Local structure and effective pair potential of rock-salt type and disordered rock-salt type AgI under pressure

Akira Yoshiasa1, Hiroshi Arima2, Hiroshi Fukui2, Osamu Ohtaka2, Osamu Kamishima3, Maki Okube4, and Yoshinori Katayama5
1Graduate School of Science, Kumamoto University, Kumamoto 860-8555, Japan
2Graduate School of Science, Osaka University, Toyonaka 560-0043, Japan
3Institute Multidisciplinary Research Adv Mat, Tohoku University, Miyagi 980-8577, Japan
4Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-850 Japan.
5Japan Atomic Energy Agency , Hyogo 679-5148, Japan

e-mail: yoshiasa@sci.kumamoto-u.ac.jp

Abstract. X-ray absorption fine structure (XAFS) observations on iodine K edge of AgI have been performed under high pressure and high temperature up to 6.0 GPa and 1000K to investigate the local structure and effective potentials in high pressure phases. In EXAFS analysis, we have directly carried out the numerical integration of EXAFS function. The anharmonic effective pair potentials \( V(u) = \alpha u^2/2 + \beta u^3/3! \) for I-Ag bond have been determined under pressures. \( \alpha \)-AgI and disordered rock-salt type phase have superionic conduction behaviors. Ag ions occupy both octahedral and tetrahedral sites in the disordered phase and twenty percent of Ag ions occupy the tetrahedral site as a maximum value at 2GPa. The transition between the rock-salt type and disordered rock-salt type phases is a broad disorder type within the same structure. From the viewpoint of the local structure analyses on XANES and EXAFS spectra, some sudden changes are recognized near the phase transition point. Pressure influences greatly the effective pair potential of anti-bonding side and anharmonicity decreases with increasing pressure. Phonon dispersion relation of the rock-salt type AgI under pressure has been derived from EXAFS experiments. Analysis of EXAFS Debye-Waller factor is useful because the force constant can be decided directly even at high pressure and high temperature.

1. Introduction
AgI is a much studied material because of the super ionic behavior of Ag ions in \( \alpha \)-AgI phase with bcc sub-lattice structure and in the disordered rock-salt type phase with fcc sub-lattice structure. We have determined the precise P-T phase diagram of AgI (Fig. 1) by in-situ high-pressure high-temperature synchrotron experiments [1]. The wurtzite type structure of AgI undergoes a first-order phase transition to \( \alpha \)-AgI phase. The rock-salt type phase transforms to the disordered rock-salt type phase by a higher-order phase transition under pressure. An in-situ neutron diffraction study under high pressure and high temperature showed that the super ionic behavior in the disordered rock-salt type phase is related to the diffuse transition with a small anomaly in lattice constant and a continuous increase in occupation of interstitial tetrahedral sites by Ag ion with increasing temperature [2].
Figure 1. P-T phase diagram of AgI [1]. The rock-salt type phase transforms to disordered rock-salt type phase with increasing temperature at 2.0 GPa and 620 K.

X-ray absorption fine structure (XAFS) spectra yields information on the local environments and bonding distances around a particular kind of atom under high pressure and high temperature. The usefulness of extended X-ray absorption fine structure (EXAFS) as a probe of vibration dynamics of local structure was discussed by many authors [3-5]. The analysis of EXAFS Debye-Waller factor provides an effective pair potential with temperature-independent and pressure-dependent shape [5-7]. We investigated the anharmonic effective pair potentials in AgI, AgBr and CuBr under high pressure using the EXAFS technique and revealed the pressure dependent effective pair potential and super ionic conduction mechanism in α-AgI type phases [7-10].

In this study, XAFS measurements of AgI under high pressure and high temperature up to 6.0 GPa and 1000 K have been performed to investigate the local structure in α-AgI, the rock-salt type and disordered rock-salt type phases. The transition between the rock salt-type and disordered rock-salt type phases has been discussed based on the local structure analysis. We have demonstrated the pressure dependence of anharmonic effective pair potentials for I-Ag bond in the rock-salt type phase. Phonon dispersion relation of the rock-salt type AgI under pressure has been derived from the EXAFS experiments.

2. Experimental and analysis
XAFS measurements were performed on a bending magnet beamline, BL14B1, at the SPring-8, Hyogo, Japan. High-pressure and high-temperature conditions were generated using a cubic-type 180 ton apparatus, SMAP2 [11], installed on the beamline. AgI powder with a nominal purity of 99.99 % was provided by Furuuchi Chemical Co. (Tokyo, Japan). The powder was finely ground and mixed with BN powder to dilute the sample. The powder mixture occupied half the volume of the sample chamber and the rest was filled with the pressure calibrant [10,12]. The chamber was put between a pair of graphite-disc heaters and encased in a cubic-shaped pressure-transmitting medium made of boron and epoxy resin. Details of the high-pressure cell assembly have been described elsewhere [11,12]. Generated pressure was determined with an accuracy of about 0.2 GPa [12]. Temperature was monitored with a thermocouple inserted between the two disc heaters.

Figure 2. Fourier transforms of the I K-edge EXAFS for AgI at 2.0 GPa 673 K. No phase shift correction is made.
XAFS spectra near the I K-edge were measured in the transmission mode under high pressure up to 6.0 GPa and 1000 K. The synchrotron radiation was monochromatized by a Si(311) double-crystal monochromator and focused vertically by two millers. The size of the X-ray beam was reduced to 0.3 x 0.3 mm². The intensities of the incident and transmitted beam were measured by ionization chambers.

The EXAFS interference function, \( \chi(k) \), was extracted from the measured absorption spectrum using the standard procedure, where \( k \) denotes the wave number of photoelectrons: \( k = 2m(E-E_0)/\hbar^2 \)^{1/2}. The \( \chi(k) \) was normalized using MacMaster coefficients according to the EXAFS workshop report [13]. Figure 2 shows examples of Fourier transforms of \( \chi k^3 \) in the range 3.0 Å⁻¹ < \( k < 13.0 \) Å⁻¹ at 2.0 GPa 673 K.

We consider the vibration of cation and anion, interacting via an anharmonic pair potential \( V(u) \): \( V(u)=au^2/2+bu^3/3! \), where \( a \) and \( b \) are the potential coefficients and \( u \) is the deviation of the bond distance from the location of the potential minimum. In the parameter fitting, we have directly carried out the numerical integration of EXAFS function and evaluated the precise anharmonic effective pair potentials by comparing Fourier-filtered observed and calculated EXAFS interference functions, \( \chi(k) \) [5,8]. On the nonlinear least-squares parameter fitting, according to the EXAFS workshop report [13], the equal deformation of observed and calculated EXAFS functions improves the accuracy of the parameter fitting. We could not determine the individual I-Ag distance for the octahedral and tetrahedral sites in the disordered rock-salt type phase separately because of large correlation among the parameters. Single shell model, therefore, was adopted. Because no evident pressure dependence for the experimental threshold energies and mean free path at this experimental resolving power was revealed, we assumed that the threshold energies and mean free path have negligible pressure dependence in this pressure range. The reliability of fit parameter, \( R \), between the experimental and calculated EXAFS functions was less than 0.041. Details on the measurement and analysis have been shown elsewhere [7-10].

Figure 3. Experimental I K-edge XANES spectra of the rock-salt type (373, 473, 573 K), disordered rock-salt type (673 and 773 K) and liquid phases (873 and 973 K) at 2.0 GPa. The shape of the XANES changed suddenly near 573 K.
3. Results and discussion

3.1. Local structure changes near the phase transition points to super ionic conductors.

X-ray absorption near-edge structure (XANES) spectra are quite sensitive to the electronic states and three-dimensional atomic configuration around X-ray absorbing atoms. XANES spectra are useful for determining the coordination environments of I ions under high temperature and high pressure [9,11]. XANES spectra of the rock-salt type (373, 473, 573 K), disordered rock-salt type (673 and 773 K) and liquid phases (873 and 973 K) at 2.0 GPa are shown in Fig. 3, where the XANES spectra seem to change suddenly near the phase transition point between the rock-salt type and disordered rock-salt type phases though the edge features change gradually with increasing temperature. The edge features of the melt AgI are comparable to that of the disordered phase, but the main peak positions shift to lower energies. It is known that the melt AgI has two distinct local structures of tetrahedral and octahedral coordination [14].

The I-Ag distances are plotted as a function of temperature at 1.0, 4.0 and 6.0 GPa in Fig 4a. The distances from iodine to silver ions in the octahedral sites of the rock-salt type phase decreases with pressure. At 1.0 GPa, the rock-salt type phase transforms to α-AgI and the coordination number change six-fold to four-fold at 550 K. The I-Ag distances become rapidly short at the first-order phase transition point with increasing temperature.

Figure 4b shows the temperature dependence of I-Ag distances at 2.0 GPa. The rock-salt type phase transforms to the disordered rock-salt type around 620 K at this pressure. Ag ions occupy both the octahedral and tetrahedral sites of the fcc sub-lattice formed by I ions in the disordered phase. Our EXAFS analyses provide the average distances from iodine to silver ions in the tetrahedral and octahedral sites. From the viewpoint of the local structure analyses on XANES and EXAFS spectra (Figs. 3 and 4b), some discontinuous or sudden changes are recognized near the phase transition point. The tetrahedral site in the disordered rock-salt type phase seems to be occupied at higher temperature than 573 K by silver ions. The Ag ions which occupy the tetrahedral site increase rapidly between 573K and 673K. Twenty percent of Ag ions occupy the tetrahedral site as a maximum value at 2GPa (Fig. 4b).

3.2. Pressure dependence of anharmonic effective pair potential in rock-salt type AgI.

We have determined the anharmonic effective pair potential V(u)=au²/2+bu³/3!. A smaller value of potential coefficient a represent a weaker bonding and a broader potential. The potential coefficients a at 2.0, 4.0 and 6.0 GPa are 1.66(5), 1.70(6) and 1.88(6) eV/Å², respectively. The coefficient a for the I-Ag bond in the rock-salt type AgI is significantly smaller than that of the tetrahedral site (2.5(1) eV/Å³) in α-AgI at 1.0 GPa. The octahedrally coordinated ion in the rock-salt type structure has a broader effective pair potential and a larger mean square relative displacement of thermal vibration than the tetrahedrally coordinated ion. The rock-salt type AgI and AgBr take the similar pressure dependence [8].

The parameter b refers to the skewness of effective pair potential, arising from anharmonic motion. The potential coefficients b at 2.0, 4.0 and 6.0 GPa are -2.6(6), -2.1(5), -1.9(7) eV/Å³, respectively. Figure 5 shows the anharmonic effective pair potentials for I-Ag bonds under the pressure. The effective pair potentials are influenced by pressure and become steeper with increasing pressure. Pressure influences greatly the potential of anti-bonding side and anharmonicity decreases with increasing pressure.

EXAFS provides the information about thermal vibration of local structure. The derived values refer to short-range correlation of the atomic motion. We try to estimate the phonon dispersion relations using the potential coefficient a by calculating the dynamical matrix with rigid-ion model [15], where unknown parameters such as the effective charge were used temporarily from a model adopted for stable phase at ambient conditions. Details of the calculation were given in Ref. 16.
phonon dispersion relation along [100] is shown in Fig. 6 along with the experimental data obtained by neutron inelastic scattering [17]. The obtained results for AgI derived from the EXAFS are compared with those for AgBr at ambient pressure from the Neutron inelastic scattering. Neutron inelastic scattering experiments have many difficulties under the high pressure and high temperature. On the other hand, analysis of EXAFS Debye-Waller factor is useful because the force constant can be decided directly even at high pressure and high temperature. We can also use the EXAFS Debye-Waller factor analysis for the assignments of vibration mode in complicated systems under pressure.

Figure 4. Temperature dependence of the I-Ag distances in AgI at 1.0, 4.0 and 6.0 GPa (a). Occupancies of Ag ions in the tetrahedral site were estimated by average I-Ag distances at 2.0 GPa (b).

Figure 5. Anharmonic effective pair potentials for I-Ag bond in the rock-salt type phases at 2.0 GPa (straight line), 4.0 GPa (dotted line) and 6.0 GPa (dashed line).

Figure 6. Comparison of the calculated phonon dispersions of the rock-salt type AgI at 6.0 GPa with the experimental data of rock-salt type AgBr at 0.1 MPa [17]. The curves are derived from the EXAFS experiments.
Acknowledgments
We thank Y. Okajima for her technical support during the XAFS measurements. The results were achieved with BL14B1 of SPring-8 under the Facilities Utilization system of Japan Atomic Energy Agency

References
[1] Ohtaka O, Takebe H, Yoshiasa A, Fukui H and Katayama Y 2002 Solid State Comm. 123 213
[2] Keen D A, Hull S, Hayes W and Gardner N J G 1996 Phys. Rev. Lett. 77 4914
[3] Stern E A, Livinš P and Zhang Z, 1991 Phys. Rev. B43 8850
[4] Dalba G, Fornasini P, Gotter R, Cozzii S, Ronchetti M and Rocca, F 1994 Solid State Ionic, 69 13
[5] Yoshiasa A and Maeda H Solid State Ioniics 1999 121 175
[6] Dalba G, Fornasini P and Rocca F 1993 Phys. Rev. B47 8502
[7] Yoshiasa A, Murai K, Nagai T and Katayama Y 2001 Jpn. J. Appl. Phys. 40 2395
[8] Yoshiasa A, Fukui H, Arima H, Okube M, Katayama Y, Murai K, Sugahara M and Ohtaka O 2007 The American Institute of Physics, Conf. Proc. 882 569
[9] Yoshiasa A, Okube M, Ohtaka O, Kamishima O and Katayama Y 2000 Jpn. J. Appl. Phys. 39 6747
[10] Yoshiasa A, Nagai T, Murai K, Yamanaka T, Kamishima O and Shimomura O 1998 Jpn. J. Appl. Phys. 37 728
[11] Utsumi W, Funamori K, Katayama Y, Okada T and Shimomura O 2002 J. Phys.: Condens. Matter 14 10497.
[12] Yoshiasa A, Nagai T, Ohtaka O, Kamishima O and Shimomura O 1999 J. Synchrotron Rad. 6 43
[13] Lytle F W, Sayers D E and Stern E A 1989 Physica B, 158 701
[14] Arima H, Ohtaka O, Hattori T, Katayama Y, Utsumi W and Yoshiasa A 2007 J. Phys.: Condens. Matter, 19 076104.
[15] Brüesch P 1982 Phonons: Theory and Experiments I Springer Sciences 34 in Solid-State Sciences.
[16] Kamishima O, Ishii T, Maeda H and Kashino S 1997 Jpn. J. Appl Phys. 36 247
[17] Dorner B, von der Osten W and Bührer W 1976 J. Phys. C9 723