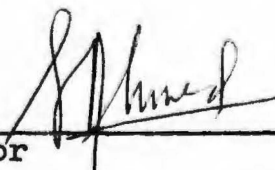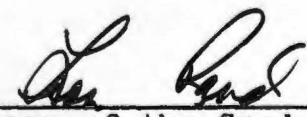# PHASE TRANSFORMATION IN PURE SELENIUM

by

Michael J. Buczek

Submitted in Partial Fulfillment of the Requirements

for the Degree of

Master of Science in Engineering

in the

Metallurgical Engineering

Program

Advisor   June 12, 1975   Date

Dean of the Graduate School   June 16, 1975   Date

YOUNGSTOWN STATE UNIVERSITY

August, 1975

ABSTRACT

PHASE TRANSFORMATION IN PURE SELENIUM

Michael J. Buczek

Master of Science in Engineering

Youngstown State University, 1975

Pure selenium transforms upon cooling from the hexagonal close packed to the diamond cubic phase. The lattice parameters of the hexagonal close packed phase are a=4.3615A and c=4.9633A. The lattice parameter of the diamond cubic phase is a=5.0672A. The enthalpy of phase transformation on cooling associated with this phase transformation is 77 cal/mole. There is an indication that the hexagonal close packed phase can be stabilized upon annealing at elevated temperatures. The habit plane of transformation is close to the 011 plane of the cubic phase.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

PHASE TRANSFORMATION IN PURE SELENIUM

Introduction

Selenium, the 40th most abundant element on earth, was discovered in 1817 by J.J. Berzelius in the form of a residue leftover during studies concerning processes for production of sulfuric acid. Selenium, atomic number 34 and atomic weight 78.96, falls between bismuth and gold in the periodic chart and is rarely found in its native state. Its most frequent recovery is as a by-product in the refinement of base metal ores of lead, copper, and nickel.

After its discovery in 1817, some fifty years passed until selenium became more than a laboratory curiosity. In 1873, W. Smith found that the electrical resistance of selenium decreased with an increase in the intensity of light. This discovery was an important step in the development of the photoelectric cell.

Industrial usage of selenium is also quite important. The glass and ceramic industry uses selenium as a decolorizer. When added to glass, it tends to prevent the greenish tint caused by the presence of iron. When combined with cadmium, a ruby-red tint is produced in glass. The steel industry has also found a use for this element as not only a degasifier in stainless steel, but also as an aid in machinability.

The rubber industry employs selenium as a vulcanizing agent in concentrations of 0.1 to 2.0 percent. Selenium dioxide is used as an oxidizing agent in the preparation of cortisone. Selenium in the oxychloride form is a most powerful solvent for paint and varnish, rubber resins, glue, and synthetic phenolic resins, at one time considered insoluable.

The density of selenium (20°C) is 4.8 gm/cc and the melting and boiling points are 217°C (423°F) and 688°C (1270°F), respectively.[1] Selenium, in fact, has the sixth lowest boiling point of all elements, just below that of tin.

Selenium's chemical behavior can be classified as being between that of sulfur and tellurium. During compound formation, selenium acts as a non-metal. Selenium will tend to form acidic compounds, especially when in its higher valency states. Selenium exists in three valance levels. They are -2 in the hydride, +4 in the dioxide, and +6 in the selenates.[2]

Selenium is a member of the oxygen-sulfur family. Like sulfur, it exists in a number of allotropic forms, although they are not as well defined as those of sulfur. The stable form of selenium exists as the hexagonal structure. The atoms are arranged in three-fold spiral chains with axes

---

[1]M. Hansen, Constitution of Binary Alloys (New York, N.Y.: McGraw-Hill Book Company, 1958) p. 440.

[2]C.A. Hampel, Rare Metals Handbook (New York, N.Y.: Reinhold Publishing Company, 1954) p. 369.

parallel to the crystallographic c-axis.[3,4] Bonding between atoms is covalent, while that between the chains is Van der Walls type. The hexagonal form of selenium is a good conductor of electricity and is slowly formed by heating amorphous selenium at $90^{\circ}C$ to $217^{\circ}C$ ($194^{\circ}F$ to $423^{\circ}F$) or monoclinic selenium (discussed later) at $120^{\circ}C$ ($248^{\circ}F$).[5,6] The lattice parameters for the hexagonal structure are a=4.3662A and c=4.9536A.[7]

Two cubic modifications of selenium have been reported.[8,9] These cubic modifications have been produced by vacuum evaporation of selenium at $20^{\circ}C$. They appear to have a diamond cubic lattice which transforms to hexagonal selenium at $130^{\circ}C$.

Amorphous selenium is produced by quenching molten selenium.[10,11] The structure of amorphous selenium has been

---

[3]Das and Bever, "Thermodynamics Investigation of Crystallic and Amorphous Se-Te Alloys," Met. Trans. (June 1973) p. 1457.

[4]K.W. Bagnall, The Chemistry of Selenium, Tellurium, and Polonium (London, England: Elsevier Publishing Company, 1966).

[5]Hampel, p. 369

[6]Das and Bever, p. 1457

[7]"Powder Diffraction File," Joint Committee on Powder Diffraction Standards 6-0362 (Philadelphia, PA).

[8]Bagnall

[9]Andrievskii and Nabitovitch, Kristallografiya, 5 (1960), 465.

[10]Hampel, p. 369

[11]Das and Bever, p. 1457

determined by Raman scattering, dissociation behavior and viscosity measurements. The structure consists of long polymer chains and eight member monomer rings in various proportions.

Monoclinic selenium is formed by crystallization from carbon disulfide. The monoclinic form separates when the carbon disulfide solution is evaporated.[12,13,14]

In the present investigation, attempts have been made to investigate the phase transformation in pure vacuum evaporated selenium by x-ray and thermodynamic studies. The x-ray studies conducted determined the crystal structure of the low and high temperature modifications of pure selenium. The thermodynamic properties of both phases, including the enthalpy of phase transformation, were also determined by separate investigation.

---

[12]Bagnall

[13]"Selenium," Van Norstrands Scientific Encyclopedia, (New York: D. Van Norstrand Company, Inc., 1947).

[14]Iizima, Taynai and Nicolet, "Preparation and Identification of Selenium Monoclinic Crystals Grown from Selenium-Saturated CS_2," Proceeding of the International Symposium (Montreal, Canada: 1967).

CHAPTER II

EXPERIMENTAL PROCEDURE

A. Sample Preparation

Two pure selenium specimens were used in this investigation. One sample (Sample A) was prepared from material produced by Material Research, Inc., (99.999% pure) while the second specimen (Sample B) was obtained from a research laboratory. This sample, B, was vacuum deposited selenium (99.9999% pure).

Sample A was melted in 3/4-inch diameter quartz tubing. Before melting the quartz tubing was cut into one foot lengths and one end sealed with an oxy-acetylene torch. A section of the tube near the open end was then necked down to approximately 1/8-inch in diameter to facilitate sealing when the contents were under vacuum. Each tube was then scrupulously cleaned with potassium dicromate, water, acetone, and ether. The selenium was also rinsed in acetone and ether prior to insertion into the tubes. After the material was placed in a tube, the tube was attached to a Kinney high vacuum pump, and allowed to run until a vacuum of 10^{-6} torr or less was attained. The tube was then sealed in the necked down region using an oxy-acetylene torch. Each tube was then placed into an upright electric muffle furnace for melting. The temperature was kept at 650°C. After the sample was

molten it was shaken vigorously at regular intervals to assure removal of entrapped gases. The sample was kept in the molten state for one hour then removed from the furnace and allowed to solidify. Sample A was then annealed at a temperature -55°C below the solidus temperature (220°C) for 15 days then furnace cooled to room temperature. This annealing operation was done to substantiate an earlier claim that the as-cast and annealed selenium has a regular hexagonal structure.

For x-ray studies Sample B was prepared from powder obtained from the as- received vacuum evaporated sample. The powders were bonded together by Duco cement to form a compact sample.

For thermodynamic studies Sample C was prepared by melting the vacuum evaporated selenium under vacuum of 10^{-6} torr. The weight was approximately 50 grams.

Thermodynamic studies were done by Mr. J. Patel and Dr. S. Ahmed. The procedure for this is described below.

B. Thermodynamic Studies

The apparatus used for the thermodynamic studies was a modified Olsen Calorimeter. The calorimeter consists of a thermos flask in which the calorimeter media is placed. The thermos flask is surrounded by styrofoam insulation. A teflon cap covers the top of the flask. Besides acting as an insulator the cap supports a thermopile (consisting of six thermocouples), a sample thermocouple, and a quartz

thermometer. The sample is located at the thermocouple tip and is surrounded by a thin-walled copper capsule. A magnetic stirrer is located at the bottom of the thermos flask. Instruments used for signal conditioning are a nanovolt amplifier, which amplifies the output of the thermopile and acts as a zero suppression unit, a K-3 potentiometer, which measures the zero suppression voltage, and an x-y recorder. A weighted amount (1160 grams) of spectro-quality isopropyl alcohol was placed into the cleaned thermos flask. The flask was then placed into the styrofoam jacket and the teflon cap placed on top of the flask, allowing the thermopile to be inserted into the media. The quartz thermometer was also placed into the media through the proper hole in the teflon cap. The magnetic stirrer was then turned on. A sample was placed on the sample thermocouple and put into a furnace. When the temperature of the sample reached approximately 200°C, the sample and thermocouple were quickly removed from the furnace, and the copper capsule secured around it. The capsule was then rapidly placed into the media through the hole in the center of the teflon cap. The change in temperature of the media and the sample were simultaneously measured and recorded.

C. X-Ray Studies

Specimen A was cut longitudinally for x-ray studies. One side of the longitudinal section was ground flat and carefully mechanically polished to reduce the amount of cold work at the surface. A Norelco diffractometer with copper

radiation and a nickel filter was used to determine the intensity and the Bragg angle (2θ) for all samples at different temperatures.

CHAPTER III

EXPERIMENTAL RESULTS

A. Thermodynamic Results

Thermodynamic parameters were calculated from studies done on the Modified Olsen Calorimeter. The experimental results consisted of a plot of the change in temperature of the calorimeter media as a function of temperature of the sample. From this data, the enthalpy per mole (H) of each sample was determined using the following equation:[15]

$$H = K(wCp\Delta T) \qquad (1)$$

where,   w = weight of the calorimeter media

ΔT = change in temperature of the isopropyl alcohol

Cp = specific heat for isopropyl alcohol at a specific temperature

K = constant determined using,

$$\frac{\text{atomic weight Se (\% Se)}}{\text{weight of the sample}}$$

A plot of ΔH versus T was then made, where T is the temperature of the sample in degrees Kelvin. These curves were corrected for exchange of heat between the system and

---

[15]M. Buczek, L. Mady, B. Carothers, Thermodynamic Properties of Dilute Tl-Cd Alloys, Undergraduate Thesis, Youngstown State University, June 1971.

surroundings as a function of time. The corrected ΔH values are shown in Figure 1 versus temperature.

The Gibbs free energy was then determined for Sample C by use of the Gibbs-Helmholtz equation as follows:[16]

$$\frac{\partial \frac{\Delta F}{T}}{\partial \frac{1}{T}} = \Delta H$$

$$\int_{T_1}^{T_2} \partial \frac{\Delta F}{T} = \int_{T_1}^{T_2} \Delta H \, \partial \frac{1}{T}$$

$$\frac{\Delta F_2}{T_2} - \frac{\Delta F_1}{T_1} = \int_{T_1}^{T_2} \Delta H \, \partial \frac{1}{T}$$

Since the standard state is at a temperature T_1 ($452^{\circ}K$), $\Delta F_1/T_1 = 0$. Therefore, $\Delta F = T_2 \int_{T_1}^{T_2} \Delta H \, \partial \frac{1}{T}$. (2)

From this equation, the values of ΔF were determined by plotting ΔH_c versus $1/T$. The area under this curve was then multiplied by the proper temperature to give ΔF. These results are presented in Figure 2.

It should be noted that the free energy curves of the low and high temperature phase intersect at the transformation temperature on cooling ($T_c = 441^{\circ}K$), not at the equilibrium temperature T_o.

---

[16] L. Darken and R. Gurry, Physical Chemistry of Metals (New York, N.Y.: McGraw-Hill Book Company, 1953) p. 223.

B. X-Ray Results

The x-ray results are shown in Tables 1 through 5 as specified below:

Table 1 - Sample A at room temperature

Table 2 - Sample A at 167°C

Table 3 - Sample A at 178°C

Table 4 - Sample B at room temperature

Table 5 - Sample B at 170°C

The Bragg angle values were tabulated and indexed to determine the Miller Indices of the plane associated with each θ value.[17] After indexing, the crystal structures were determined as specified below:

1. Hexagonal Close Packed

This method of indexing involved the manipulation of $\sin^2\theta$ values to find multiple integers which define relationships between them. Each crystal structure has a characteristic relationship between $\sin^2\theta$ values, and identification of these relationships leads to a solution to the crystal structure. For the hexagonal close packed system the $\sin^2\theta$ values must follow the relation:

$$\sin^2\theta = \frac{\lambda^2}{3a^2}(h^2+hk+k^2) + \frac{\lambda^2}{4c^2}l^2 \qquad (3)$$

---

[17]B. Cullity, Elements of X-Ray Diffraction (Reading Massachusetts: Addison Wesley Publishing Company, 1956) p. 459.

Permissible values of (h^2+hk+k^2) are 1, 3, 4, 7, 9, 12, 13, 16, 19, 21, etc. To arrive at these multiples, the $\sin^2\theta$ values are divided by 1, 3, 4, etc., and these numbers examined to find $\sin^2\theta$ values which are equal or multiples of each other. In this manner the proper indices can be assigned to each $\sin^2\theta$ value and the subsequent crystal structure determined.

2. Diamond Cubic

In the diamond cubic structure, the $\sin^2\theta$ values follow the relationship:

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2+k^2+l^2) \tag{4}$$

The $(h^2+k^2+l^2)$ term is always integral and the $\lambda^2/4a^2$ term is constant for any one pattern. Manipulation of the term $(h^2+k^2+l^2)$ to find a set of integers which will yield a constant quotient when divided one by one into tabulated $\sin^2\theta$ values results in the indices hkl for each $\sin^2\theta$ value.

The calculation of the lattice parameters for each phase is then accomplished by substituting hkl values back into the two previously mentioned equations and solving for lattice parameters a and c.

The a and c values for the different samples in the hexagonal phase at various temperatures (Sample A) are shown in Table 6 and Figures 3 and 4. The lattice parameter of the diamond cubic phase (Sample B) is also shown in Table 6.

CHAPTER IV

DISCUSSION OF RESULTS

Pure selenium undergoes a phase transformation on cooling from hexagonal close packed to diamond cubic structure at $441^{\circ}K$. This is accompanied with an enthalpy of phase transformation of 77 cal/mole. The specific heats (dH/dT) of pure selenium obtained from enthalpy data are shown in Table 7.

The x-ray results indicate that the hexagonal phase has lattice parameters of a=4.3615A and c=4.9633A. The diamond cubic structure has a lattice parameter of a=5.0672A. It appears the diamond cubic structure is composed of two unit cells as has been observed in other alloy systems. One of these unit cells transforms to a unit cell of the hexagonal close packed structure. It was observed that the annealing process stabilizes the hexagonal close packed structure. This was observed in Sample A which remained hexagonal close packed at room temperature. This stabilization was successfully utilized to determine the coefficient of expansion of lattice parameters a and c of the hexagonal phase using Figures 3 and 4. These results are presented in Table 8. These coefficient

of expansion values were utilized to calculate room temperature
a and c values of the high temperature hexagonal phase which
transformed from the room temperature diamond cubic phase.
It may be noted that the lattice parameters for Samples A
and B in the hexagonal phase agree well.

The Wechsler-Lieberman-Read Theory (WLR) allows deter-
mination of the habit plane from knowledge of the lattice
parameters of both phases. The equations that are useful in
obtaining h, k, and l values are given below. These are
equations 32, 33, and 34 in the WLR paper:[18]

$$h = \frac{1}{2\eta_1}\left\{ \sqrt{\frac{\eta_1^2 + \eta_2^2 - 2\eta_1^2\eta_2^2}{1 - \eta_2^2}} - \sqrt{\frac{2 - \eta_1^2 - \eta_2^2}{1 - \eta_2^2}} \right\} \qquad (5)$$

$$k = \frac{1}{2\eta_1}\left\{ \sqrt{\frac{\eta_1^2 + \eta_2^2 - 2\eta_1^2\eta_2^2}{1 - \eta_2^2}} + \sqrt{\frac{2 - \eta_1^2 - \eta_2^2}{1 - \eta_2^2}} \right\} \qquad (6)$$

$$l = \frac{1}{\eta_1}\sqrt{\frac{\eta_1^2 - 1}{1 - \eta_2^2}} \qquad (7)$$

[18]M.S. Wechsler, et al, "On the Theory of Formation of
Martensite," Journal of Metals, Trans, AIME, Volume 197, (New
York, N.Y.: Nov. 1953)

To calculate the η values one needs to know the lattice parameters of the diamond cubic phase at room temperature and the extrapolated value of the hexagonal close packed phase at room temperature. These values are given in Table 9 along with the volume of each unit cell and the percent change in cell volume associated with the transformation.

These lattice parameters were then used to calculate η_1 and η_2 and subsequently h, k, and l. The calculation of η_1, η_2 and hkl are as follows:

$$\eta_1 = \frac{2a}{a_o} = \frac{2(4.3675)}{5.0672} = 1.219 \tag{8}$$

$$\eta_2 = \frac{c}{a_o} = \frac{4.9623}{5.0672} = 0.979 \tag{9}$$

$$h = \frac{1}{2(1.219)} \left\{ \sqrt{\frac{(1.219)^2+(0.979)^2-2(1.219)^2(0.979)^2}{1-(0.979)^2}} \right.$$
$$\left. - \sqrt{\frac{2-(1.219)^2-(0.979)^2}{1-(0.979)^2}} \right\} = -.0627i$$

$$k = \frac{1}{2(1.219)} \left\{ \sqrt{\frac{(1.219)^2+(0.979)^2-2(1.219)^2(0.979)^2}{1-(0.979)^2}} \right.$$
$$\left. + \sqrt{\frac{2-(1.219)^2-(0.979)^2}{1-(0.979)^2}} \right\} = 2.603i$$

$$1 = \frac{1}{1.219} \sqrt{\frac{(1.219)^2 - 1}{1 - (0.979)^2}} = 2.79$$

It appears that the habit plane is close to the 011 plane of the diamond cubic phase.

The Bain distortion in this case involves the movement of atoms as indicated in Figure 5. This involves expansions on the a-axis of 16.2% and on the c-axis of 20.9%.

This investigation directly results in the determination of the crystal structures of the high and low temperature modifications of pure selenium.

Pure selenium transforms upon cooling from the hexagonal close packed to the diamond cubic phase. The lattice parameters of the hexagonal close packed phase are a=4.3615A and c=4.9633A. The lattice parameter of the diamond cubic phase is a=5.0672A. The enthalpy of phase transformation on cooling associated with this phase transformation is 77 cal/mole. There is an indication that the hexagonal close packed phase can be stabilized upon annealing at elevated temperatures. The habit plane is close to the 011 plane of the cubic phase.

APPENDIX A

<u>Figures</u>
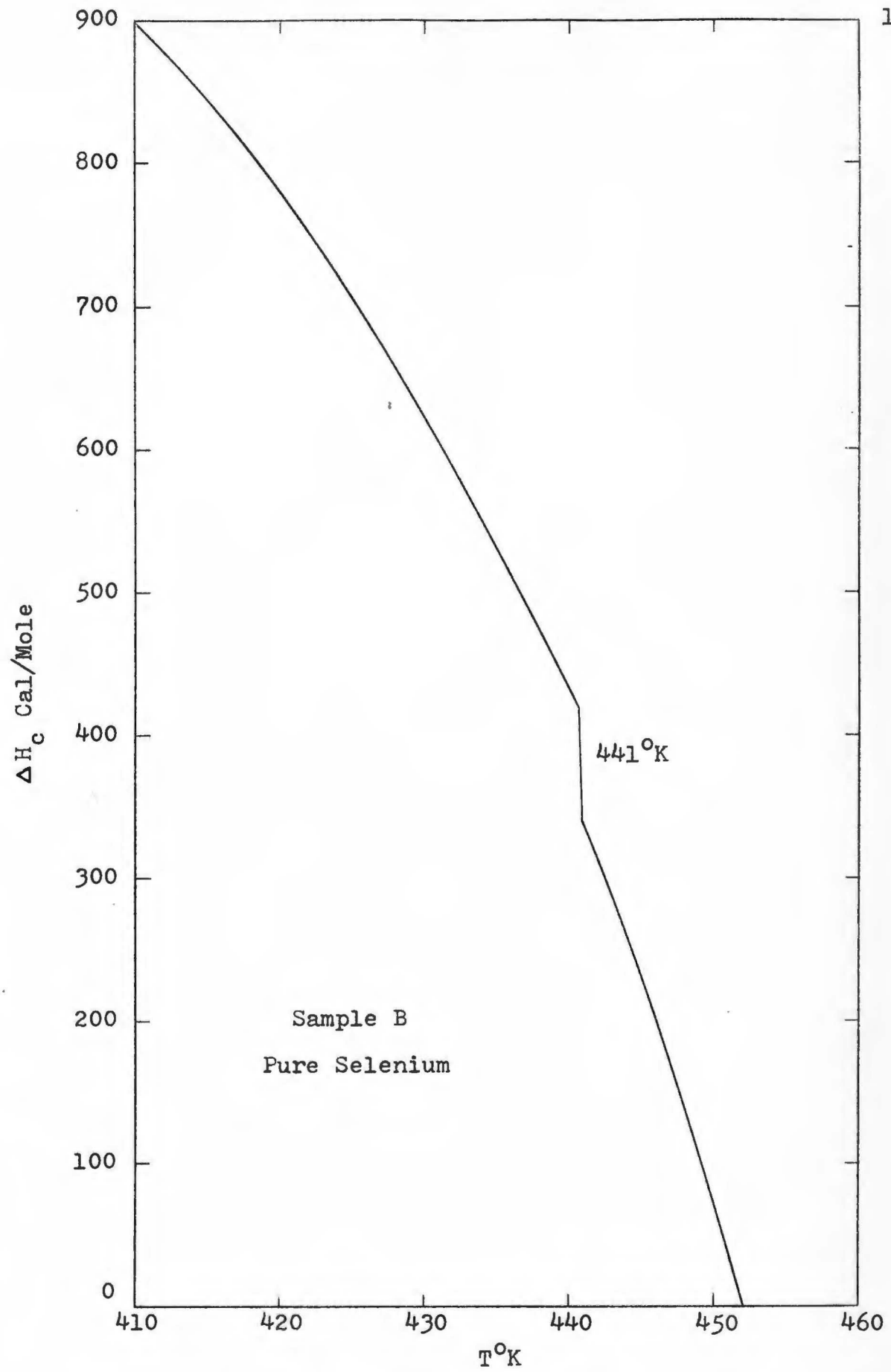
Fig. 1. ΔH_c as a Function of Temperature.
(Unpublished Result of J. Patel and S. Ahmed. Used with Permission.)
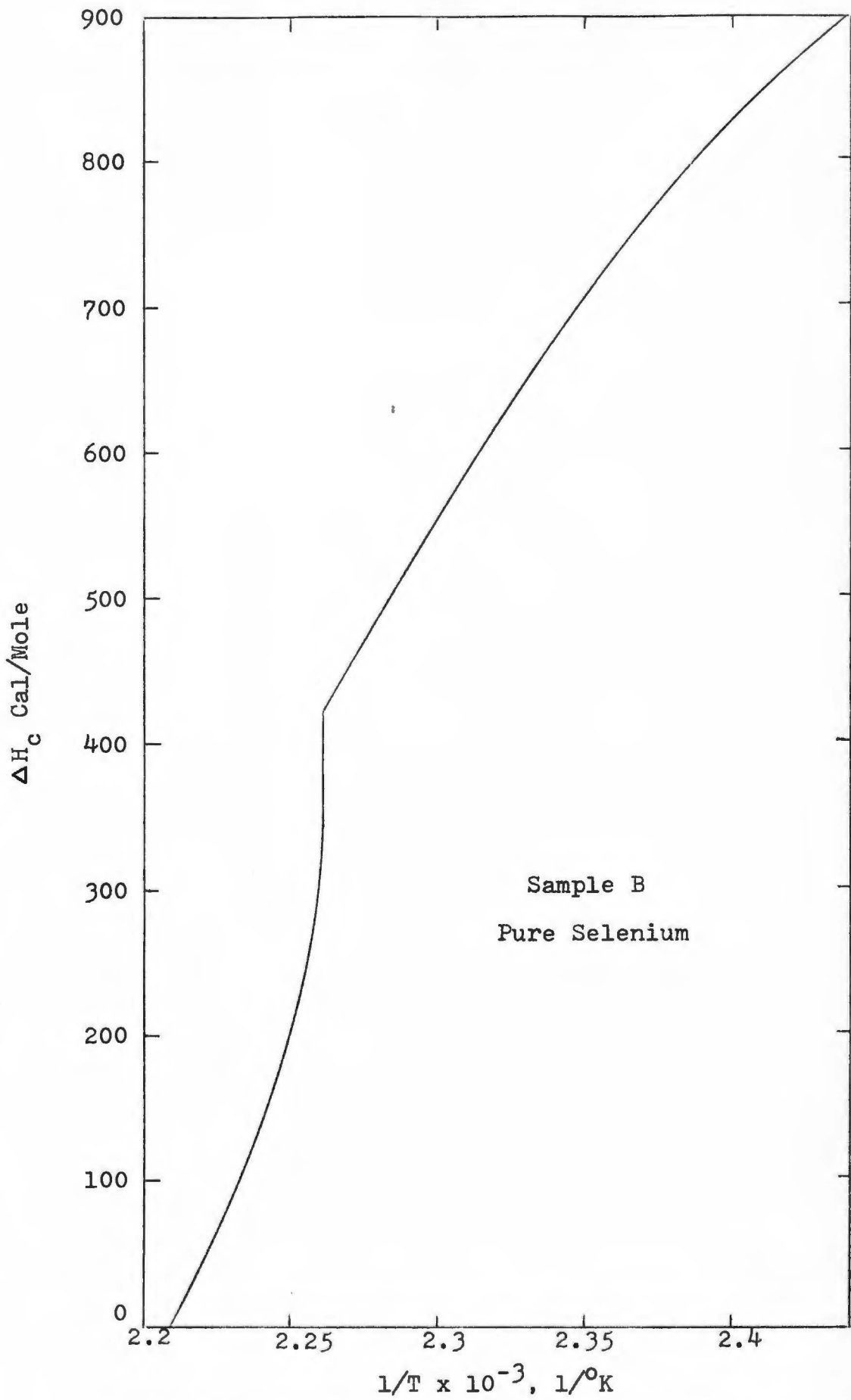
Fig. 2. ΔH_c Values as a Function of $1/T$.
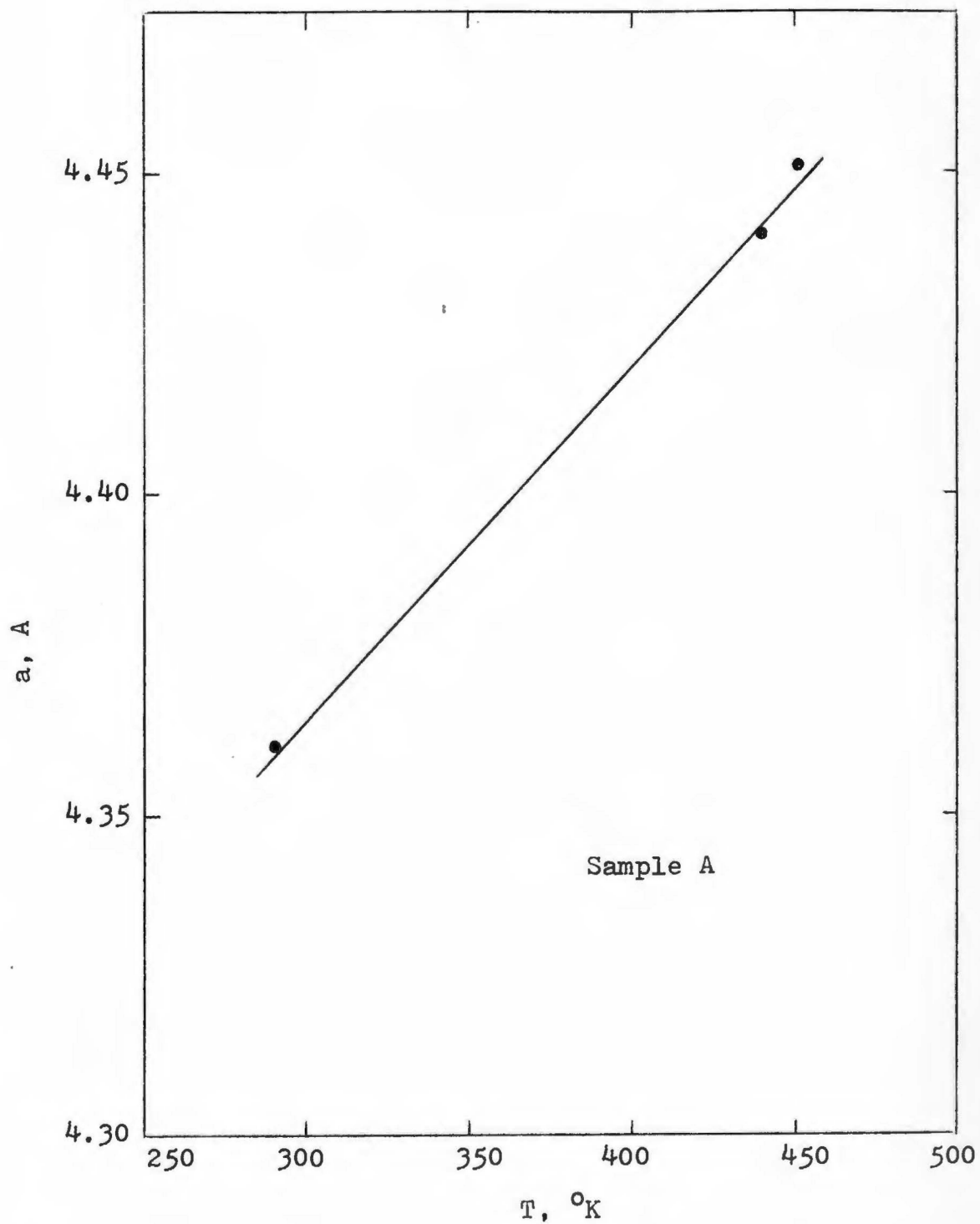
Fig. 3. Variation in Lattice Parameter a for
Hexagonal Selenium as a Function of Temperature.
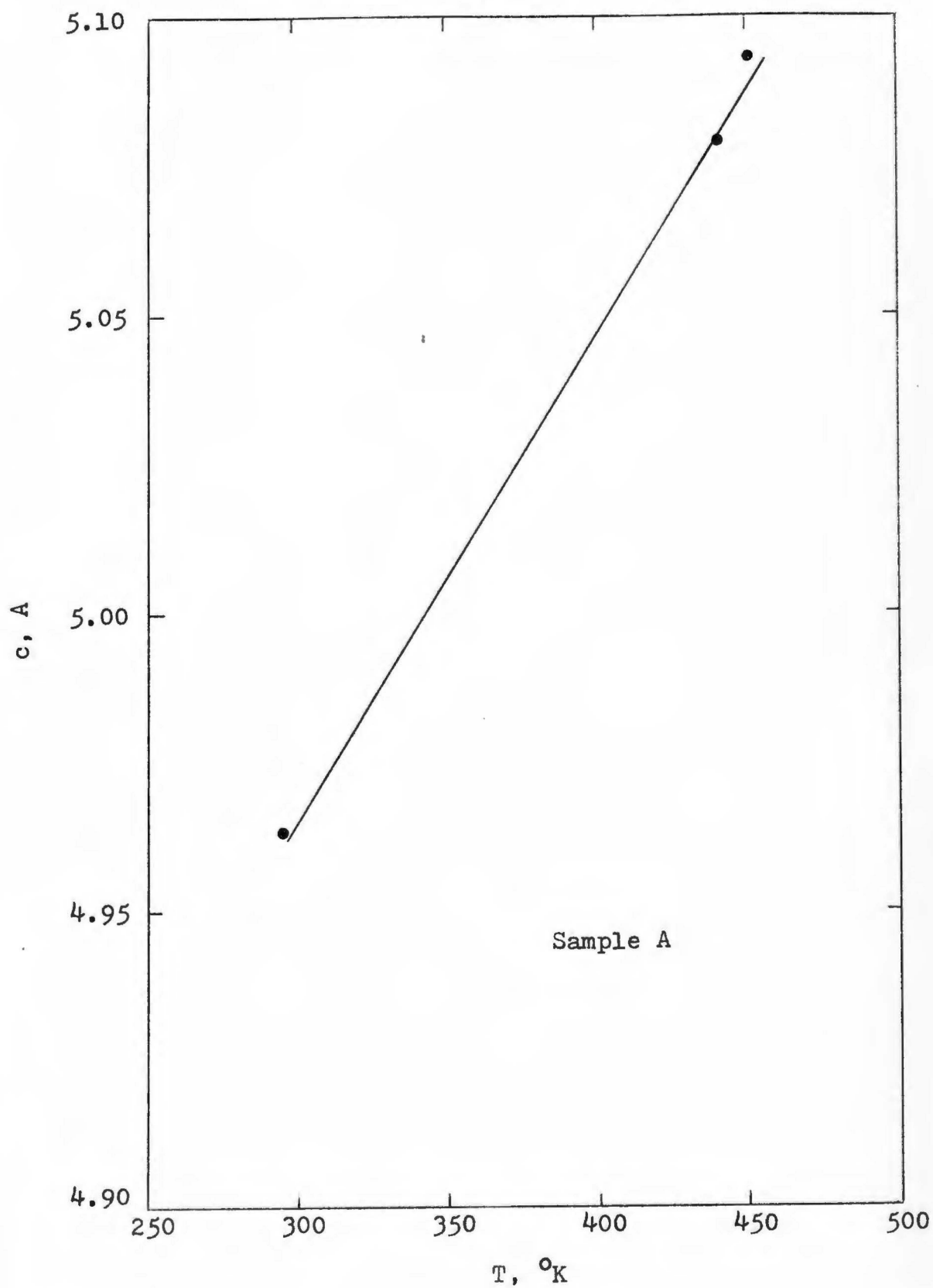
Fig. 4. Variation of Lattice Parameter c for Hexagonal Selenium as a Function of Temperature.
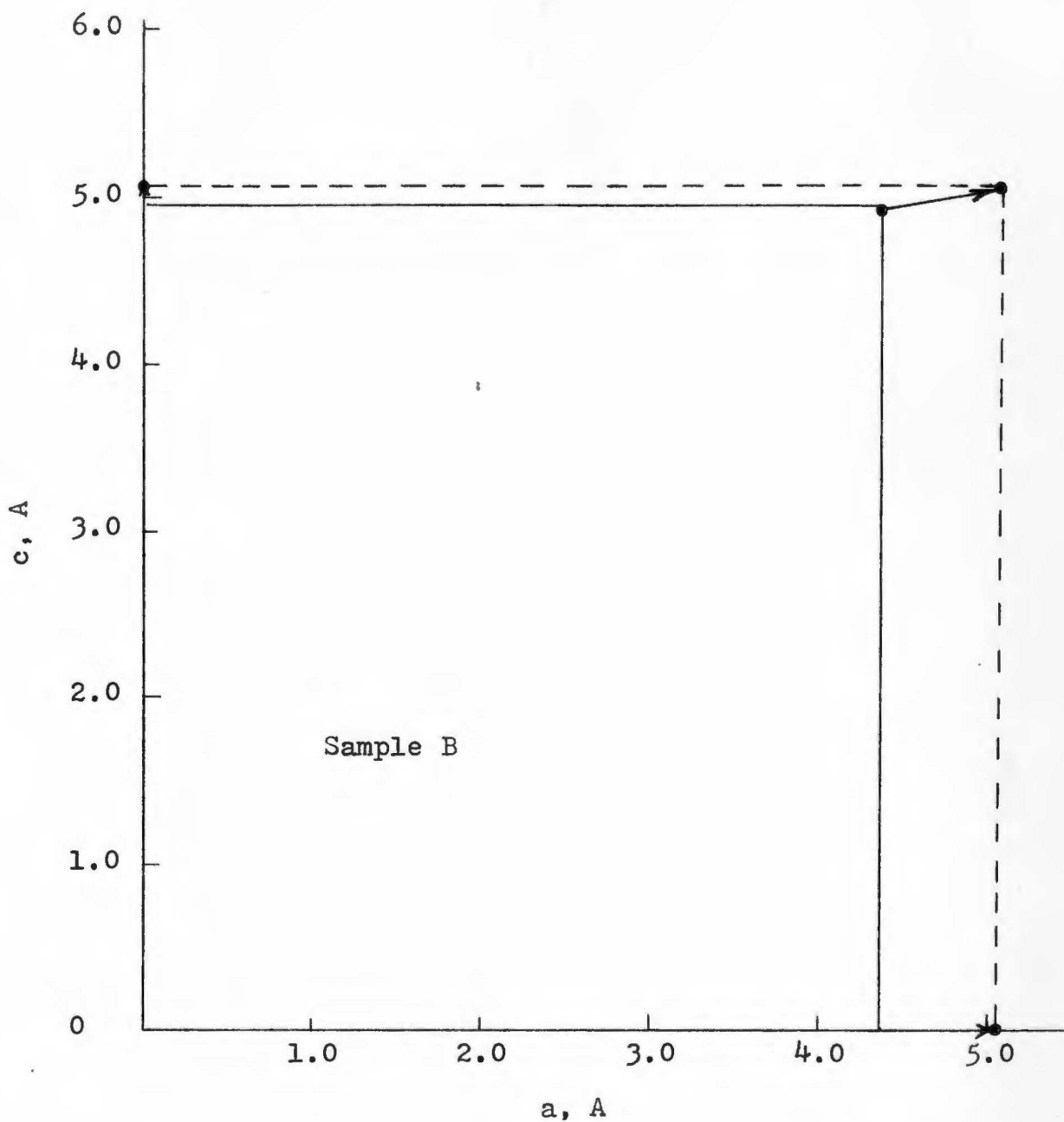
Fig. 5. Bain Distortion Associated with the
Transformation from Hexagonal Close Packed to Diamond Cubic.

APPENDIX B

<u>Tables</u>

TABLE 1

DETERMINATION OF INTERPLANAR SPACING d, LATTICE PARAMETERS a AND c, AND
MILLER INDICES hkil FOR HEXAGONAL SELENIUM (SAMPLE A) AT ROOM TEMPERATURE

2θ	θ	$\sin\theta$	$\sin^2\theta$	d
23.56	11.78	0.2041	0.0416	3.7739
29.70	14.85	0.2563	0.066	3.0053
41.36	20.68	0.3531	0.125	2.1814
43.60	21.80	0.3714	0.138	2.0739
45.40	22.70	0.3859	0.149	1.9960
48.10	24.05	0.4075	0.166	1.8902
51.80	25.90	0.4368	0.191	1.7634
56.10	28.05	0.4702	0.221	1.6381
65.30	32.65	0.5395	0.291	1.4277
68.30	34.15	0.5614	0.315	1.3720
89.70	44.85	0.7052	0.497	1.0922
92.60	46.30	0.7229	0.523	1.0655

TABLE 1 CONT.

DETERMINATION OF INTERPLANAR SPACING d, LATTICE PARAMETERS a AND c, AND MILLER INDICES hkil FOR HEXAGONAL SELENIUM (SAMPLE A) AT ROOM TEMPERATURE

θ	$\sin^2\theta$	$\sin^2\theta/3$	$\sin^2\theta-A$	$\sin^2\theta-3A$	hkil
11.78	0.0416	0.014	-	-	$10\bar{1}0$
14.85	0.066	0.022	0.024	-	$10\bar{1}1$
20.68	0.125	0.042	0.083	-	$11\bar{2}0$
21.80	0.138	0.046	0.096	0.012	$10\bar{1}2$
22.70	0.149	0.049	0.107	0.023	$11\bar{2}1$
24.05	0.166	0.055	0.124	0.040	$20\bar{2}0$
25.90	0.191	0.064	0.149	0.065	$20\bar{2}1$
28.05	0.221	0.074	0.179	0.095	$11\bar{2}2$
32.65	0.291	0.097	0.249	0.165	$21\bar{3}0$
34.15	0.315	0.105	0.273	0.189	$21\bar{3}1$
44.85	0.497	0.166	0.437	0.371	$21\bar{3}3$
46.30	0.523	0.174	0.481	0.397	0004

TABLE 1 CONT.

DETERMINATION OF INTERPLANAR SPACING d, LATTICE PARAMETERS a AND c, AND MILLER INDICES hkil FOR HEXAGONAL SELENIUM (SAMPLE A) AT ROOM TEMPERATURE

θ	sinθ	d	hkil	a	c
11.78	0.2041	3.7739	$10\bar{1}0$	4.3606	4.9719
14.85	0.2563	3.0053	$10\bar{1}1$	-	-
20.68	0.3531	2.1814	$11\bar{2}0$	4.3572	-
21.80	0.3714	2.0739	$10\bar{1}2$	-	-
22.70	0.3859	1.9960	$11\bar{2}1$	-	-
24.05	0.4075	1.8902	$20\bar{2}0$	4.3659	-
25.90	0.4368	1.7634	$20\bar{2}1$	-	-
28.05	0.4702	1.6381	$11\bar{2}2$	-	-
32.65	0.5395	1.4277	$21\bar{3}0$	4.3621	-
34.15	0.5614	1.3720	$21\bar{3}1$	-	-
44.85	0.7052	1.0922	$21\bar{3}3$	-	-
46.30	0.7229	1.0655	0004	<u>-</u>	<u>4.9546</u>
				4.3615	4.9633

TABLE 2

DETERMINATION OF INTERPLANAR SPACING d LATTICE PARAMETERS a AND c, AND MILLER INDICES hkil FOR HEXAGONAL SELENIUM (SAMPLE A) AT 167°C

2θ	θ	$\sin\theta$	$\sin^2\theta$	d
23.00	11.50	0.1994	0.0397	3.8628
29.00	14.50	0.2504	0.0627	3.0760
40.50	20.25	0.3461	0.1198	2.2255
43.20	21.60	0.3681	0.1355	2.0925
44.60	22.30	0.3795	0.1439	2.0296
47.40	23.70	0.4019	0.1616	1.9165
51.00	25.50	0.4305	0.1853	1.7892
55.40	27.70	0.4648	0.2161	1.6572
60.90	30.45	0.5068	0.2568	1.5198
64.26	32.13	0.5318	0.2829	1.4484
67.26	33.63	0.5538	0.3067	1.3908

TABLE 2 CONT.

DETERMINATION OF INTERPLANAR SPACING d, LATTICE PARAMETERS a AND c, AND MILLER INDICES hkil FOR HEXAGONAL SELENIUM (SAMPLE A) AT 167°C

θ	$sin^2\theta$	$sin^2\theta/3$	$sin^2\theta-A$	hkil
11.50	0.0397	0.0132	-	$10\bar{1}0$
14.50	0.0627	0.0209	0.0230	$10\bar{1}0$
20.25	0.1198	0.0399	0.0801	$11\bar{2}0$
21.60	0.1355	0.0452	0.0958	$10\bar{1}2$
22.30	0.1439	0.0479	0.1042	$11\bar{2}1$
23.70	0.1616	0.0539	0.1219	$20\bar{2}0$
25.50	0.1853	0.0618	0.1456	$20\bar{2}1$
27.70	0.2161	0.0720	0.1764	$11\bar{2}2$
30.45	0.2568	0.0856	0.2171	$20\bar{2}2$
32.13	0.2829	0.0943	0.2432	$21\bar{3}0$
33.63	0.3067	0.1022	0.2670	$21\bar{3}1$

TABLE 2 CONT.

DETERMINATION OF INTERPLANAR SPACING d, LATTICE PARAMETERS a AND c,
AND MILLER INDICES hkil FOR HEXAGONAL SELENIUM (SAMPLE A) AT 167°C

θ	$\sin\theta$	d	hkil	a	c
11.50	0.1994	3.8628	$10\bar{1}0$	4.4637	5.0787
14.50	0.2504	3.0760	$10\bar{1}0$	-	-
20.25	0.3461	2.2255	$11\bar{2}0$	4.4506	-
21.60	0.3681	2.0925	$10\bar{1}0$	-	-
22.30	0.3795	2.0296	$11\bar{2}1$	-	-
23.70	0.4019	1.9165	$20\bar{2}0$	4.4248	-
25.50	0.4305	1.7892	$20\bar{2}1$	-	-
27.70	0.4648	1.6572	$11\bar{2}2$	-	-
30.45	0.5068	1.5198	$20\bar{2}2$	-	-
32.13	0.5318	1.4484	$21\bar{3}0$	4.4241	-
33.63	0.5538	1.3908	$21\bar{3}1$	-	-
				4.4408	5.0787

TABLE 3

DETERMINATION OF INTERPLANAR SPACING d, LATTICE PARAMETERS a AND c, AND MILLER INDICES hkil FOR HEXAGONAL SELENIUM (SAMPLE A) AT 178°C

2θ	θ	$\sin\theta$	$\sin^2\theta$	d
23.10	11.55	0.2000	0.0400	3.8513
29.10	14.55	0.2512	0.0631	3.0663
40.80	20.40	0.3486	0.1215	2.2096
43.30	21.65	0.3689	0.1361	2.0879
44.70	22.35	0.3803	0.1446	2.0254
47.50	23.75	0.4027	0.1622	1.9127

TABLE 3 CONT.

DETERMINATION OF INTERPLANAR SPACING d, LATTICE PARAMETERS a AND c, AND MILLER INDICES hkil FOR HEXAGONAL SELENIUM (SAMPLE A) AT 178°C

θ	$\sin^2\theta$	$\sin^2\theta/3$	$\sin^2\theta$-A	hkil
11.55	0.0400	0.0133	-	10$\bar{1}$0
14.55	0.0631	0.0210	0.0231	10$\bar{1}$1
20.40	0.1215	0.0405	0.0815	11$\bar{2}$0
21.65	0.1361	0.0454	0.0961	10$\bar{1}$2
22.35	0.1446	0.0482	0.1046	11$\bar{2}$1
23.75	0.1622	0.0541	0.1222	20$\bar{2}$0

TABLE 3 CONT.

DETERMINATION OF INTERPLANAR SPACING d, LATTICE PARAMETERS a AND c, AND MILLER INDICES hkil FOR HEXAGONAL SELENIUM (SAMPLE A) AT 178°C

θ	sinθ	d	hkil	a	c
11.55	0.2000	3.8513	$10\bar{1}0$	4.4686	5.0930
14.55	0.2512	3.0663	$10\bar{1}1$	-	-
20.40	0.3486	2.2096	$11\bar{2}0$	4.4562	-
21.65	0.3689	2.0879	$10\bar{1}2$	-	-
22.35	0.3803	2.0254	$11\bar{2}1$	-	-
23.75	0.4027	1.9127	$20\bar{2}0$	4.4291	-
				4.4513	5.0930

TABLE 4

DETERMINATION OF LATTICE PARAMETER a AND MILLER INDICES hkl
FOR DIAMOND CUBIC SELENIUM AT ROOM TEMPERATURE (SAMPLE B)

2θ	θ	$\sin^2\theta$	$h^2+k^2+l^2$	$^2/4a^2$	a	hkl
24.4	12.2	0.04466	8	0.00558	10.3175	220
30.6	15.3	0.06965	11	0.00633	9.6955	311
42.2	21.1	0.12959	19	0.00682	9.3340	331
44.5	22.25	0.14337	24	0.00597	9.9737	422
46.2	23.1	0.15267	27	0.00565	10.2304	511,333
52.6	26.3	0.19631	35	0.00550	10.3301	531
56.4	28.2	0.22330	40	0.00558	10.3176	620
63.6	31.8	0.27768	51	0.00544	10.4474	711,551
66.2	33.1	0.29823	56	0.00533	10.5636	642
					10.1344	

$\lambda = 1.54178$

TABLE 5

DETERMINATION OF INTERPLANAR SPACING d, LATTICE PARAMETERS a AND c,
AND MILLER INDICES hkil FOR HEXAGONAL SELENIUM TRANSFORMED FROM
DIAMOND CUBIC SELENIUM AND AT 170°C (SAMPLE B)

2θ	θ	$\sin\theta$	$\sin^2\theta$	d
23.00	11.50	0.1994	0.0397	3.8628
29.10	14.55	0.2512	0.0631	3.0663
40.80	20.40	0.3486	0.1215	2.2096
43.20	21.60	0.3681	0.1355	2.0925
44.70	22.35	0.3803	0.1446	2.0254
-	-	-	-	-
51.00	25.50	0.4305	0.1853	1.7892
55.00	27.50	0.4617	0.2132	1.6843
60.70	30.35	0.5053	0.2553	1.5482

TABLE 5 CONT.

DETERMINATION OF INTERPLANAR SPACING d, LATTICE PARAMETERS a AND c,
AND MILLER INDICES hkil FOR HEXAGONAL SELENIUM TRANSFORMED FROM
DIAMOND CUBIC SELENIUM AND AT 170°C (SAMPLE B)

θ	$\sin^2\theta$	$\sin^2\theta/3$	$\sin^2\theta-A$	hkil
11.50	0.0397	0.0132	-	$10\bar{1}0$
14.55	0.0631	0.0210	0.0231	$10\bar{1}1$
20.40	0.1215	0.0405	0.0815	$11\bar{2}0$
21.60	0.1355	0.0452	0.0958	$11\bar{2}0$
22.35	0.1446	0.0482	0.1046	$11\bar{2}1$
-	-	-	-	-
25.50	0.1853	0.0618	0.1456	$20\bar{2}1$
27.50	0.2132	0.0710	0.1735	$11\bar{2}2$
30.25	0.2553	0.0851	0.2156	$20\bar{2}2$

TABLE 5 CONT.

DETERMINATION OF INTERPLANAR SPACING d, LATTICE PARAMETERS a AND c,
AND MILLER INDICES hkil FOR HEXAGONAL SELENIUM TRANSFORMED FROM
DIAMOND CUBIC SELENIUM AND AT 170°C (SAMPLE B)

θ	sinθ	d	hkil	a	c
11.50	0.1194	3.8628	$10\bar{1}0$	4.4637	5.0787
14.55	0.2512	3.0663	$10\bar{1}1$	-	-
20.40	0.3486	2.2096	$11\bar{2}0$	4.4562	-
21.60	0.3681	2.0925	$11\bar{2}1$	-	-
22.35	0.3803	2.0254	-	-	-
-	-	-	-	-	-
25.50	0.4305	1.7892	$20\bar{2}1$	-	-
27.50	0.4617	1.6843	$11\bar{2}2$	-	-
30.25	0.5053	1.5482	$20\bar{2}2$	-	-
				4.4599	5.0787

TABLE 6

LATTICE PARAMETER VALUES FOR THE HEXAGONAL CLOSE PACKED
PHASE (SAMPLE A) AT VARIOUS TEMPERATURES AND THE DIAMOND
CUBIC PHASE (SAMPLE B) AT ROOM TEMPERATURE

Hexagonal Close Packed Phase

Room temperature

a = 4.3615A

c = 4.9633A

167°C

a = 4.4408A

c = 5.0787A

170°C

a = 4.4513A

c = 5.0930A

Diamond Cubic Phase

Room temperature

a = 5.0672A

TABLE 7

SPECIFIC HEAT OF THE HEXAGONAL CLOSE PACKED
AND DIAMOND CUBIC PHASES OF SELENIUM

Hexagonal Close Packed

Temperature Range -- 445-450°K

Specific Heat -- 35 cal/mole/°K

Diamond Cubic

Temperature Range -- 425-435°K

Specific Heat -- 17.5 cal/mole/°K

TABLE 8

COEFFICIENTS OF EXPANSION FOR THE STABILIZED
HEXAGONAL CLOSE PACKED PHASE OF SELENIUM

Coefficient of expansion along the a-axis

5.50×10^{-4} A/°K

Coefficient of expansion along the c-axis

8.25×10^{-4} A/°K

TABLE 9

EXTRAPOLATED LATTICE PARAMETER VALUES FOR THE HEXAGONAL
CLOSE PACKED PHASE AND ACTUAL LATTICE PARAMETER FOR THE
DIAMOND CUBIC PHASE

Hexagonal close packed phase

Extrapolated values to room temperature

$$a = 4.3675A$$

$$c = 4.9623A$$

$$Volume = 0.866a^2c = 81.97A^3$$

Diamond cubic phase

Actual value at room temperature

$$a = 5.0672$$

$$Volume = a^3 = 130.11A^3$$

Volume change on transformation is 36 percent.

BIBLIOGRAPHY

Books

Bagnall, K.W. The Chemistry of Selenium, Tellurium, and Polonium. London, England: Elseview Publishing Company, 1966.

Cullity, B. Elements of X-Ray Diffraction. Reading, MASS: Addison Wesley Publishing Company, 1956.

Darken, L. and Gurry, R. Physical Chemistry of Metals. New York, N.Y.: McGraw-Hill Book Company, 1953.

Hampel, C.A. Rare Metals Handbook. New York, N.Y.: Reinhold Publishing Company, 1954.

Hansen, M. Constitution of Binary Alloys. New York, N.Y.: McGraw-Hill Book Company, 1958.

"Powder Diffraction File," Joint Committee on Powder Diffraction Standards 6-0362. Philadelphia, PA.

Articles

Andrievskii and Nabitovitch. Kristallografiya, 5. 1960.

Buczek, M., Mady, L., Carothers, B. Thermodynamic Properties of Dilute Tl-Cd Alloys. Undergraduate Thesis, Youngstown State University, 1971.

Das and Bever. "Thermodynamics Investigation of Crystallie and Amorphous Se-Te Alloys," Met. Trans., 1973.

Iizima, Taynai and Nicolet. "Preparation and Identification of Selenium Monoclinic Crystals Grown from Selenium-Saturated CS_2," Proceeding of the International Symposium. Montreal, Canada, 1967.

"Selenium." Van Norstrands Scientific Encyclopedia. New York: D. Van Norstrands Company, Inc, 1947.

Wechsler, M.S., et al. "On the Theory of Formation of Martensite," Journal of Metals, Trans, AIME, Volume 197. New York, N.Y., 1953.