RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 38, NUMBER 14 15 NOVEMBER 1988-I

Structural phase transitions and equations of state for selenium under pressure

G. Parthasarathy* and W. B. Holzapfel
Universität Gesamthochschule, Paderborn, Fachbereich Physik, D-4790 Paderborn, Federal Republic of Germany

(Received 24 June 1988)

Pressure-induced structural phase transitions in hexagonal Se were studied for the first time by high-pressure energy dispersive x-ray-diffraction techniques up to 50 GPa. The observed phase transitions are as follows: from hexagonal to monoclinic at 14(1) GPa, from monoclinic to tetragonal at 28(2) GPa, and from tetragonal to rhombohedral at 41(3) GPa. All the observed phase transitions are reversible with hysteresis. The high-pressure behavior of selenium is compared with that of tellurium. The room-temperature equation-of-state data for all the phases are presented.

Selenium and tellurium are known to exhibit several interesting physical phenomena,[1] one of which is the pressure-induced semiconductor-metal transition.[2-5] The high-pressure metallic phases are superconducting at sufficiently low temperatures.[6-8] There has been also considerable interest in theoretical understanding of the electronic structure of Se and Te at high pressures.[9-15] However, so far all the theoretical work[9-15] on Se and Te is limited to pressures below 14 GPa, due to the lack of structural data for these materials in the extended pressure range.

In a recent communication,[16] we have reported that Te undergoes many structural phase transitions under high pressure. Since the elements in many groups of the periodic system exhibit a close homology in their high-pressure behavior,[17-20] one could anticipate that Se might exhibit as similar a sequence of structural phase transition as Te.

In a high-pressure x-ray investigation McCann and Cartz[21] found that hexagonal and amorphous Se transform irreversibly at 14(1) GPa to similar unidentified structures. On the contrary, Moodenbaugh, Wu, and Viswanathan[7] have reported that the pressure-induced transition in hexagonal Se is reversible. In a recent study,[22] it has been reported that Se undergoes several pressure-induced transitions up to 50 GPa. In that study[22] the observed interplanar spacings d_{hkl} at 4.5 GPa (in particular strong diffraction lines at 2.286 Å, 2.606 Å) indicate that the starting material was already a phase mixture. It is well known for Se that a sample with phase mixture yields differing results.[23,24] However, in none of the above studies, have structures of high-pressure phases been solved.

These facts have motivated the present study on the room-temperature phase diagram of hexagonal Se up to 50 GPa.

In the present Rapid Communication, we report results of energy dispersive x-ray diffraction on hexagonal selenium under pressure at room temperature. We find that hexagonal Se I transforms to a monoclinic phase Se II at 14(1) GPA, Se II transforms to a tetragonal phase Se III at 28(2) GPa, and Se III transforms to a rhombohedral phase Se IV at 41(3) GPa. All the observed phase transitions are reversible with hysteresis. We also present the room-temperature equation-of-state data for all the observed phases of Se, which hopefully helps theorists to evaluate the structural stability of Se at high pressures.

The powdered samples of Se with 99.999% purity yielded at room temperature and ambient pressure an x-ray-diffraction pattern of the pure hexagonal phase with $a = 4.366(1)$ Å and $c = 4.958(2)$ Å in excellent agreement with the literature values[25] $a = 4.3655(10)$ Å and $c = 4.9576(24)$ Å. The diamond-anvil technique[26,27] was used for generating high pressure and the well-known ruby fluorescence technique[28-31] served for pressure measurement. Liquid nitrogen was used as a pressure transmitting medium in three of the present experiments and a mixture of methanol:ethanol:water in the ratio 16:3:1 was applied in the other two experiments to check on possible effects of nonhydrostatic stresses.[32] All the five different experiments yielded consistent results. The hysteresis of the phase transitions was studied by taking data not only on increasing but also on decreasing pressure. The values of the transition pressures quoted in the paper correspond, therefore, within the given uncertainties to the equilibrium transition pressures. The precision in the pressure determination with respect to the nonlinear ruby scale[33] is estimated to be better than 0.5 GPa at 40 GPa.

The structural data were obtained by energy dispersive x-ray diffraction. The details of the experimental technique have been described elsewhere.[34-36]

The variation of the observed lattice spacings d_{hkl} of Se as a function of pressure are represented in Fig. 1. The appearance and disappearance of the diffraction lines illustrates clearly the structural phase transitions in Se under high pressure. It is also seen from Fig. 1 that all the observed phase transitions are reversible with hysteresis. The indexing (hkl) of the observed lattice spacings is presented in Table I for the different phases together with the observed and fitted d_{hkl} values. The variation of the lattice spacings for hexagonal Se I corresponds closely to the data reported earlier in the literature.[37,38] The values of the lattice parameters at 15 GPa [$a = 3.640(1)$ Å and $c = 5.160(2)$ Å] indicate that the axial ratio c/a of Se I increases from 1.135(1) at ambient pressure to 1.417(1) at 15 GPa. The observed variation of c/a with pressure is consistent with the published data.[34,35] A pressure-

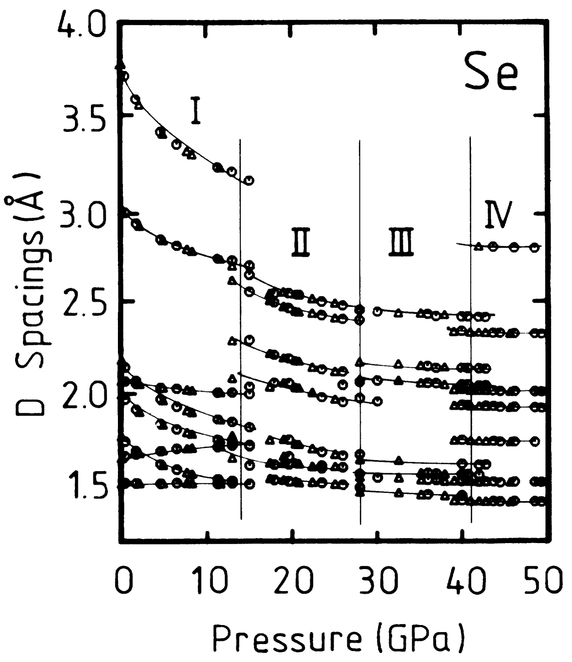

FIG. 1. Effect of pressure on *d* spacings for various phases of selenium. Circles and triangles indicate data collected on increasing and decreasing pressure, respectively. The lines drawn through the experimental data points are only guides for the eye.

induced phase transition occurs in hexagonal Se at a *c/a* ratio of 1.417, which corresponds to the value of the *c/a* ratio of Te at 4.0(2) GPa (Ref. 16) where it undergoes its first phase transition. Since the initial *c/a* ratios for Se and Te are 1.13 and 1.33, respectively, one could already expect from simple scaling rules that Se would require a higher pressure for this transformation to occur. The data for Se II could be assigned only to a monoclinic structure apparently similar to the structure of Te II phase,[39] however, with three atoms per unit cell. Since the intensities of the observed reflections may be affected by the preferred orientations in the sample a complete structure determination cannot be made with these data; however, the values of the unit-cell parameters (Table I) and the different numbers of atoms in the unit cell indicate clearly that Se II has a different structure than Te II.

It is quite evident from Fig. 1 that Se II transforms to Se III at 28(2) GPa. On the basis of the known high-pressure sequence of Te (Ref. 16) one may be tempted to assign an orthorhombic structure to Se III; however, the observed pattern can be indexed unambiguously only to a tetragonal structure with four atoms per unit cell. The observed and calculated interatomic spacings for Se III at 40(2) GPa are also listed in Table I.

In Fig. 1, new diffraction lines at 41(3) GPa illustrate the appearance of a new phase Se IV. The diffraction pattern for Se IV can be indexed as rhombohedral with two

TABLE I. Selected structural data for each of the high-pressure phases of selenium including atomic volume *V*, lattice parameters *a*, *b*, *c*, and β (where adequate), as well as indexing (*hkl*) for the experimental lattice spacings d_{obs} and the best-fit values d_{calc}.

	Se I $P=4.6(2)$ GPa, $V=22.67(14)$ Å^3 $a=3.939(1)$ Å, $c=5.062$ Å			Se II $P=19.0(9)$ GPa, $V=14.96(8)$ Å^3 $a=3.2712(7)$ Å, $b=4.1264(8)$ Å $c=3.3484(9)$ Å, $\beta=96.80(2)°$	
(*hkl*)	d_{obs}	d_{calc}	(*hkl*)	d_{obs}	d_{calc}
10.0	3.412(3)	3.411	110	2.548(3)	2.552
10.1	2.828(2)	2.829	$10\bar{1}$	2.468(3)	2.474
10.2	2.034(2)	2.033	101	2.200(3)	2.197
11.0	1.969(1)	1.970	020	2.062(2)	2.063
11.1	1.835(2)	1.836	021	1.756(2)	1.753
00.3	1.687(1)	1.687	002	1.661(2)	1.662
20.1	1.617(1)	1.616	200	1.620(3)	1.624
10.3	1.512(2)	1.512	$20\bar{1}$	1.540(4)	1.533
	Se III $P=40(2)$ GPa, $V=12.71(3)$ Å^3 $a=4.585(2)$ Å, $c=2.418(1)$ Å			Se IV $P=46.2(23)$ GPa, $V=12.08(1)$ Å^3 $a=4.658(2)$ Å, $c=3.858(2)$ Å	
(*hkl*)	d_{obs}	d_{calc}	(*hkl*)	d_{obs}	d_{calc}
001	2.418(2)	2.418	10.1	2.788(2)	2.788
101	2.140(1)	2.139	11.0	2.328(2)	2.329
210	2.051(1)	2.051	20.0	2.016(2)	2.017
111	1.938(2)	1.939	00.2	1.929(2)	1.929
220	1.621(1)	1.621	10.2	1.740(1)	1.740
211	1.564(1)	1.564	21.0	1.524(1)	1.525
300	1.528(2)	1.528	21.1	1.420(1)	1.418
310	1.450(2)	1.450			

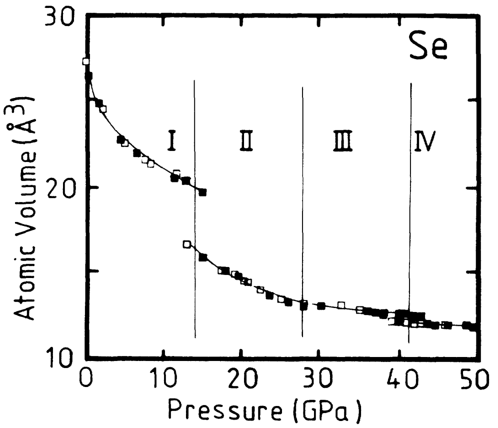

FIG. 2. Effect of pressure on the atomic volume of selenium in the different phases. The closed and open squares indicate data collected on increasing and decreasing pressure, respectively. The continuous lines represent equations of state obtained by least-squares fits. The fit parameters are given in Table II.

atoms per unit cell. The lattice spacings for Se IV at 46.2(23) GPa (Table I) yield the lattice parameters $a = 2.981(2)$ Å and $\alpha = 102.76(12)°$ for the rhombohedral cell and $a = 4.6581(12)$ Å and $c = 3.858(2)$ Å for the equivalent hexagonal cell.

From a comparison with the high-pressure behavior of Te (Ref. 16) one might expect that Se IV would ultimately also transform to a body-centered-cubic structure Se V, when c/a approaches a value $c/a = 0.812$. However, within the pressure range 39–49 GPa, $c/a = 0.828(2)$ of Se IV remains constant within the experimental uncertainty. This observation seems to indicate that the possible Se IV-Se V transition may require much higher pressure than the upper limit of the present experimental investigation.

The variation of the atomic volume for all the presently studied phases of Se under pressure at room temperature are represented in Fig. 2 which shows clearly that the transitions Se I-Se II and Se III-Se IV are first-order phase transitions with volume discontinuities of 20 and 3.5%, respectively. On the other hand, the volume change at the Se II-Se III phase transition appears to be smaller than 1%. The curves in Fig. 2 represent fits of first-order Murnaghan equations

$$(V/V_r) = [(B_r'/B_r)(P - P_r) + 1]^{-1/B_r'} \qquad (1)$$

where free parameters V_r, B_r, and B_r' represent the volume per atom, bulk modulus, and its pressure derivative at the references pressure P_r. The values in Table II represent the results of the least-squares fits. The values of P_r were chosen thereby in the center of the stability region of each phase to obtain minimum uncertainties in B_r. For Se I, the values of B_r and B_r' are found to be consistent with the earlier piston-cylinder data on hexagonal selenium. For the other phases, Table II presents the first sets of data for B_r and B_r'.

TABLE II. Values for the equation-of-state parameters P_r, V_r, B_r, and B_r' obtained from least-squares fits of the experimental data by Eq. (1).

Phases	P_r (GPa)	V_r (Å^3)	B_r (GPa)	B_r'
I	7.7	21.56(13)	48.1(20)	4.33(4)
II	20.4	14.50(8)	63.7(36)	2.53(8)
III	35.2	12.94(5)	263(14)	5.2(2)
IV	44.5	12.12(6)	458(40)	6.5(5)

Since Se and Te show a close structural homology at low pressures,[1,9,10] this homology has been studied for the low-pressure phase Se I and Te I also in a more extended pressure ranges by single-crystal x-ray diffraction[38] and Raman scattering.[40] These studies[38,40] indicated already that deviations from simple scaling laws are observed as pressure approaches the first phase-transition pressure in either of these elements.

In addition, the present investigation shows remarkable differences at the structural phase transition between the phase I and II for Se and Te. The fact that the I-II-phase transition in Se occurs at a higher pressure with even a larger volume discontinuity (Fig. 2) than in Te,[16] and the further observation that Se II, Se III, and Se IV seem to have no structural resemblance with the corresponding phases of Te, are considered as strong evidence for a breakdown of structural homology rules for these group-VI*A* elements, at least in the present pressure range of investigations. However, if the c/a value for Se IV reaches the value 0.612, Se IV would change into a *bcc* phase Se V, which has been observed in Te as Te V at pressures in excess of 27 GPa at room temperature.[16] In the present pressure range of investigations the value of c/a for the Se IV phase (0.827) is found to be pressure independent. So it is difficult to estimate the transition pressure for a possible Se IV-Se V transition, keeping in mind that a bcc phase has been considered as a stable high-pressure phase for the group-VI*A* elements.[20] However, since there are no first-principles calculations available on the structural stability of the group-VI*A* elements under high pressure, one cannot exclude that a structural homology will be resumed for these elements at very high pressure.

As mentioned earlier, the theoretical understanding of the high-pressure behavior of selenium is very limited[9-12,14,15] due to the lack of structural data. We hope that the present results will stimulate theorists to study the stability of the different phases of selenium and their electronic structure, in order to obtain ultimately a better understanding of the physics of group-VI*A* elements.

We gratefully acknowledge the help of Olaf Schulte with the experimental work. This work has been funded in part by the German Minister for Research and Technology (BMFT) under the Contract No. 05-340-AxBO. One of us (G.P.) is grateful to the Alexander von Humbolt Foundation for financial support.

*Permanent address: Materials Research Laboratory, Indian Institute of Science, Bangalore 560012, India.

[1]See *The Physics of Selenium and Tellurium*, edited by E. Gerlach and P. Groose (Springer-Verlag, Berlin, 1979).

[2]A. S. Balchan and H. G. Drickamer, J. Chem. Phys. **34**, 1948 (1961).

[3]B. M. Riggleman and H. G. Drickamer, J. Chem. Phys. **37**, 446 (1962).

[4]F. P. Bundy and K. J. Dunn, J. Chem. Phys. **71**, 1550 (1979).

[5]G. Parthasarathy, K. J. Rao, and E. S. R. Gopal, Solid State Commun. **52**, 867 (1984).

[6]J. Wittig, Phys. Rev. Lett. **15**, 159 (1969).

[7]A. R. Moodenbaugh, C. T. Wu, and R. Viswanathan, Solid State Commun. **13**, 1413 (1973).

[8]F. P. Bundy and K. J. Dunn, Phys. Rev. Lett. **44**, 1623 (1980).

[9]J. D. Joannopoulos, M. Schüter, and M. L. Cohen, Phys. Rev. B **11**, 2186 (1975).

[10]R. M. Martin, G. Lucovsky, and K. Helliwell, Phys. Rev. B **13**, 1383 (1976).

[11]H. Wendel, R. M. Martin, and D. J. Chadi, Phys. Rev. Lett. **38**, 656 (1977).

[12]J. D. Joannopoulos, Th. Starkloff, and M. Kastner, Phys. Rev. Lett. **38**, 660 (1977).

[13]G. Doerre and J. D. Joannopoulos, Phys. Rev. Lett. **43**, 1040 (1979).

[14]J. von Boehm and H. M. Isomäki, Phys. Rev. B **24**, 6945 (1981).

[15]H. M. Isomäki and J. von Boehm, Phys. Rev. B **35**, 8019 (1987).

[16]G. Parthasarathy and W. B. Holzapfel, Phys. Rev. B **37**, 8499 (1988).

[17]H. Olijnyk, S. K. Sikka, and W. B. Holzapfel, Phys. Lett. **103A**, 137 (1984).

[18]Y. K. Vohra, K. E. Brister, S. Desgreniers, A. L. Ruoff, K. J. Chang, and M. L. Cohen, Phys. Rev. Lett. **56**, 1944 (1986).

[19]S. J. Duclos, Y. K. Vohra, and A. L. Ruoff, Phys. Rev. Lett. **58**, 775 (1987).

[20]L. G. Liu and W. A. Bassett, *Elements, Oxides, and Silicates* (Oxford Univ. Press, New York, 1986), pp. 24–91.

[21]D. R. McCann and L. Cartz, J. Chem. Phys. **56**, 2552 (1972).

[22]H. K. Mao, G. Zou, and P. M. Bell, Carnegie Inst. Washington Yearb. **80**, 283 (1980).

[23]S. N. Vaidya and G. C. Kennedy, J. Phys. Chem. Solids **33**, 1377 (1972).

[24]A. K. Singh and G. C. Kennedy, J. Phys. Chem. Solids **35**, 1545 (1974).

[25]J. Donohue, *The Structure of the Elements* (Wiley, New York, 1974), p. 370.

[26]G. K. Huber, K. Syassen, and W. B. Holzapfel, Phys. Rev. B **15**, 5123 (1977).

[27]A. Jayaraman, Rev. Mod. Phys. **55**, 65 (1983).

[28]R. A. Forman, G. J. Piermarini, J. D. Barnett, and S. Block, Science **176**, 284 (1972).

[29]J. D. Barnett, S. Block, and G. J. Piermarini, Rev. Sci. Instrum. **44**, 1 (1973).

[30]G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. **46**, 2774 (1975).

[31]G. J. Piermarini and S. Block, Rev. Sci. Instrum. **46**, 973 (1975).

[32]G. J. Piermarini (private communication).

[33]H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[34]K. Syassen and W. B. Holzapfel, Europhys. Conf. Abstr. **1A**, 75 (1975).

[35]W. B. Holzapfel and W. May, in *High Pressure Research in Geophysics,* Advances in Earth and Planetary Sciences, Vol. 12, edited by S. Akimoto and M. M. Manghnani (Reidel, London, 1982), p. 73.

[36]W. B. Holzapfel, Rev. Phys. Appl. **19**, 705 (1984).

[37]D. R. McCann, L. Cartz, R. E. Schmunck, and Y. D. Harker, J. Appl. Phys. **43**, 1432 (1972).

[38]R. Keller, W. B. Holzapfel, and H. Schulz, Phys. Rev. B **16**, 4404 (1977).

[39]K. Aoki, O. Shimomura, and S. Minomura, J. Phys. Soc. Jpn. **48**, 551 (1980).

[40]K. Aoki, O. Shimomura, S. Minomura, N. Koshizuka, and T. Tsushima, J. Phys. Soc. Jpn. **48**, 906 (1980).