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ANISOTROPY OF COMPRESSIBILITY AND THERMAL EXPANSION OF HEXAGONAL SELENIUM

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ABSTRACT

The anisotropic compressibility behavior of hexagonal Selenium has been determined by high pressure x-ray diffraction and also by high pressure neutron (time-of-flight) methods up to 52 kbars. The coefficients are: a-axis 31.9 ± 7, c-axis -14.3 ± 4, Volume 49.7 ± 15 $\text{kbars}^{-1} \times 10^{-4}$. The c-axis expands under pressure, where it is known that the c-axis contracts with increase of temperature. From measurements of the intensities of the diffracted beams, the changes of the Se-Se bond lengths and bond angle with pressure have been measured. The bond angle increases from 102.5° at room temperature and pressure to 105.7° at 52 kbars. The anisotropic behavior can be explained by the bond angles along the chain opening up with increase of pressure, the bond lengths along the chains remaining essentially constant and the distances between the chains decreasing markedly.

INTRODUCTION

Selenium is known to have a highly anisotropic thermal expansion behavior with a contraction of the c-axis with increase of temperature,[1] and anisotropic compressibilities have been reported with increase of the c-axis with increase of pressure.[2] Tellurium also exhibits analogous anisotropic physical properties.[3,4] The two properties of expansion and compressibility are related by the Grüneisen rule and thermodynamically.[5] To follow this anisotropic behavior, it is necessary to determine the changes of atomic positions within the unit cell, changes of bond angles and bond lengths, as pressure or temperature are changes, and these can be determined from the intensities of the diffraction pattern lines. However, the magnitude of the atomic displacements that can be measured experimentally is much greater with change of pressure than with change of temperature. Thus, generally speaking, a temperature difference of 1000°C or a pressure difference of 10 kilobars will produce the same magnitude of volume change. Static pressures can be obtained experimentally to several hundreds of kilobars. In the present study on Selenium, diffraction patterns have been recorded at pressures approaching 200 kilobars. There is also presently a discrepancy in various reported values of the volume compressibility of Se.[6,7,8]

EXPERIMENTAL

The anisotropy of compressibility of Selenium has been determined by two independent methods, neutron time-of-flight (TOF) as well as by x-ray diffraction. In neutron (TOF) diffraction, a polyenergetic neutron beam is chopped into bursts, impinges on the sample in a high pressure system, and diffraction occurs by Bragg's Law, though here with variable λ, Θ fixed. The diffracted neutrons spread out in time and are detected after a fixed flight path by proportional counters.[9] The TOF equation is $d = (hT)/2mL\sin\Theta$ where d is the crystal plane spacing, h Planck's constant, T time-of-flight, m neutron mass, L length of path and Θ the fixed Bragg diffraction angle. The high pressure system used was developed by Brugger and co-workers.[10] Fig. 1 shows a typical hexagonal Se diffraction pattern with NaCl used as an internal pressure standard.[11] The high pressure x-ray camera used was developed by Bassett and co-workers[12] and was mounted on a GE X-ray Diffractometer. A typical diffraction pattern is shown in Fig. 2 obtained by step scanning. Details of the experimental systems will be published elsewhere.[13]

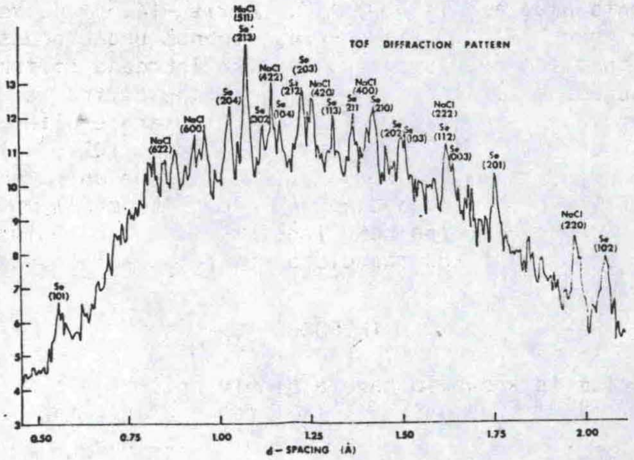

Fig. 1. Neutron TOF diffraction pattern of selenium.

From the displacement of the diffraction lines, the compressibility coefficients along the a and c-axes have been determined. These are shown in Fig. 3 up to pressures of 80 kbars. It is seen that the c-axis expands whilst the a-axis contracts with increase of pressure, and the coefficients are listed in Table 1.

To determine the bond lengths and angles, intensities of diffraction lines must be measured and these were obtained from the high pressure x-ray diffraction system up to 52 kbars. The n (TOF) system was not working at optimum conditions and further developments are being carried out by Dr. T. G. Worlton and co-workers at Argonne National Laboratory where the system has been moved from Idaho Nuclear Corp.

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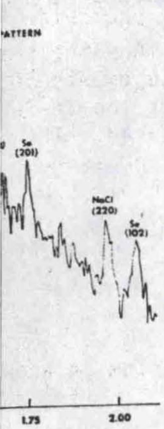

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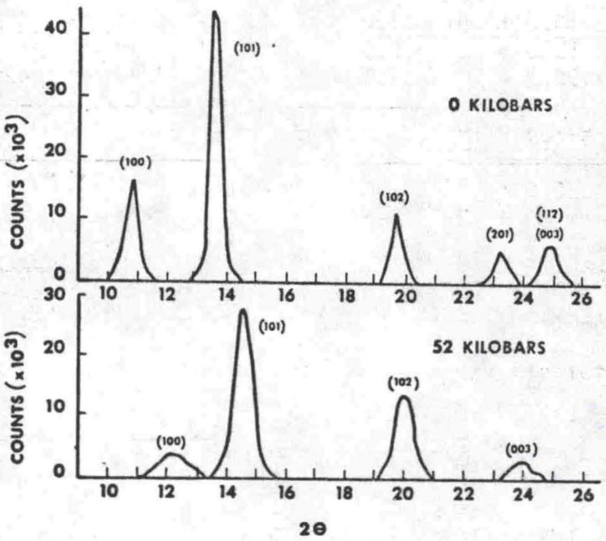

Fig. 2. X-ray diffraction pattern of selenium.

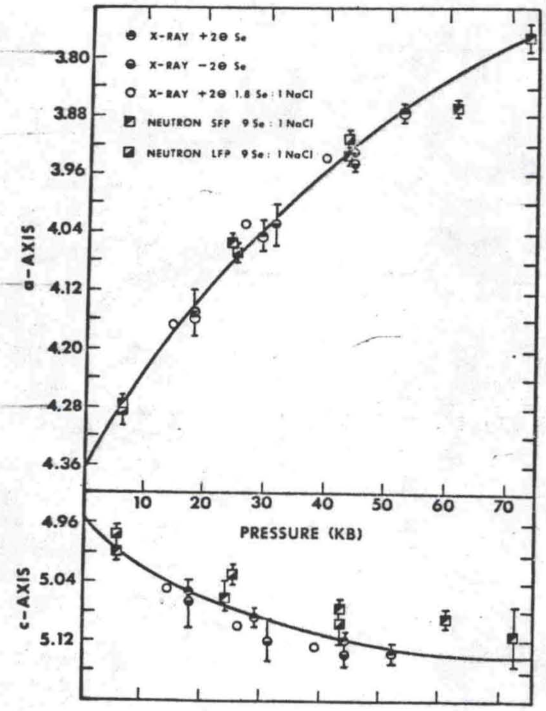

Fig. 3. Change of selenium lattice parameters with pressure.

Table I Zero Pressure Compressibilities ($\times 10^{-4}$ kbar^{-1})

	Neutron TOF SFP	 LFP	X-ray Diffractometer +2Θ	 -2Θ
a-axis:	36.0 ± 5	33.0 ± 10	30.8 ± 5	29.0 ± 10
c-axis:	-15.6 ± 2	-8.5 ± 7	-15.5 ± 2	-16.0 ± 5
Volume:	56.2 ± 10	57.7 ± 25	45.3 ± 12	42.8 ± 20
	X-ray Film	Average		
a-axis:	30.9 ± 5	31.9 ± 7		
c-axis:	-15.8 ± 2	-14.3 ± 4		
	46.5 ± 10	49.7 ± 15		

DETERMINATION OF BOND ANGLE AND BOND LENGTHS

The crystal structure details of Se are as follows.

LATTICE PARAMETER (26°C)

$a = 4.3662$ A.U. $c = 4.9536$ A.U.

SPACE GROUP $P3_121$

THREE ATOMS PER UNIT CELL

WYCKOFF ATOMIC POSITIONS

$$u00,\ \overline{uu}\tfrac{2}{3},\ 0u\tfrac{1}{3}$$

$$u = 0.2254$$

The atomic position parameter u is obtained from the intensities of the diffraction lines.[14] From the atomic position parameter u, the bond lengths and angles can be derived, where the bond length along the chain,

$$B1 = \left[\left(\frac{c}{3}\right)^2 + 3(ua)^2\right]^{1/2},$$

the bond length between chains

$$B4 = \left[\left(\frac{c}{3}\right)^2 + (3ua)^2 - a^2(3u-1)\right]^{1/2},$$

and the chain bond angle, BA is given by

$$\text{Arcos}\ \left[2(B1)^2 - (B2)^2\right]/2(B1)^2$$

where B2 is the distance of second nearest Se along the chain.

The values of u obtained from the experimental data are given in Table II where it is seen that u changes from about 0.23 at RTP (room temperature and pressure) to about 0.25 at 52 kbars. Using this variation with pressure of u, the bond lengths and angles are

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5	29.0 ± 10
2	-16.0 ∓ 5
12	42.8 ± 20

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shown in the graphs of Fig. 4 and the values presented in Table III.

Table II Variation of Atomic Position Parameter (u) with Pressure

Pressure (kbar)	Parameter u
RTP	0.230
RTP	0.227
18	0.241
18	0.240
29	0.249
31	0.248
44	0.250
44	0.250
52	0.248
RTP	0.227
RTP	0.227

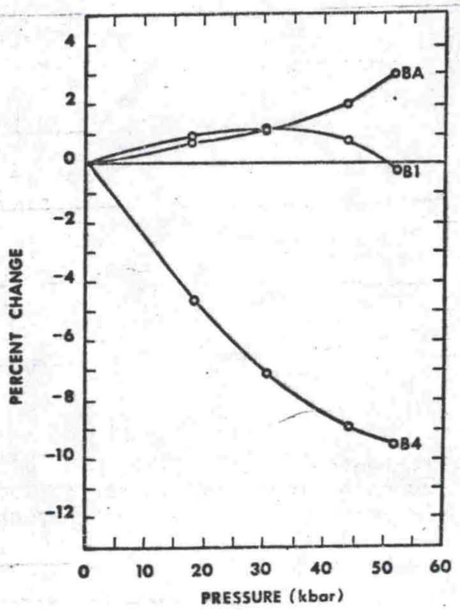

Fig. 4. Change of selenium bond lengths (BI and B4) and chain bond angle (BA) with pressure. B4 is distance between chains and BI nearest neighbors distance along chains.

Table III Variation of Bond Lengths and Angles with Pressure

Pressure (kbar)	Bond Lengths (A.U.) Along Chain	Perpendicular to Chain	Bond Angle
0	2.39	3.42	102.5
18	2.42	3.27	103.3
30	2.43	3.18	103.7
44	2.42	3.12	104.7
52	2.39	3.09	105.7
Standard Deviations	±0.03	±0.03	±1.0

DISCUSSION

The anisotropic behavior of the compressibility is thus explained by the bond angles along the chain opening up with increase of pressure, the bond lengths along the chain remaining approximately constant, and the chains packing more closely together. The bond angle opens up from about 102.5° at RTP to about 105.7° at 52 kbars. It is now possible to see that the atomic readjustments with increase of temperature will be extremely small, and that the Se-Se-Se bond angle will change by about 0.1° for a temperature change of 200°C. Such a small angular change would be most difficult to measure.[15]

The thermal expansion and compressibility of hexagonal Te and Se are compared in Table IV where they are seen to be very similar.

Table IV Comparison of Hexagonal Te and Se

	Te	Se
Compressibilities (x10^{4}kbar^{-1})		
a-axis	28.0	31.9
c-axis	-5.0	-14.3
Thermal Expansion Coefficients (x10^{-6}°C^{-1})		
a-axis	27.5	74.1
c-axis	-1.7	-17.9

Both Te and Se transform at high pressures at the same c/a ratio of 1.42. For Se this occurs at about 140 ± 10 kbars.[13]

The high pressure x-ray and neutron diffraction systems used permitted only a very limited amount of diffraction information to be recorded, so that at present only those crystal structures depending on one or two atomic position parameters can be studied at pressure to derive bond angles and lengths. For more versatile studies a single crystal high pressure diffraction system will be necessary.

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