PHYSICAL REVIEW B **71**, 214104 (2005)

Crystal structure of the superconducting phases of S and Se

Olga Degtyareva,[1] Eugene Gregoryanz,[1] Maddury Somayazulu,[2] Ho-kwang Mao,[1] and Russell J. Hemley[1]
[1]*Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road North West, Washington D.C. 20015, USA*
[2]*HPCAT, Carnegie Institution of Washington, Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, USA*

(Received 27 October 2004; revised manuscript received 10 January 2005; published 16 June 2005)

Compressed S and Se are studied by x-ray diffraction with synchrotron radiation up to 160 GPa. Phase IV of S is shown to have a body-centered monoclinic structure and is stable between 83 and 153 GPa, where it transforms to S-V with a primitive rhombohedral β-Po structure. Observation of the modulation reflections in S-IV up to 135 GPa shows that its crystal structure is incommensurately modulated, the same as known for Se and Te. Our study on the stability range of the modulated phase of Se (Se-IV) shows that Se-IV transforms to the β-Po phase Se-V at around 80 GPa. Pressure dependence of the structural parameters of these high-pressure phases in S and Se are discussed in relation to their superconducting behavior.

DOI: 10.1103/PhysRevB.71.214104 PACS number(s): 61.50.Ks, 62.50.+p

I. INTRODUCTION

Recent discoveries of incommensurate host-guest structures[1–4] and incommensurately modulated structures[5–7] in elemental metals at high pressure suggest that aperiodic structures are a common phenomenon among the elements under pressure. An aperiodic structure with large modulations in atomic positions is found in the metallic phases of group-VI elements Te and Se, Te-III and Se-IV,[6,7] and is described as an incommensurately (IC) modulated structure with two atoms in the body-centered monoclinic (bcm) average cell with modulation along the *b* axis. According to the harmonic modulation wave, atoms are displaced from their ideal positions mainly along the *c* axis. The bcm structure can be considered as a distortion of the β-Po (primitive rhombohedral) structure. On compression, the monoclinic distortion of Te-III and Se-IV decreases and the bcm average structure approaches the β-Po; at the same time the modulation reflections become weaker indicating a decrease of the modulation amplitude.

To distinguish between the modulated monoclinic and the rhombohedral β-Po structures, one needs to obtain high-resolution diffraction data with low background and high signal-to-noise ratio. Such experimental studies[6] show that Te-III with a modulated bcm structure, stable above 4.5(2) GPa, transforms directly to a body-centered cubic (bcc) structure (Te-V, Ref. 8) at 29.2(7) GPa omitting β-Po structure. The modulated bcm phase of Se-IV is stable from 29 GPa to at least 70 GPa.[7] Assuming a continuous phase transition from a modulated bcm to β-Po structure, extrapolation of the Se-IV structural parameters suggested a transition pressure of 82 GPa,[7] whereas the β-Po phase of Se is known to transform to bcc at 140 GPa.[9] These results[6,7] revised the phase transition sequence of the metallic Te and Se reported earlier.[9–15] However, the question of whether the modulated Se-IV phase transforms to β-Po above 70 GPa remains open and the nature of this transition (first or second order) is unclear.

The lighter group-VI element S with its metallic phases has been reported to be isostructural with Te and Se.[16,17] S-IV, stable above 83 GPa with a base-centered orthorhombic (bco) structure,[16,17] the same as previously reported for Te-III and Se-IV,[9,11] transforms to β-Po at 162(5) GPa, which is stable up to at least 212 GPa.[17] The stability of the bco structure for S (Refs. 18,19) as well as for Se (Ref. 20) and Te (Ref. 21), was not confirmed by theoretical calculations. Thus, in light of recent experimental reports of incommensurately modulated phases of Te-III and Se-IV,[6,7] the structure of S-IV should be reexamined with advanced experimental techniques. Moreover, the metallic phases of S, Se, and Te discussed above are known to be superconductors with a variable and complex pressure dependence of superconducting transition temperature (Ref. 22, and references therein). Accurate determination of the crystal structures of metallic S and Se is crucial for understanding the complex behavior of T_c in the group-VI elements.

Here we report the determination of the crystal structure of S-IV, stable above 83 GPa, as incommensurately modulated. We observe the structural modulation in S-IV up to 135 GPa, the highest pressure a modulated structure has been reported so far. The incommensurately modulated phases in both S and Se are confirmed to transform to the β-Po structure. Superconducting properties and pressure dependence of T_c in S and Se are discussed in light of present structural data.

II. EXPERIMENTAL METHODS

Samples of 99.999% purity S (Puratronic) and 99.99% purity of Se (Alfa Aesar) were loaded in Mao-Bell piston-cylinder diamond anvil cells with an opening allowing probing up to 27° of 2θ of the angle-dispersive x-ray diffraction. Powder x-ray diffraction data were collected at beam line 16-ID-B (HPCAT) at the Advanced Photon Source. Focused monochromatic beams of different wavelengths ($\lambda = 0.36 - 0.42$ Å) were used and the data were recorded on MAR image plate calibrated with a CeO_2 or Si standard. Samples of S and Se were studied at room temperature up to pressures of 160 and 150 GPa, respectively. Samples were loaded in the diamond anvil cells with neon as a pressure transmitting medium in order to obtain the diffraction patterns of high-pressure phases with less stress and strain. Our diffraction patterns show that the starting material was always the

©2005 The American Physical Society

known ambient orthorhombic S-I and trigonal Se-I phases. To determine the pressure, we used *in situ* fluorescence measurements of ruby chips that were loaded in the sample chamber. The well resolved ruby spectra show that neon provides quasihydrostatic condition. Powder diffraction data were integrated azimuthally using FIT2D,[23] and structural information was obtained using JANA2000.[24]

III. RESULTS

With an increase in pressure above 36 GPa, we obtain diffraction patterns that correspond to the S-III phase, reported recently as having body-centered tetragonal structure with 16 atoms in the unit cell (space group $I4_1/acd$).[25,26] Our present data give the following lattice parameters for S-III at 76 GPa: $a=7.706(1)$Å, $c=3.061(1)$Å, atomic volume $V_{\mathrm{at}}=11.36$ Å^3. Diffraction lines of S-IV phase appear at 83 GPa observed together with the remaining S-III, and the diffraction patterns of pure S-IV are observed above 94 GPa. We obtained a quasisingle crystal of S-IV, which gave several arcs on a diffraction pattern (Fig. 1, upper panel). At each pressure, three patterns were collected from the sample placed at 0° and ±4.0° between the diamond-anvil cell axis and the incident beam, to obtain information from a larger portion of the reciprocal space. The integrated profile is obtained from integration of the diffraction arcs. The resulting integrated diffraction pattern obtained from S-IV at 102(3) GPa is shown in Fig. 1 (lower panel). The fitting of this pattern with the previously proposed bco structure[16] (upper tick marks in Fig. 1) shows that some reflections remain unfit. These extra reflections are similar in their positions to the modulation reflections reported in literature for the modulated phases Te-III and Se-IV (Refs. 6,7) and found in our own diffraction data on Se-IV (Fig. 2). Application of the incommensurately modulated structure model proposed for Te-III (Ref. 6) to the diffraction pattern of S-IV at 102(3) GPa shows that the positions of the extra reflections can be fit as modulation reflections (lower tick marks in Fig. 1, lower panel).

The structure of S-IV is IC modulated body-centered monoclinic with two atoms in the average unit cell [Figs. 3(a) and 3(b)] with the lattice parameters 102(3) GPa (obtained from the least-square fit of the diffraction peak positions) $a=2.8217(8)$Å, $b=3.4698(9)$Å, $c=2.2187(4)$Å, $\beta=112.95(3)°$, atomic volume $V_{\mathrm{at}}=10.00(1)$Å^3 at 102(3) GPa, and the superspace group $I'2/m(0q0)s0$, where I' denotes centering in 4D.[27] As was proposed for Te-III and Se-IV,[6,7] the atoms in S-IV are displaced from their ideal positions (0 0 0) and (1/2 1/2 1/2) along x and z direction due to a harmonic modulation with wavevector along the b axis. The amplitude of the atomic displacements in S-IV could not be determined in present work because of the insufficient diffraction intensity information. However, the reliably determined peak positions of the modulation reflections allow us to determine the period of the modulation wave in S-IV, which is incommensurate with the lattice period b^* resulting in modulation vector $(0q0)=[0,0.289(1),0]$ at 102(3) GPa.

Using this structural model, all the observed diffraction reflections can be indexed (Fig. 1) using four integers h,k,l,m, according to $\mathbf{H}=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*+mq\mathbf{b}^*$, where $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*$ define the reciprocal lattice of the bcm structure. Several modulation reflections [with $\mathrm{mod}(m)=1$] are clearly visible in the diffraction image of S-IV at 102(3) GPa (Fig. 1). The pressure dependence of the value of the modulation wavevector $(0q0)$ for S-IV is obtained from the least-square fit of the 5 to 10 (main and modulation) diffraction reflections using the U-FIT computer program,[28] and the result is shown in the inset to Fig. 4. The value of the modulation vector q decreases in S-IV from (0,0.289(1),0) at 102(3) GPa down to (0,0.269(1),0) at 129(3) GPa. The modulation reflections decrease in intensity with pressure but are still visible in the 129 GPa diffraction pattern of S-IV [Fig. 2(a)]. Only a faint trace of one modulation reflection is found in the 135 GPa diffraction image, and in the 146 GPa image the modulation reflections are completely absent. Thus, similar to the behavior reported for Te-III and Se-IV,[6,7] the intensity of the modulation reflections in S-IV decreases with pressure. In S-IV, the disappearance of the modulation reflections at 140(5) GPa correspond to the transition from IC modulated to a non-modulated phase.

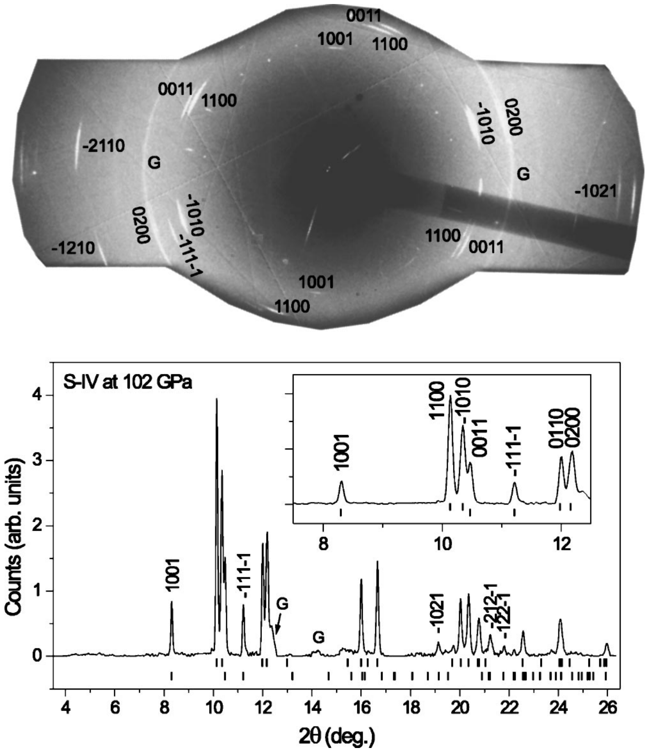

FIG. 1. (Upper panel) A diffraction image of S-IV at 102(3) GPa. Some of the diffraction reflections are indexed with their *hklm* indices. A powder line from the tungsten gasket is marked “G.” (Lower panel) Diffraction profile of incommensurate S-IV at 102 GPa, obtained from the integration of the above image, collected with $\lambda=0.3675$ Å. The upper and lower tick marks below the profile show the peak positions of the main and first-order satellite reflections, respectively. The inset shows the low-angle reflections. Some of the diffraction reflections are indexed with their *hklm* indices. Diffraction peaks from gasket are marked “G.”

With increasing pressure, we observe a decrease in the doublet splitting of the main reflections 1100 and −1010 (at 2θ around 10.2°) and reflections 0110 and 0200 (at 2θ

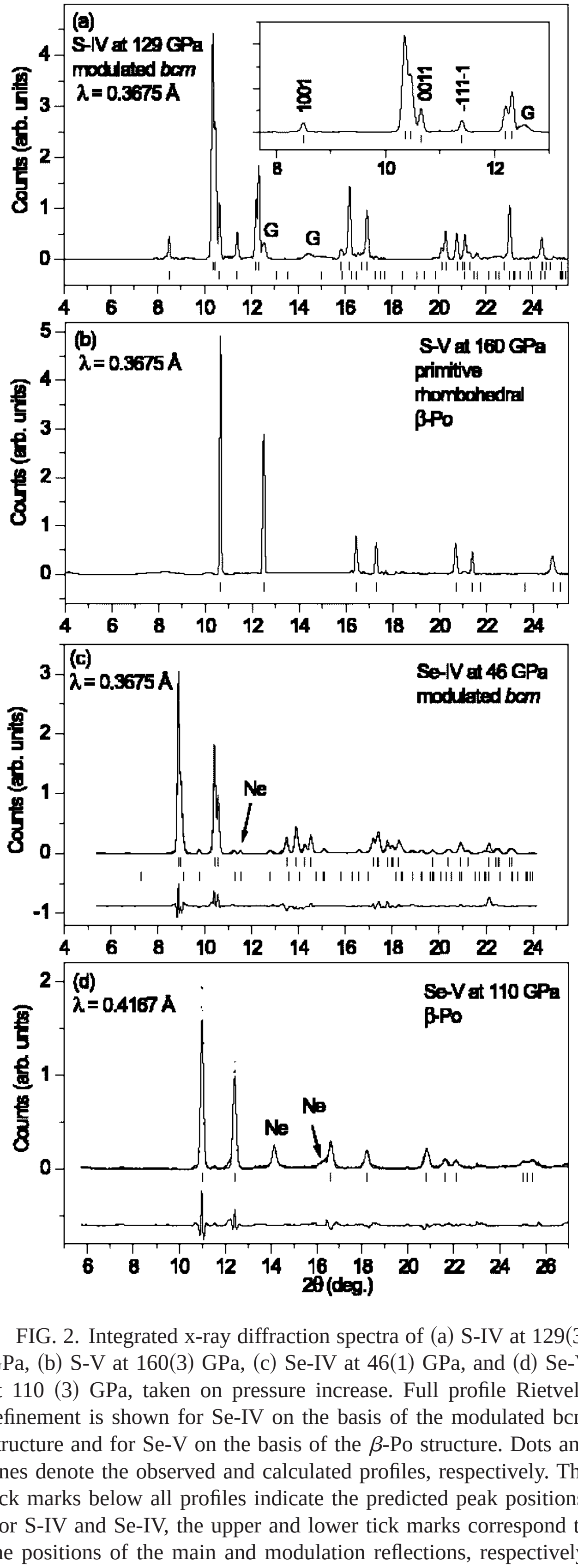

FIG. 2. Integrated x-ray diffraction spectra of (a) S-IV at 129(3) GPa, (b) S-V at 160(3) GPa, (c) Se-IV at 46(1) GPa, and (d) Se-V at 110 (3) GPa, taken on pressure increase. Full profile Rietveld refinement is shown for Se-IV on the basis of the modulated bcm structure and for Se-V on the basis of the β-Po structure. Dots and lines denote the observed and calculated profiles, respectively. The tick marks below all profiles indicate the predicted peak positions. For S-IV and Se-IV, the upper and lower tick marks correspond to the positions of the main and modulation reflections, respectively. Below the tick marks is the difference curve between the observed and calculated profiles. “G” denotes the diffraction reflections from the gasket material (tungsten), and “Ne” indicates the diffraction peaks from neon used as pressure transmitting medium.

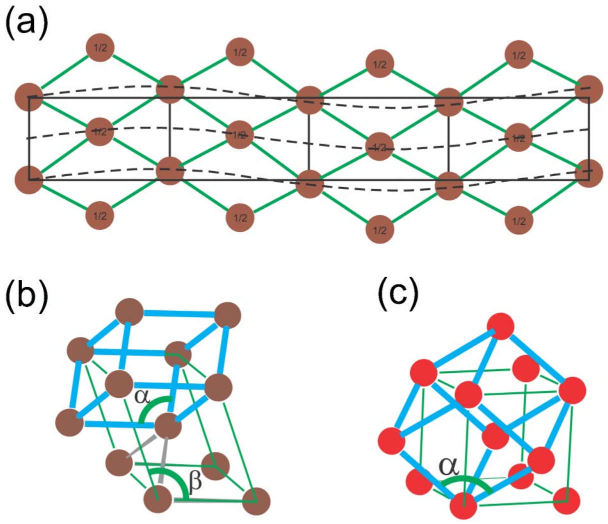

FIG. 3. (Color online.) Structural relationship of the metallic phases in the group-VI elements. (a) The modulated bcm structure of Te-III and Se-IV (four unit cells) viewed down the *a* axis (from Ref. 6). The six nearest-neighbor distances for each atom are shown, and those atoms at the body centers are labeled with “1/2.” The modulation wave is indicated by the dashed lines. (b) Relationship between the average bcm structure (thin lines) and a primitive rhombohedral structure of β-Po (thick lines). The monoclinic angle β and the rhombohedral angle α are shown. (c) Structural relation between the primitive rhombohedral structure (thick lines) and the body-centered cubic structure (thin lines). The rhombohedral angle $\alpha(=109.47°)$ is indicated.

around 12.1°) [Figs. 1 and 2(a)] in the pressure range of 100 to 150 GPa, becoming a singlet within errorbar at 156 GPa corresponding to the phase transition from (non-modulated) bcm structure to β-Po at 153(5) GPa. The pattern of S at 160 GPa [Fig. 2(b)] is fit with primitive rhombohedral β-Po structure, with $a_h=3.3780(1)$Å, $c_h=2.6919(3)$Å (in hexagonal setting), and $a_r=2.147(1)$Å, $\alpha_r=103.77(1)°$ (in rhombohedral setting), and resulting atomic volume $V_{\mathrm{at}}=8.87$ Å^3. Pressure dependence of the lattice parameters across the bcm to β-Po transition in sulfur is shown in Fig. 4. The transition pressure of 153(5) GPa is lower than the pressure of 162(5) GPa reported in Ref. 17. In contrast to the results reported in Ref. 17 based on low-resolution energy-dispersive x-ray data, present data allowed us to observe small splittings of the reflections associated with the monoclinic distortion of the β-Po structure, because of the spatial separation of these reflections in the diffraction images (Fig. 1).The extent to which residual devatoric stresses contribute to the splitting remains to be determined.

We also performed high-pressure studies of the metallic phases of the next member of the chalcogen family Se. On pressure increase above 29 GPa, we obtain the Se-IV phase with an incommensurately modulated bcm structure, in accordance with previous study.[6,7] Our Rietveld refinement of Se-IV at 46(1) GPa [Fig. 2(c)] gives the following structural parameters: $a=3.2226(1)$Å, $b=3.9896(1)$Å, $c=2.5596(1)$, $\beta=113.265(4)°$, and $V_{\mathrm{at}}=15.12(1)$Å^3 and $(0q0)=(0,0.2847(6),0)$. The value of the modulation vector q is observed to decrease with pressure in the pressure range

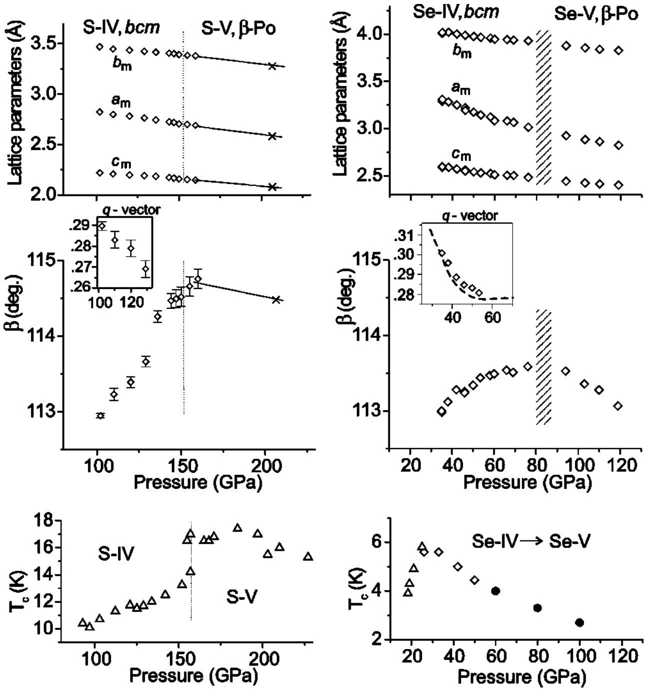

FIG. 4. Upper and middle panel: Pressure dependence of lattice parameters for the body-centered monoclinic (bcm) S-IV and Se-IV and rhombohedral β-Po S-V and Se-V structures (in monoclinic setting). Open diamonds denote data from the present work. The data at 206 GPa for S-V denoted with "x" is taken from Ref. 17. Insets in the middle panel show the pressure dependence of the modulation vector q, with open diamonds denoting data from present work, and the dashed line denoting data from Ref. 7. Solid lines are guides to the eye. Lower panel: Pressure dependence of the temperature of superconducting transition in S and Se, with open symbols denoting experimental data (triangles from Ref. 22, diamonds from Ref. 35) and solid symbols denoting data from theoretical work.[37] Vertical dotted lines and dashed areas denote proposed transition pressures.

between 35 and 53 GPa (Fig. 4, inset in the middle panel), in accordance with Ref. 7. The refined modulation parameters, which characterize the displacements of atoms from their ideal positions due to the modulation wave, are $B_{1x}=0.020(2)$ and $B_{1z}=0.083(1)$ at 46(1) GPa.[29] These values are in agreement with those reported previously for Se-IV.[7] In our work, we were able to measure the modulation reflections up to pressure of 53 GPa, whereas Ref. 7 reports the observation of the modulation reflections up to the maximum pressure of 70 GPa reached in that study. The difference in the observations can be possibly accounted for by the different pressure transmitting media used in the two studies.

On pressure increase from 29 to 70 GPa, the splitting of the main reflections in Se-IV decreases, as does the intensity of the modulation reflections, indicating a reduction of the monoclinic distortion. Modulation reflections can be used to obtain accurate lattice parameters of Se-IV and to determine the degree of the monoclinic distortion.[7] For the diffraction patterns of Se obtained in present work between 70 and 90 GPa, it is impossible to distinguish between the bcm and β-Po structures; although the patterns resemble those that would be expected from a primitive rhombohedral phase, we cannot rule out a slight monoclinic distortion. At 90 GPa, the observed diffraction pattern can be fit with primitive rhombohedral β-Po structure, indicating that Se-IV transformed to Se-V at a pressure around 80 GPa. Rietveld refinement of the Se-V phase at 110(3) GPa [Fig. 2(d)] on the basis of β-Po structure gives the lattice parameters $a_h=3.8411(5)$Å, $c_h=2.8614(2)$Å (in hexagonal setting), and $a_r=2.414(1)$Å, $\alpha_r=105.42(1)°$ (in rhombohedral setting), with atomic volume $V_{\mathrm{at}}=12.18(1)$Å^3. We observe the Se-V phase to be stable up to 140(3) GPa, where it transforms to Se-VI with a bcc structure, in accordance with Ref. 9. The relationship between the β-Po and bcc structures is shown in Fig. 3(c).

The pressure dependence of the lattice parameters of the bcm and β-Po phases in S and Se is shown in Fig. 4 (upper and middle panels). The relation between the bcm structure and the primitive rhombohedral β-Po structure can be seen in Fig. 3(b), where $a_m=a_r(3+6\cos\alpha_r)^{1/2}=c_h$, $b_m=a_r(2-2\cos\alpha_r)^{1/2}=a_h$, $c_m=a_r$, and $\beta_m=\arccos[-(1/3+2/3\cos\alpha_r)^{1/2}]$. The continuous change of the lattice parameters across the transition from the modulated bcm to β-Po phase indicates a nearly second order character for both S and Se. We point out that the presence of residual stresses complicates the identification of the true order of such transition.[30] To examine the possible weak first-order character of the bcm to β-Po transition, more detailed structural studies in the vicinity of the transition should be performed as a function of compression and decompression.

The structural data obtained in the present work in combination with the data available in the literature allow us to analyze the interatomic distances of Se over a wide pressure range from ambient pressure up to 150 GPa, through the transition from semiconducting to metallic state. Apart from Se phases II and III,[31,32] the data on the interatomic distances of all the known phases of Se are summarized in Fig. 5. These are Se-I (trigonal structure with triangular atomic chains),[33] Se-VII (tetragonal structure with squared atomic chains),[25] Se-IV (modulated bcm) (Ref. 7 and present work), Se-V (rhombohedral β-Po) and Se-VI (bcc) (Ref. 9 and present work). Se-VII can be obtained at room temperature after heating Se-III to 450 K, and also known to transform to Se-IV above 29 GPa on pressure increase.[25]

The nearest interatomic distance of the chain structures Se-I and Se-VII (2.36 Å) is determined by covalent bonding and is pressure independent. The second nearest interatomic distance (four distances) of Se-I and Se-VII corresponds to the interchain distance and decreases drastically with pressure. In the metallic Se-IV phase with a modulated bcm structure, a new interatomic distance of 2.6 Å appears, indicating a change in the atomic bonding in comparison to Se-VII. The distance of 2.6 Å is unaffected by modulation and connects the atoms in linear chains running along the c axis of the bcm cell of Se-IV. In addition, in Se-IV there are $2+2$ distances that are modulated and their values are ranging between min and max values shown in Fig. 5. The minimum value of the modulated distance in Se-IV is limited by the covalent bonding. At higher pressure, in the β-Po Se-V structure, the $2+2+2$ distances become equal and decrease slightly with pressure. The ultimate high-pressure phase of Se, Se-VI, has $8+6$ nearest neighbors in its bcc structure. A

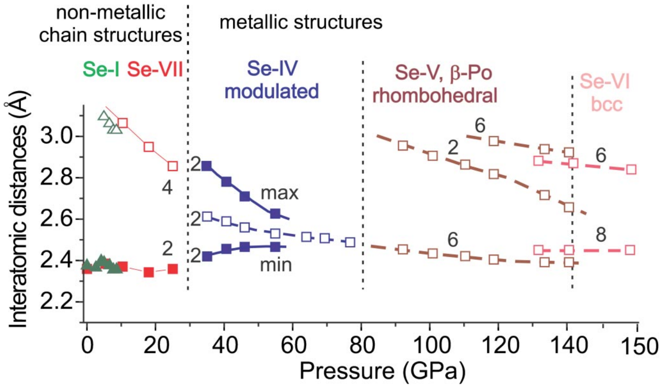

FIG. 5. (Color online.) Interatomic distances for the Se phases up to 150 GPa. The data on Se-I (green triangles) are taken from Ref. 33, the data on Se-VII (red squares) are taken from Ref. 25. The data on Se-IV, V, and VI (blue, brown, and pink squares) are from present work and are in agreement with the literature data.[7,9] The numbers indicate how many of the distances are present in the structure. The vertical dotted lines indicate the proposed transition pressures.

very similar picture of interatomic distances is expected for sulfur in its nonmetallic phases II and III (triangular and squared chain structures),[25] modulated bcm structure of phase IV and β-Po structure of phase V.

IV. DISCUSSION

Superconducting transition temperature in Te and Se in the pressure range corresponding to the modulated bcm and β-Po phases show strongly nonlinear behavior with a maximum $T_c = 4.2$ K at 5.3 GPa in Te and 5.8 K at 25 GPa in Se with a decrease of T_c on further compression[22,34,35] (for T_c in Se, see Fig. 3, lower panel). Theoretical calculations of T_c for Se and Te in this pressure range, using the β-Po structure, reproduce the value of T_c and its decrease with increasing pressure.[36,37] A jump to a higher T_c of 7.4 K is observed in Te at higher pressure of 35 GPa (Ref. 35) (probably corresponding to a phase transition to bcc, Ref. 8), confirmed theoretically.[36] For bcc Se, T_c is calculated to be 10–11 K at 120–130 GPa with a decrease in T_c with further increase in pressure,[37,38] this is consistent with experimental data at 150–170 GPa.[22]

Metallic sulfur is superconducting with T_c of 10 K at 93 GPa, and the superconducting transition temperature rises up to 14 K at 157 GPa,[39] in contrast to a negative dT_c/dP observed in the heavier superconducting Se and Te.[35] A jump in T_c up to 17 K is observed in S at 157 GPa, which is attributed to the bco-β-Po phase transition[39] (Fig. 4, lower panel). The T_c for β-Po phase of sulfur is calculated as 17 K at 160 GPa (Refs. 37,40) in agreement with the experiment. For a predicted bcc phase in S at 585 GPa, T_c is calculated as 15 K.[18] Another theoretical work that shows a simple cubic phase to be stable in S between β-Po and bcc phases, predicts T_c below 10 K at pressure of 280 GPa.[37,40]

One can assume that the differences in the pressure dependence of T_c and electronic structure reported for S and Se (Ref. 37) are connected with the difference in the pressure dependence of structural parameters for the metallic phases. In Fig. 4, the pressure dependence of T_c in S and Se (lower panel) is shown in comparison with the pressure dependence of the structural parameters of the modulated bcm and β-Po phases. The differences in T_c correlate with the different behavior of both the modulation vector q and the cell angle of the bcm structure. The value of q for S decreases linearly with pressure, in contrast to the strong nonlinearity of q observed in Se.[7] Also, the pressure dependence of the cell angle β of the modulated bcm structure is distinct in S-IV and Se-IV. Additional first-principles calculations would be helpful to examine the relationship between the different structural behavior of the metallic phases of S and Se and their electronic structure, including the different pressure dependence of T_c in these phases.

Group-VI elements S, Se, and Te now all confirmed to have an incommensurately modulated phase at high pressure and all appear to have superconducting states at low temperatures and high pressures. First-principle calculations should be now employed to investigate the possibility of an electronic nesting instability, a possible development of a charge-density wave (CDW) and enhancement of electron-phonon coupling at the origin of the incommensurability. Further theoretical studies would be helpful to examine correlation and possible competition of incommensurate modulations and a superconducting state in these systems.

V. CONCLUSION

We have shown that phase IV of sulfur stable above 83 GPa is incommensurately modulated, as found earlier for Se-IV and Te-III. The modulated bcm structure of S-IV and Se-IV is shown to transform to the β-Po structure of S-V and Se-V at pressures of 153 and approximately 80 GPa, respectively. Analysis of the interatomic distances in Se from ambient pressure to 150 GPa shows changes in bonding properties on compression from covalent to metallic. The pressure dependence of structural parameters in the metallic phases is found to be essentially different for S and Se, which may account for the difference in the pressure dependence of superconducting transition temperatures in these materials.

Note added in proof. Recent study on metallic phases of sulfur[41] confirms the incommensurate nature of sulfur above 83 GPa and reports Rietveld refinement of S-IV at 100.2 GPa. It also indicates an existence of another previously unreported phase of S stable between S-III and S-IV with a triclinic structure, the same as recently reported for Te-II and Se-III.[32]

ACKNOWLEDGMENTS

We thank V. F. Degtyareva for stimulating discussions. This work and HPCAT was supported by DOE-BES, DOE-NNSA (CDAC), DOD-TACOM, NSF, NASA, and the W.M. Keck Foundation. The authors acknowledge financial support from NSF, through Grant No. EAR-0217389. The Advanced Photon Source is supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

[1] R. J. Nelmes, D. R. Allan, M. I. McMahon, and S. A. Belmonte, Phys. Rev. Lett. **83**, 4081 (1999).

[2] M. I. McMahon, T. Bovornratanaraks, D. R. Allan, S. A. Belmonte, and R. J. Nelmes, Phys. Rev. B **61**, 3135 (2000).

[3] M. I. McMahon, O. Degtyareva, and R. J. Nelmes, Phys. Rev. Lett. **85**, 4896 (2000).

[4] M. I. McMahon, S. Rekhi, and R. J. Nelmes, Phys. Rev. Lett. **87**, 055501 (2001).

[5] K. Takemura, K. Sato, H. Fujihisa, and M. Onoda, Nature (London) **423**, 971 (2003).

[6] C. Hejny and M. I. McMahon, Phys. Rev. Lett. **91**, 215502 (2003).

[7] M. I. McMahon, C. Hejny, J. S. Loveday, L. F. Lundegaard, and M. Hanfland, Phys. Rev. B **70**, 054101 (2004).

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

[9] Y. Akahama, M. Kobayashi, and H. Kawamura, Phys. Rev. B **47**, 20 (1993).

[10] J. C. Jamieson and D. B. McWhan, J. Chem. Phys. **43**, 1149 (1965).

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

[12] M. Takumi, T. Masamitsu, and K. Nagata, J. Phys.: Condens. Matter **14**, 10 609 (2002).

[13] Y. Akahama, M. Kobayashi, and H. Kawamura, Solid State Commun. **83**, 273 (1992).

[14] Y. Akahama, M. Kobayashi, and H. Kawamura, Solid State Commun. **83**, 269 (1992).

[15] T. Kruger and W. B. Holzapfel, Phys. Rev. Lett. **69**, 305 (1992).

[16] Y. Akahama, M. Kobayashi, and H. Kawamura, Phys. Rev. B **48**, 6862 (1993).

[17] H. Luo, R. G. Greene, and A. L. Ruoff, Phys. Rev. Lett. **71**, 2943 (1993).

[18] O. Zakharov and M. L. Cohen, Phys. Rev. B **52**, 12 572 (1995).

[19] A. Nishikawa, K. Niizeki, and K. Shindo, Phys. Status Solidi B **211**, 373 (1999)

[20] A. Nishikawa, K. Niizeki, K. Shindo, and K. Ohno, J. Phys. Chem. Solids **56**, 551 (1995).

[21] F. Kirchhoff, N. Binggeli, G. Galli and S. Massidda, Phys. Rev. B **50**, 9063 (1994).

[22] E. Gregoryanz, V. V. Struzhkin, R. J. Hemley, M. I. Eremets, H. K. Mao, and Y. A. Timofeev, Phys. Rev. B **65**, 064504 (2002).

[23] A. P. Hammersley, FIT2D, European Synchrotron Radiation Facility, 1998.

[24] V. Petricek and M. Dusek, Institute of Physics, Praha, Czech Republic, 2000.

[25] O. Degtyareva, E. Gregoryanz, M. Somayazulu, P. Dera, H. K. Mao, and R. J. Hemley, Nat. Mater. **4**, 152 (2005)

[26] H. Fujihisa, Y. Akahama, H. Kawamura, H. Yamawaki, M. Sakashita, T. Yamada, K. Honda, and T. Le Bihan, Phys. Rev. B **70**, 134106 (2004).

[27] *Mathematical, Physical, and Chemical Tables*, 2nd ed. edited by E. Prince, Vol. C of International Tables for Crystallography (Kluwer Academic, Dordrecht, 1999), Sec. 9.8

[28] M. Evain, U-FIT, A cell parameter refinement program, Institut des Matriaux Jean Rouxel, Nantes, 1992.

[29] B_{1x} and B_{1z} are the refinable modulation parameters in a sum of Fourier amplitudes that define modulation:

$$u_\alpha(\bar{x}_4) = \sum_{n=1}^{\infty}[A_{n\alpha}\cos(2\pi n\bar{x}_4) + B_{n\alpha}\sin(2\pi n\bar{x}_4)]$$

with $\alpha=x,y,z$ where $\bar{x}_4$ is the forth space coordinate, and $A_{n\alpha}$and $B_{n\alpha}$ are the amplitudes of the *n*th order Fourier components.

[30] R. J. Hemley, J. Shu, M. A. Carpenter, J. Hu, H. K. Mao, and K. J. Kingma, Solid State Commun. **114**, 527 (2000).

[31] Y. Ohmasa, I. Yamamoto, M. Yao, and H. Endo, J. Phys. Soc. Jpn. **64**, 4766 (1995).

[32] C. Hejny and M. I. McMahon, Phys. Rev. B **70**, 184109 (2004).

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

[34] I. V. Berman, Zh. I. Binzarov, and P. Kurkin, Sov. Phys. Solid State **14**, 2192 (1973).

[35] Y. Akahama, M. Kobayashi and H. Kawamura, Solid State Commun. **84**, 803 (1992).

[36] F. Mauri, O. Zakharov, S. de Gironcoli, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **77**, 1151 (1996).

[37] S. P. Rudin, A. Y. Liu, J. K. Freericks, and A. Quandt, Phys. Rev. B **63**, 224107 (2001).

[38] M. Otani and N. Suzuki, Phys. Rev. B **63**, 104516 (2001).

[39] V. V. Struzhkin, R. J. Hemley, H. K. Mao, and Y. A. Timofeev, Nature (London) **390**, 382 (1997).

[40] S. P. Rudin and A. Y. Liu, Phys. Rev. Lett. **83**, 3049 (1999).

[41] C. Hejny, L. F.Lundegaard, S. Falkoni, *et al.*, Phys. Rev. B **71**, 020101(R) (2005).