Volume compression of period 4 elements: Zn, Ge, As, and Se up to multimegabar pressures

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Keywords: x-ray diffraction, structural phase transition, atomic volume

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In general, elements tend to be transformed to a close-packed monatomic metal at ultra-high pressure. From the viewpoint of high-pressure science, it is important to clarify the details of these structural phase transitions experimentally. In addition, comparing atomic volumes of monatomic metals in elements of the same period is essential for understanding the systematics in the condensation state of these elements electronically. Recently, we have compared atomic volumes of the period 5 elements: Ag, Cd, Sn, Sb, Te, I, and Xe in the multimegabar region and found one systematic behavior [1]. That is, in the high-pressure monatomic metal phases, as the atomic number increases, the atomic volume also increases.

Our interest focuses on investigating this systematicity in the period 4 elements. We extended X-ray diffraction experiments of Zn, Ge, As, and Se up to multimegabar pressures; 250, 251, 253, and 320 GPa, respectively, at 298 K on the BL10XU at SPring-8 by the angle-dispersive method. Pressure was estimated based on the Pt EoS scale [2]. In addition, up to now, previous X-ray studies of Zn, Ge, As, and Se have been reported at pressures up to 126 GPa [3], 190 GPa [4], 122 GPa [5], and 150 GPa [6], respectively.

Figure 1 shows diffraction patterns of the highest pressure phase for each element. The hcp phase of **Zn** was stable up to 250 GPa. The c/a ratio of lattice constants decreased rapidly with pressure. It reached to ~1.6 at around 30 GPa and became almost constant. A decrease in the optical reflectance of the sample above 50 GPa is of interest in suggesting certain change in the electronic structure such as to semimetallic. **Ge** transformed to the hcp phase at ~180 GPa after the structure sequence: diamond-β-Sn-*Imma*-sh-*Cmca*. In the stable region of the *Cmca* phase, the hcp phase with the relatively larger atomic volume than the *Cmca* phase coexisted and the both volumes reversed at ~180 GPa. The hcp phase was stable up to 251 GPa. **As** transformed to the bcc phase from the monoclinic host-guest $I'2/c$ phase at 133 GPa and the bcc phase was stable up to 253 GPa. The atomic volume of the host-guest phase was determined assuming that gest atoms form a tetragonal lattice. **Se** transformed to the bcc phase from the β-Po type phase at 140 GPa and the bcc phase was stable up to 320 GPa though a bcc-fcc phase transition has been predicted theoretically [7].

Figure 2 shows compression curves of metallic high-pressure phases of period 4 elements: Zn, Ge, As, and Se,
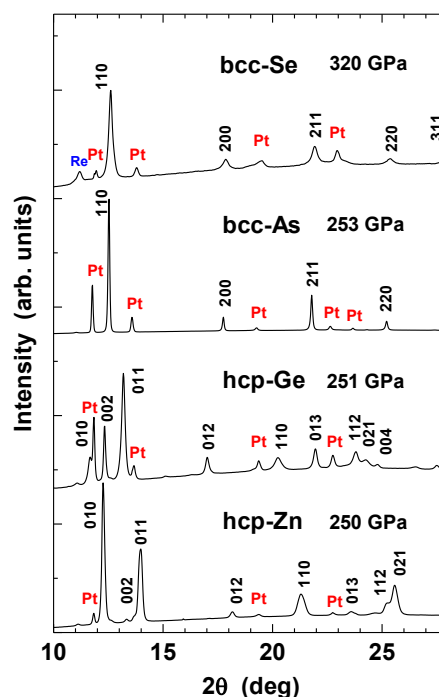

Figure 1. Diffraction patterns of the highest pressure phase for each element; Zn, Ge, As, and Se.
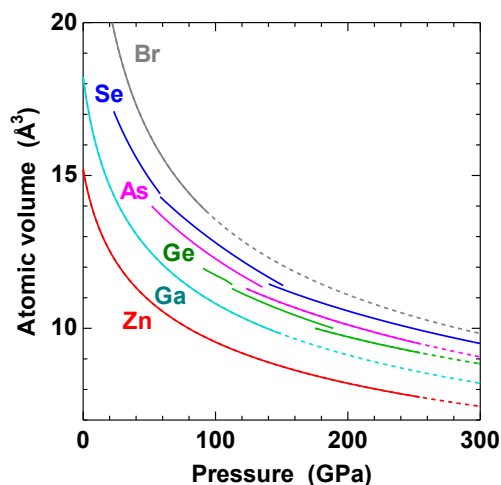

Figure 2. Compression curves of metallic high-pressure phases of period 4 elements: Zn, Ga, Ge, As, Se, and Br.

together with data of Ga [8] and Br [9] reported previously. Period 4 elements exhibit the same systematicity as period 5 elements. In other words, as the atomic number increases, the atomic volume also increases. In general, atoms in metallic crystals are described to consist of a positively charged ion core surrounded by the valence electron gas. As the atomic number increases, the number of protons increases and the ionic core contracts to shield the positive charges. As a result, the expansion of the valence electron gas with the increase in the number of electrons will exceed the contraction. Therefore, the systematicity is considered to be universal for the typical elements.

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