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Electronic structures and the space group of orthorhombic selenium under high pressure

Masaaki Geshi¹, Tatsuki Oda² and Yasuaki Hiwatari²

¹ Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Canada K1K 4M3

² Department of Computational Science, Faculty of Science, Kanazawa University, Kanazawa, 920-1192, Japan

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Abstract

We have performed first-principles electronic structure calculations for high-pressured phases of selenium by using the full-potential linearized augmented-plane-wave method. We present electronic structures and the optimized atomic positions in the unit cell for the third and fourth phases. From the positions obtained, the space group of the fourth phase was determined as $P2_1/m$, which is almost consistent with the experimental results.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Pressure-induced structural phase transitions of selenium have been investigated since the development of high-pressure x-ray diffraction experimental techniques [1, 2]. The most stable structure under ambient pressure is a trigonal structure. This structure is transformed into a monoclinic structure (M-I) with increasing pressure at 17 GPa [2], from the M-I structure into another monoclinic structure (M-II) at about 23 GPa [1], from the M-II structure into an orthorhombic structure at 28 GPa [1], from the orthorhombic structure into a β -Po-type rhombohedral structure at 60 GPa [1], from the β -Po-type structure into a bcc structure at 140 GPa [1]. At some of these phase transitions large discontinuities of the lattice parameters were not observed in x-ray diffraction experiments—especially at the transition from the orthorhombic to the β -Po-type structure. At this transition, the twelve diffraction lines that were observed for the orthorhombic structure were decreased to four lines with the changes: doublet to singlet and decaying intensity. No clear discontinuous change of volume was observed in the experiments. These experimental results suggest that the transition is of second order. The orthorhombic structure was identified by the monoclinic angle being 90° without specifying the atomic positions, because of the difficulty of experiments under high pressure. The space group of this structure was not determined by the experiment [1]. Nishikawa *et al* [3] carried

out first-principles calculations for both orthorhombic and β -Po-type structures, and adopted the space group $Cmcm$ for the former structure.

The M-II phase, which is the lower-pressured phase of the orthorhombic structure, is the first metallic phase in the sequence of high-pressured phases. This phase is discussed in connection with the second high-pressured phase of tellurium (Te-II), because the latter phase has a similar crystal structure and is the first of the metallic phases [2, 4]. The structure of the Te-II phase is constituted by puckered layers, in which there are long-short-bond zigzag chains. The space group for Te-II was reported to be $P2_1$ [4].

We have performed first-principles electronic structure calculations for all phases and have already presented a process of transformation from the trigonal to the M-I structure [5], atomic positions in the unit cell [5], and electronic structures for M-I, β -Po-type, and bcc structures [5–7]. It is difficult to extract all of these properties under high pressure from experiment. Our calculated results have significantly contributed to much of the understanding of complex high-pressured phases for selenium. In this paper, we present the electronic structures of the orthorhombic and M-II phases. Furthermore, the atomic positions obtained by the calculations allow us to determine the space group of the orthorhombic structure. The result relating to the orthorhombic phase is partially described elsewhere [8].

2. Calculation method

We performed a structural optimization of atomic positions in the orthorhombic framework fixed at experimental lattice parameters without assuming any symmetry operation of the point group by using the full-potential linearized augmented-plane-wave (FLAPW) method. The calculation was carried out with the WIEN97 code [9]. We used the generalized gradient approximation [10] and took electrons in $[\text{Ar}](3d)^{10}$ states as core electrons. The muffin-tin radius of 2.0 au and the energy cut-off of 16 Ryd were taken to construct the basis of augmented plane waves. For the self-consistent calculations, 1824 k -points were sampled. The lattice constants were taken as the experimental values at 28.0, 34.9, and 54.2 GPa [1] for the orthorhombic structure and at 26 GPa for M-II structure [2].

3. Results

3.1. Orthorhombic structure

The four atomic positions in the unit cell were optimized and interpreted as $(x, y, 1/4)$, $(-x, -y, 3/4)$, $(x + 1/2, y + 1/2, 1/4)$, $(-x + 1/2, -y + 1/2, 3/4)$ ($x = y = 1/8$). These positions have two intrinsic symmetry operations in addition to the translational symmetry of crystal. One is reflection in the mirror plane perpendicular to the c -axis on each atom and the other is rotation about the screw axis along the c -axis through the centre point between nearest neighbours. Because these operations are related to only one axis, the space group is classified among monoclinic space groups. (Orthorhombic space groups contain operations related to a -, b -, and c -axes.) We finally identify the space group as $P2_1/m$ and the atomic positions described above as a dual set for the 2e site in Wyckoff notation. This identification is consistent with the extinction law observed in the x-ray diffraction pattern [1] and does not need the angle between the a - and b -axis (monoclinic angle) to be 90° . Judging from the experimental results [1, 2], the monoclinic angle of the real system could be about 90° over the whole range of pressure of interest.

The most striking feature different from those for $Cmcm$ is a non-vanishing value of x . This indicates a relatively flat band below the Fermi level in the electronic band dispersion along the (100) direction. The total energy of the structure is always at least 5 mRyd lower

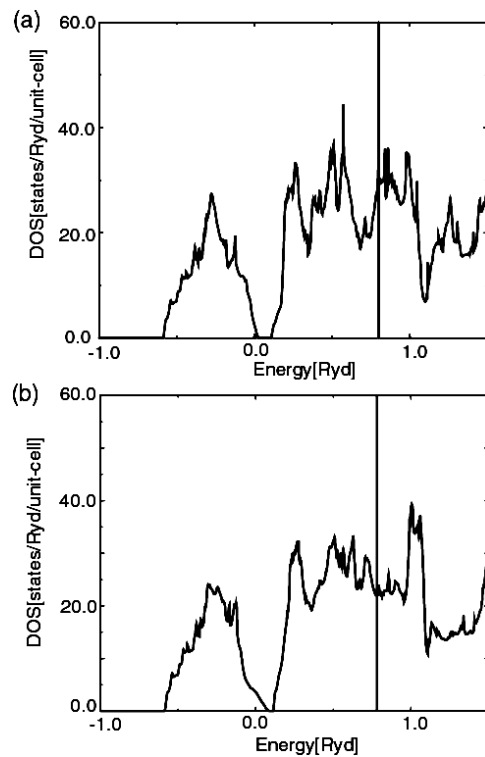


Figure 1. The DOSs at 28 GPa for the space groups Cmc (a) and $P2_1/m$ (b). Vertical lines indicate the Fermi level.

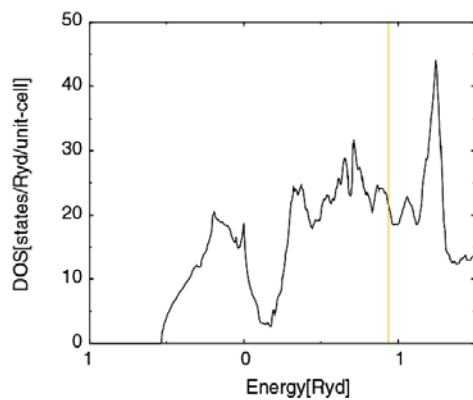


Figure 2. The DOS at 54.2 GPa for the space group $P2_1/m$.

than that of Cmc in the pressure range of interest. In the density of states (DOS), as shown in figure 1, for the space group $P2_1/m$, the deep dip below the Fermi level disappears, whereas in the DOS for Cmc it appears. When pressure increases, the s band touches the p band; however, the basic shape of the DOS does not change. In the experiment in [1] the transition to the β -Po-type structure was considered to be of a second order. The DOS for the group $P2_1/m$ near the transition pressure, as shown in figure 2, is very similar to that of the β -Po-type structure [8].

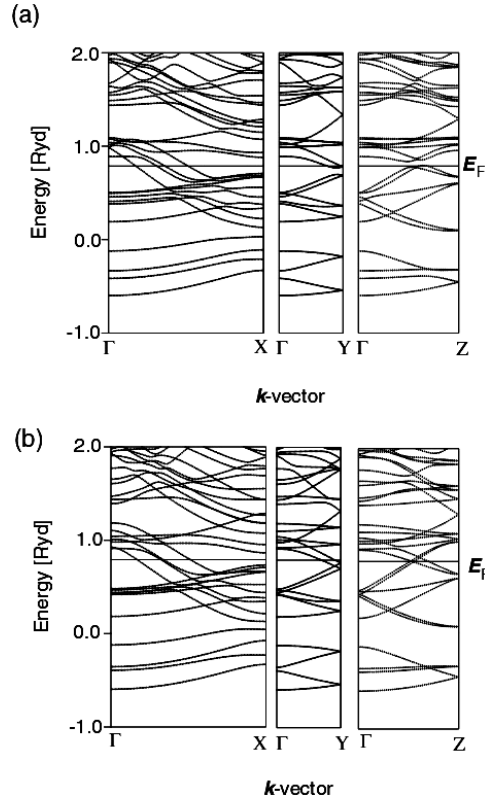


Figure 3. Band dispersions of the M-II structure. (a) The internal parameters obtained by Aoki *et al* [4] and (b) those optimized in this work are used.

It is also found that the β -Po-type structure can be continuously transformed to the $P2_1/m$ structure. The monoclinic angle γ of the orthorhombic phase is represented by

$$\cos \gamma = -\frac{1 + 4 \cos \alpha_r}{\sqrt{9 + 16 \cos \alpha_r}},$$

where α_r is the rhombohedral angle of the β -Po-type structure. In the experiment, $\alpha_r = 104.2^\circ$ on the phase boundary, which gives $\gamma = 89.5^\circ$. If the structure smoothly changes on the phase boundary in a real system, the monoclinic angle of the fourth phase of selenium might be somewhat distorted from the right angle.

3.2. M-II structure

The optimized atomic positions of the four atoms in the unit cell are represented as follows; (x_1, y_1, z_1) , $(-x_1, y_1 + 1/2, -z_1)$, (x_2, y_2, z_2) , $(-x_2, y_2 + 1/2, -z_2)$, ($x_1 = 0.327$, $y_1 = 0.238$, $z_1 = 0.497$; $x_2 = 0.327$, $y_2 = 0.992$, $z_2 = 0.997$). This atomic configuration also obeys the space group $P2_1$ but, unlike the case for the Te-II phase, does not form any long-short-bond alternating chain. The corresponding zigzag chain in selenium has the single bond length of 2.54 Å. Structures having an alternating chain like Te-II phase are unstable in selenium. Band dispersions are shown in figure 3. When the internal parameters obtained by Aoki *et al* [4] are used, the band gap in the Γ -Z direction is observed (see figure 3(a)).

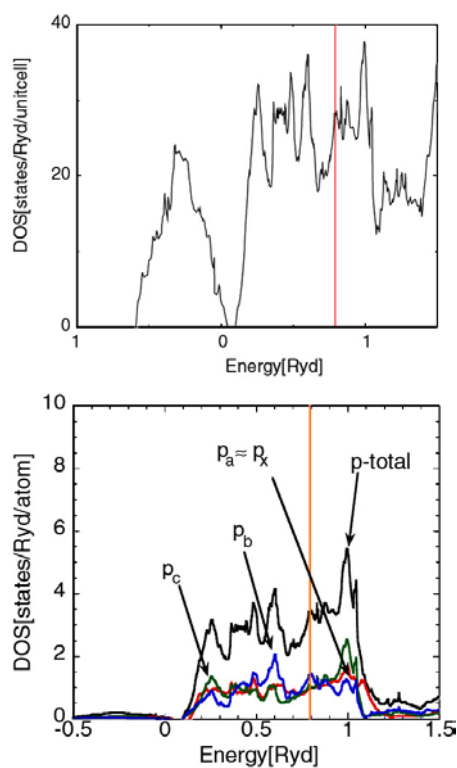


Figure 4. The total DOS (upper panel) and partial DOSs (lower panel) of M-II structure at 26 GPa.

This property was also reported in previous work for Te-II phase [11]. However, the total energy of the structure is 5 mRyd/atom higher than that of the structure optimized in this work. This implies that a phenomenon like the Peierls transition never happens. The total DOS and partial DOSs of electronic structure are shown in figure 4. These densities indicate no lone pair electrons and a complete metallic electronic structure around the Fermi level, while in the M-I phase there are partial lone pair electrons and partially metallic behaviour is observed [5]. These changes in electronic structure from M-I to M-II structure correspond well to the reduction in the resistivity [2] at interesting pressures. The three components of the partial DOSs projected onto the p orbitals have almost the same value around the Fermi level, which indicates that the electronic structure has a three-dimensional character although the M-II structure has a layer crystal structure.

We note that, as in the DOS of the *Cmcm* structure, there is a large dip just below the Fermi level in the DOS of the M-II structure. This is considered to indicate that the same kind of electronic instability as was found in the orthorhombic phase exists in the electronic state of the present M-II structure.

4. Conclusions

The electronic structures for the third and fourth phases under high pressure have been studied by using the FLAPW method, assuming the lattice constants observed in experiments. We optimized the atomic positions in the unit cell for both phases. From the positions obtained,

the space group of the fourth phase was determined as $P2_1/m$. These positions show more stable electronic structure than those in the $Cmcm$ structure and change almost continuously to the β -Po structure. The latter property naturally explains the transitions of second order that have found in experiments. The electronic structure of the M-II phase shows a completely metallic character and no lone pair electrons. Our first-principles calculation on this phase shows that the long–short-bond alternating chain that has been found in Te-II is unstable, but we do not conclude that the electronic and atomic configurations presented here will be the most stable.

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References

- [1] Akahama Y, Kobayashi M and Kawamura H 1993 *Phys. Rev. B* **47** 20
- [2] Ohmasa Y, Yamamoto I, Yao M and Endo H 1995 *J. Phys. Soc. Japan* **64** 4766
- [3] Nishikawa A, Niizeki K, Shindo K and Ohno K 1995 *J. Phys. Chem. Solids* **56** 551
- [4] Aoki K, Shimomura O and Minomura S 1980 *J. Phys. Soc. Japan* **48** 551
- [5] Geshi M, Oda T and Hiwatari Y 1999 *J. Phys. Soc. Japan* **68** 3341
- [6] Geshi M, Oda T and Hiwatari Y 1998 *J. Phys. Soc. Japan* **67** 3141
- [7] Geshi M, Oda T and Hiwatari Y 2000 *Prog. Theor. Phys. Suppl.* **138** 249
- [8] Geshi M, Oda T and Hiwatari Y 2002 *J. Phys.: Condens. Matter* **13** 9401
- [9] Blaha P, Schwarz K and Luitz J 1999 *WIEN97, a Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties* Technical University of Vienna (ISBN 3-9501031-0-4)
This is an improved and updated Unix version of the original copyrighted WIEN code, which was published by Blaha P, Schwarz K, Sorantin P and Trickey S B 1990 *Comput. Phys. Commun.* **59** 399
- [10] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [11] Doerre G and Joannopoulos J D 1979 *Phys. Rev. Lett.* **43** 1040