the quadrupole splitting (the difference between the isomer shifts of A and B) as a function of pressure is presented in Fig. 3. All points were taken as a function of increasing pressure. Following each pressure run, a measurement was taken on the sample, released to atmospheric pressure (0.001 kbar). These are labeled as atmospheric postrun points on the graphs. All the data were taken on fragments of SnSe from the same sample batch. Although there were three separate runs made, no need was found to distinguish between the three when presenting the isomer-shift and quadrupole-splitting data.

The recoilless fraction was not directly measured due to difficulties the high-pressure experiment presents in determining the exact amount of SnSe in the sample chamber, a quantity necessary for the calculation. Instead, the effective thickness was measured, a quantity
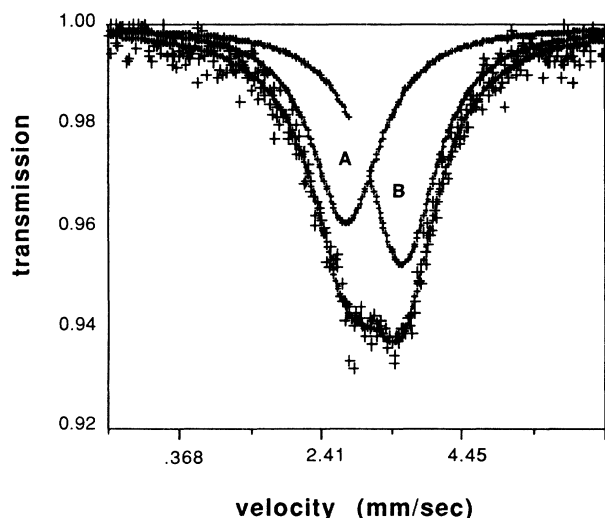

FIG. 1. The Mössbauer spectrum for SnSe at atmospheric presure (0.001 kbar). The quadrupole split line is labeled A and B for clarity. The unequal line intensities is illustrated clearly.
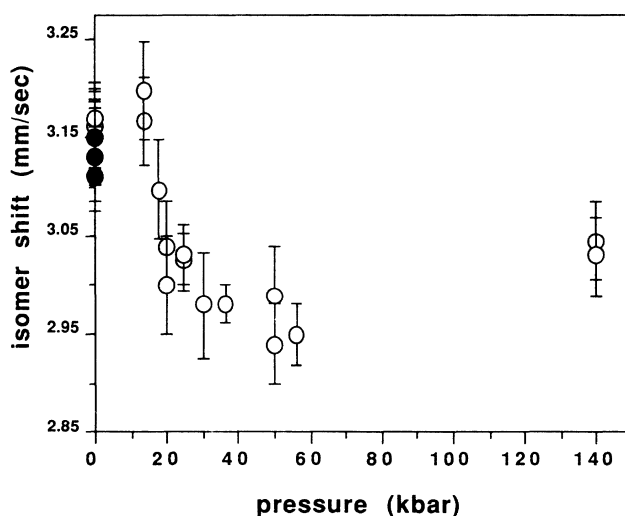
FIG. 2. Pressure dependence of the isomer shift of SnSe at room temperature. The solid circles represent atmospheric postrun points.
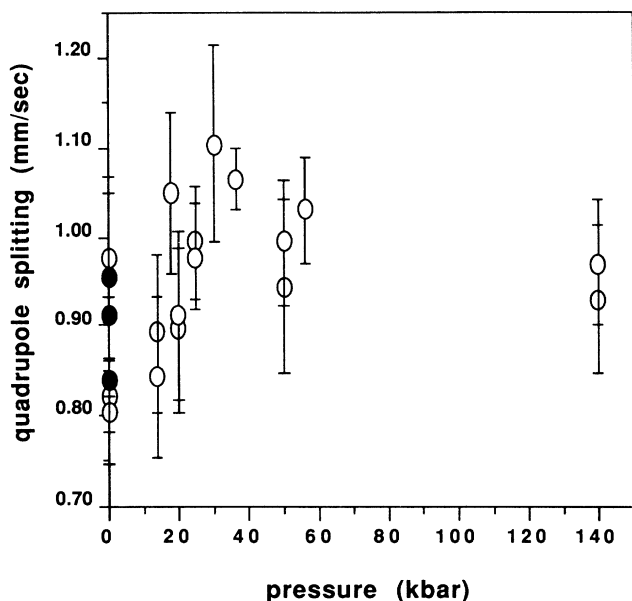
FIG. 3. Pressure dependence of the quadrupole splitting of SnSe at room temperature. The solid circles represent atmospheric postrun points.

The isomer shift δ is proportional to the difference in the probability density of the s electrons at the nucleus in the absorber (A) and the source (S):

$$\delta = \text{const} \times \{ |[\Psi_s(0)]_A|^2 - |[\Psi_s(0)]_S|^2 \} \ .$$

Screening effects of p, d, and f electrons, changes in the s-electron population, and changes in the chemical bonding of the atom all contribute to changes in the isomer shift. In SnSe, the two $5s$ and two $5p$ electrons of Sn will be most affected by changes in pressure. The differences in the location and shape of the p and s orbitals make the p electrons more sensitive to applied pressure. The volume the p orbitals occupy decreases with increasing pressure, resulting in an increase in the fraction of the wave function existing between the nucleus and the bulk of $|[\Psi_s(0)]_A|^2$, the s-electron density which involves contributions from all the s shells. The inner shells are not greatly affected by chemical bonding. The outer s shells, namely the $5s$ in Sn, contribute most to the isomer shift. The result of the increased screening of the $5s$ electrons by the $5p$ electrons is a decrease in the isomer shift.

The quadrupole splitting can also give information about the distribution of the charge around the nucleus
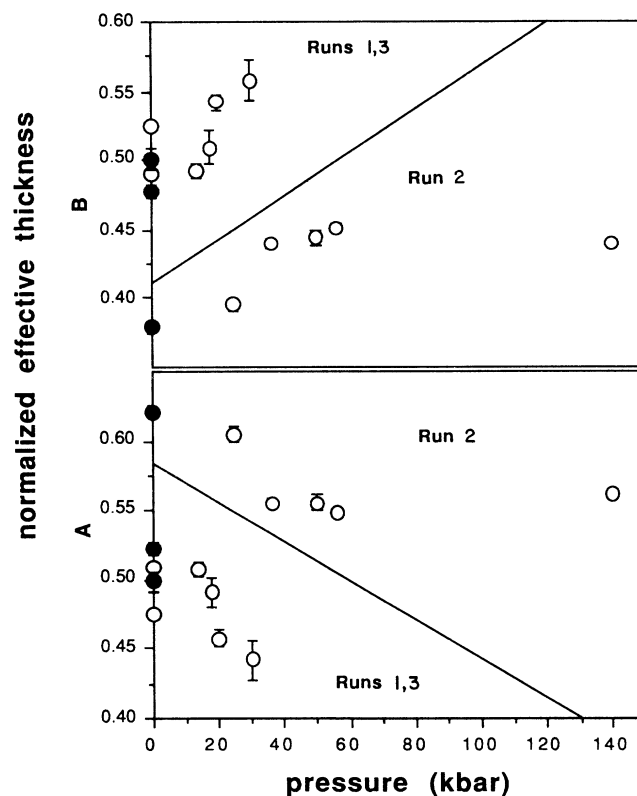
which is related to the recoilless fraction by the formula

$$T_a = f_a \sigma_0 t_a n_a \ ,$$

where T_a is the effective thickness, f_a is the recoilless fraction of the absorber, σ_0 is the Mössbauer cross section, and $t_a n_a$ is the areal density of the absorber, a quantity which varies only slightly when using a diamond-anvil cell for high-pressure experiments.[9] If the number of Sn sites does not change, a change in effective thickness means a corresponding change in the recoilless fraction, which is measured as a change in the depths of the resonances shown in Fig. 1. The effective-thickness data are presented in Fig. 4, in which both halves of the doublet (A and B) are shown normalized with respect to their sum. This inequality in the depths of A and B will be discussed later in this paper. Unlike the isomer-shift and quadruople-splitting data, the effective thickness data showed a link between the measured effective thicknesses and the different runs and, therefore, the runs are presented separately.

A. Isomer shift and quadrupole splitting

The isomer shift of the centroid shows a uniform decrease with increasing pressure between 14 and 30 kbar. In the range 30–55 kbar this decrease saturates. An additional data point taken at 140 kbar is consistent with this saturation. The isomer shift, as a measure of the electron density at the nucleus, would be expected to increase with increased pressure. A decrease in the isomer shift and thus in the electron density for [119]Sn has been observed in metallic tin[10] and in tin compounds such as SnO.[11]

FIG. 4. Normalized effective thickness vs pressure for the SnSe quadrupole split doublet. The lower graph contains the data for the A half of the doublet. The upper graph contains the data for B. The graphs are split into regions according to the different runs. Note that Run 2 is very different from Runs 1 and 3, arising possibly from a difference in sample orientation. The solid circles represent atmospheric postrun points.

because it is a measure of the interaction of the nuclear-quadrupole moment (assumed constant at these pressures) and the electric-field gradient at the nucleus. A larger quadrupole splitting results from an increase in the asymmetry of the charge around the nucleus. A larger fraction of the p-electron wave function near the nucleus would result in a larger electric-field gradient there, due to the asymmetric shape of the p orbitals. Thus the decreased isomer shift and increased quadrupole splitting with pressure both point to an increase in the asymmetry of the charge distribution.

The initial atmospheric pressure values of the quadrupole splitting show measurable differences among the different samples. This is evidence that the samples were not uniform, but composed of many crystallites containing a distribution of Sn sites as a result of strains due to grain boundaries and other defects commonly found in quenched samples. This would lead to a distribution of electric-field gradients and thus to a distribution of quadrupole splittings. Regardless of the initial value, the quadrupole splitting showed an increase with increasing pressure.

The changes in both the isomer shift and quadrupole splitting occur at pressures below 30 kbar. Above that pressure, both remain essentially constant. As was described earlier, SnSe is a layered material with strong intralayer and weak interlayer bonds. The pressure range below 30 kbar represents the range in which the interlayer distances are changing. To effect intralayer changes, pressures greater than 55 kbar (and probably greater than 140 kbar) would be required.

B. Effective thickness

The quadrupole splitting observed in the Mössbauer resonance results from the splitting of the $\frac{3}{2}$ excited state into two energy levels. The $(\pm\frac{3}{2},\frac{3}{2}+)\rightarrow(\pm\frac{1}{2},\frac{1}{2}+)$ and $(\pm\frac{1}{2},\frac{3}{2}+)\rightarrow(\pm\frac{1}{2},\frac{1}{2}+)$ transitions are the two halves of the doublet. A difference in the effective thickness of A and B means that one of these transitions is more likely to occur than the other. This inequality has been a subject of controversy in the field of Mössbauer spectroscopy, with two major influences competing as explanations of unequal line intensities.

Recall the relationship between the effective thickness and the recoilless fraction: $T_a = f_a \sigma_0 t_a n_a$. The recoilless fraction is related to the vibrational properties of the lattice:

$$f = \exp[-\langle x^2 \rangle / (\lambda/2\pi)^2] ,$$

where $\langle x^2 \rangle$ is the mean-square displacement from equilibrium of the atom along the direction of the incident γ ray, and λ is the wavelength of the incident γ ray. Therefore f will be larger for tightly bound atoms and smaller for those more loosely bound. As previously noted, the force constants within the layer in SnSe are much larger than those between the layers and therefore the mean-square displacement within the layer of the SnSe will be much smaller than that perpendicular to the layer. So the orientation of the crystallites with respect to the incident γ ray must be known and kept constant for this orientation factor to be eliminated. A tendency towards partial orientation in polycrystalline powders is called "texture." The sample orientation was not controlled in this experiment and so the effects of texture in the spectra cannot be ruled out.

The second influence on relative line intensities is the Goldanskii-Karyagin effect based on the interpretation that the recoilless fractions of each of the two transitions have different dependences on the angle between the incident γ ray and the principal axis of the electric-field gradient. Evidence of the Goldanskii-Karyagin effect was found in SnSe and SnS during a lattice-dynamical study,[12] but subsequent studies raise questions about the sign of the quadrupole constant used in the calculations and, therefore, the results obtained.[13]

The data in this study can be interpreted cautiously by looking at the difference in the effective thickness in the three runs. Run 1 (0.001–20 kbar) and Run 3 (0.001–30 kbar) both had sample fragments that were single flakes of SnSe, laid in the sample chamber perpendicular to the incoming γ rays. Run 2 (25–55 kbar, 140 kbar) had four SnSe fragments of irregular shape randomly oriented in the chamber. This difference resulted in a very different range of values for the effective thickness of Runs 1 and 3 versus Run 2. The orientation of the sample therefore had a demonstrable influence on the effective thickness. The presence or absence of the Goldanskii-Karyagin effect cannot be conclusively determined. It should also be noted that the effective thickness was more sensitive to counting statistics than were the isomer shift and quadrupole splitting, and that the previously mentioned distribution of quadrupole splittings may also be required to understand the effective-thickness data.

IV. CONCLUSIONS

This study of SnSe, using high-pressure techniques and Mössbauer spectroscopy, has produced more evidence that SnSe is a layered material intermediate between two and three dimensions. This evidence lies in the identification of two very different regions of behavior of the SnSe under pressure. For low pressures (below 30 kbar), the electron density of the Sn atoms decreases and the charge-distribution asymmetry increases. The effective-thickness data, while quantitatively inconclusive, do show great movement in this range and then a saturation for higher pressures. For higher pressures (between 30 and 55 kbar), very little change in the isomer shift, the quadrupole splitting, or effective thickness was measured. A single measurement taken at 140 kbar supports the argument that little change occurs above 30 kbar. While there are discontinuous changes with pressure in both the isomer shift and the quadrupole splitting, which might signal a phase transition, the inconclusiveness of the effective-thickness data and the reversibility, within error bars, point to this not being the case. An x-ray-diffraction study of IV-VI compound semiconductors corroborates this, finding that no phase transition occurs in SnSe up to 340 kbar.[14]

The pressure derivatives of the force constants for SnSe have not been measured, but a brief calculation using the

Table II. Ratios of intralayer (k_1) to interlayer (k_0) force constants for SnSe and other compounds. The 30-kbar value for SnSe is calculated, see text for details.

Material	k_1/k_0
As_2Se_3	14[b]
SnSe at 30 kbar	16
As_2S_3	17[b]
SnSe	21[a]
MoS_2	26.3[b]
SnS	31[a]
Graphite	100[b]

[a]Reference 3.
[b]Reference 15.

values for GeSe (Ref. 4) shows that the ratio of intralayer (k_1) to interlayer (k_0) force constants decreases from a value of 21 at atmospheric pressure[3] to 16 at 30 kbar. Table II compares these values with those of other layered compounds. At $k_1/k_0 = 100$, graphite exhibits the most layerlike behavior, while a value of $k_1/k_0 = 1$ would indicate that the interlayer and intralayer forces are of equal strength. The decrease in the value of the ratio for SnSe at 30 kbar signifies a decrease in its layerlike qualities, a move from being a predominantly two-dimensional material to a more three-dimensional one. A further extrapolation, assuming that the pressure coefficients remain constant, shows that the interlayer force constant of SnSe would become comparable to that of the intralayer vibrations at a pressure greater than 1 Mbar.

The two regions of response are attributed to the layered quality of the material. The interlayer spacing will change more rapidly than the intralayer spacing at lower pressures, since the interlayer bonds are much weaker than the intralayer bonds. The two-dimensional, layered SnSe is, under pressure, being made more three dimensional. Above 30 kbar, the less layerlike material is being squeezed, and little effect is evident in the isomer shift, quadrupole splitting, and effective thickness.

ACKNOWLEDGMENTS

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