Electron Density Distribution in Amorphous Se Determined by Reverse Monte Carlo Simulation Coupled with Anomalous X-ray Scattering Data

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The ion-electron structure factor estimated from the anomalous X-ray scattering measurements near the Se K absorption edge has been used in the reverse Monte Carlo (RMC) simulation for determining the valence electron density distribution in amorphous Se. The results clearly indicate that the origin of particular valence electron distribution for Se can be explained by two non-bonding electrons and two bonding electrons.

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1. Introduction

Liquid and amorphous metals in their pure states are considered to be binary mixtures of ions and strongly coupled plasma composed of electrons. Based on this idea, it was pointed out that the structure of liquid and amorphous metals should be explicitly described by three correlation functions of electron-electron, electron-ion and ion-ion pairs. When we use the Ashcroft-Langreth form of the partial structure factors, the total X-ray scattering intensity from the system containing N ions and zN valence electrons except for Q = 0 is expressed by

\[ I_{\text{Total}}(Q, E) = \frac{N}{N} \left[ f_i(Q, E) S_{ii}(Q) + 2 \sqrt{z} f_i(Q, E) S_{ie}(Q) \right. \]

\[ \left. + z S_{ee}(Q) \right] + (Z - z) S_{ie}^{\text{inc}}(Q) \]  (1)

where z is the number of valence electrons per atom, Z is the atomic number, Q and E are the wave vector and the energy of the incident X-rays, respectively. \( f_i(Q, E) \) is the scattering factor of an ion including its anomalous dispersion terms. \( S_{ii}(Q), S_{ie}(Q) \) and \( S_{ee}(Q) \) are the partial structure factors of ion-ion, ion-electron and electron-electron pairs, respectively and \( S_{ie}^{\text{inc}}(Q) \) is the incoherent (Compton) scattering factor of ions due to bound electrons. The partial structure factors of \( S_{ie}(Q) \) and \( S_{ee}(Q) \) are given by the following equations:

\[ S_{ie}(Q) = \frac{\rho(Q)}{\sqrt{z}} S_{ii}(Q), \]  (2)

\[ S_{ee}(Q) = \frac{\rho(Q)^2}{z} S_{ii}(Q) + S_{ie}^{\text{inc}}(Q) \]  (3)

where \( \rho(Q) \) is the electron density distribution function in Q-space and \( S_{ie}^{\text{inc}}(Q) \) is the structure factor of uniformly distributed electrons. Egelstaff et al.⁷ firstly indicated the possibility for estimating the ion-electron structure factor in liquid metals by combining the scattering experiments of X-rays, neutrons and electrons. The difference in these intensity profiles originated from their different scattering abilities for ions including nuclei and electrons provides the electron density distribution around an ion. Takeda et al.⁸ have reported a series of works on the ion-electron structure factor in liquid metals by combining their own data of X-rays and neutrons. Recently, we proposed another method for determining the electron density distribution of disordered materials by utilizing the anomalous dispersion effect near the absorption edge.⁹ Fundamentals and usefulness of the anomalous X-ray scattering (hereafter referred to as AXS) method⁹ were demonstrated by the results of amorphous Se. This method has an advantage that the electron density distribution function can be obtained without any combinations of different scattering techniques of X-rays, neutrons or electrons which may induce unavoidable errors arising from their different geometrical factors such as the absorption correction and the angular resolution. Nevertheless, the previous results of the electron density distribution for amorphous Se should be considered far from complete because the experimental data are spread in certain positions mainly arising from the scarcity of counting statistics at each Q value. Then, the reverse Monte Carlo simulation method⁷ is strongly suggested for improving quality of the electron density distribution estimated from the AXS data.

This prompts us to re-analyze the previous AXS data⁹ by applying the RMC simulation method for obtaining the electron density distribution of amorphous Se in real space through the precise determination of its ion-electron structure factor.

2. Fundamentals of Reverse Monte Carlo Simulation

The three-dimensional modeling of electron density distribution in disordered materials could be obtained by using the reverse Monte Carlo (hereafter referred to as RMC) simulation⁷ consisting of the following two main steps. In the first step, RMC simulation is carried out for determining the ionic configuration by using the experimental \( S_{ii}(Q) \) data as an input. Next, the electron density distribution around an ion is
determined so as to reproduce the experimental $S_{\text{ii}}(Q)$ data with the ionic configuration obtained in the first step.

### 2.1 RMC for distribution of ions

The algorithm of RMC method used for determining the ionic distribution is essentially identical to that originally proposed by McGreavy and Pusztai. Thus, only the essential points needed for the present work are given below.

The RMC simulation starts from an initial arrangement with $N$ ions in a cubic supercell of volume $V$, giving the average number density of $\rho_\Lambda = N/V$. The usual periodic boundary condition, in which the cube is surrounded by the images of itself, is applied and the pair distribution function for ion-ion pairs $g_{\text{ii}}(r)$ is calculated. The ion-ion structure factor $S_{\text{ii}}(Q)$ is related to $g_{\text{ii}}(r)$ by the Fourier transformation;

$$S_{\text{ii}}(Q) = 1 + \frac{4\pi \rho_\Lambda}{Q} \int_0^\infty r[g_{\text{ii}}(r) - 1] \sin(Qr)dr.$$  \hspace{1cm} (4)

The structure factor estimated is compared with the experimental results by calculating the following statistics,

$$\chi^2 = \sum_m \frac{(S_{\text{ii}}(Q_m) - S_{\text{ii}}^0(Q_m))^2}{\sigma^2_{\text{ii}}(Q_m)}$$  \hspace{1cm} (5)

where $S_{\text{ii}}^0(Q_m)$ corresponds to the calculated ion-ion structure factor and $\sigma^2_{\text{ii}}(Q_m)$ is the estimate of the uncertainty for the experimental data. New configuration is then generated with the random movement of one ion. In order to prevent ions coming unphysically close to one another, the cut-off distance is set for $g_{\text{ii}}(r)$ closer than the direct contact value of two ions. When the new configuration violates this cut-off restriction, it is rejected and the previous configuration data is restored. Otherwise the change in $g_{\text{ii}}(r)$ is calculated and new $S_{\text{ii}}^0(Q_m)$ and $\chi^2$ are obtained from this. When the new value of $\chi^2$ is smaller than the old one, the new configuration is accepted; otherwise it is accepted only with a probability less than unity. This process is iterated until $\chi^2$ shows a reasonable convergence.

### 2.2 RMC for distribution of electrons

The RMC method has been mainly used for analyzing the atomic (or ionic) configuration in materials. In this work, we extended the idea of RMC simulation to the case of electronic distribution. Additional points of this procedure are given below.

The supercell volume used in the first step is divided into $n \times n \times n$ pixels. $\rho_j$ is the electron density at a pixel $j$. The iterative calculation is started from the uniform electron density $\rho_j = \rho_\Lambda (= \rho_0 \Lambda)$. Two pixels are randomly selected as $j$ and $k$, and then the small amount of electrons $\delta \rho$ is transferred from pixel $j$ to $k$. Namely, $\rho_j$ and $\rho_k$ are varied to $\rho_j - \delta \rho$ and $\rho_k + \delta \rho$, respectively, although the total number of electrons in the supercell is always kept constant $\rho_0 V$ throughout the iteration process. When $\rho_j$ is negative, the new $\rho_j$ is rejected and the previous data is restored. Under the periodic boundary condition, the ion-electron pair distribution function, $g_{\text{ie}}(r)$, can be calculated from the electron distribution around each ion, of which coordinate was predetermined in the first step. The ion-electron structure factor, $S_{\text{ie}}(Q)$, is related to $g_{\text{ie}}(r)$ by the Fourier transformation;

$$S_{\text{ie}}(Q) = 1 + \frac{4\pi \rho_0}{\sqrt{\pi}Q} \int_0^\infty r[g_{\text{ie}}(r) - 1] \sin(Qr)dr.$$  \hspace{1cm} (6)

The estimated $S_{\text{ie}}^0(Q_m)$ is compared with the experimental results by calculating the following statistics,

$$\chi^2 = \lambda \sum_m \frac{(S_{\text{ie}}(Q_m) - S_{\text{ie}}^0(Q_m))^2}{\sigma^2_{\text{ie}}(Q_m)} - S,$$  \hspace{1cm} (7)

$$S = -\sum_j \frac{\rho_j}{\rho_0 V} \ln \frac{\rho_j}{\rho_0 V}$$  \hspace{1cm} (8)

where $\sigma^2_{\text{ie}}(Q_m)$ is the estimate of the uncertainty for the experimental data of $S_{\text{ie}}(Q)$. $S$ corresponds to the entropy which appears in so-called ‘constrained entropy’ with the Lagrange multiplier $\lambda$ for the maximum entropy method (MEM) developed for the charge density study of crystalline materials. It is worthy noting here that $\chi^2$ is expressed by a similar form to the constrained entropy in the MEM method though its sign is reversed. When the new value of $\chi^2$ is smaller than the old one, the new configuration is accepted. The electron density distribution can be deduced in such iterative way by minimizing $\chi^2$.

### 3. Results and Discussion

The electron configuration of a Se atom is known to be $4s^2\,4p^4$. Among four $4p$ electrons, two electrons participate in covalent bonds to form the chain structure, the other two behave as lone pair electrons and occupy the top of a valence band, while a conduction band is formed by anti-bonding orbitals. Thus, $4p$ electrons would play an important role in physical properties of amorphous Se. For this reason, four $4p$ electrons are regarded as valence electrons of interest ($\varepsilon = 4$) and Se$^{4+}$ is considered to be a rigid ion in this work.

Figure 1 shows the valence electron density distribution function of amorphous Se in $Q$-space, $\rho(Q)$, obtained by the AXS method at the Se $K$ absorption edge with the theoretical value for an isolated Se atom. Figure 2 shows the ion-ion structure factor $S_{\text{ii}}(Q)$ of amorphous Se, which can be estimated by normalizing the X-ray scattering intensity data with the atomic scattering factor of $f_i(Q, E) + \rho(Q)$. The resultant $S_{\text{ii}}(Q)$ might be identical with the structure factor obtained by neutron diffraction. Corresponding structure factor calculated by the RMC simulation is also drawn with solid line in this figure. Here, we took 54 atoms with the number density $\rho_\Lambda = 32.6$ nm$^{-3}$ in the RMC simulation. It is found that the RMC simulation result could reproduce the experimental data. This agreement clearly indicates that the present approach basically works well. Figure 3 shows the positions of Se ions from a representative RMC generated configuration in amorphous Se. Here, bonds between nearest neighbor Se ions are also drawn as sticks. It is well known that the amorphous Se consists of disordered chains of two-fold coordinated atoms, where atoms are covalently bonded. This characteristic structural feature can be confirmed in the configuration of Fig. 3.

Figure 4 shows the ion-electron structure factor $S_{\text{ie}}(Q)$ of
amorphous Se calculated from $\rho(Q)$ and $S_0(Q)$ by using eq. (2). The resultant data of $S_0(Q)$ are spread in certain positions mainly arising from the scarcity of counting statistics. Nevertheless, this result qualitatively agrees with that reported by Inui et al.\(^{11}\) by combining their own data of X-ray and neutron, although there are some differences in detail. Corresponding $S_0(Q)$ calculated by the RMC simulation using 100 $\times$ 100 $\times$ 100 pixels is also drawn with solid line in Fig. 4. Considering many factors including the experimental uncertainty, $S_0(Q)$ obtained by RMC method is, in the present authors’ view, rather good, because the calculated result coincides with the average values of the scattered experimental data so as to draw a smooth continuous function. Here, it should be kept in mind that this RMC simulation technique is not a unique mathematical procedure. However, the ion-electron structure factor determined through this procedure with the RMC simulation is considered to be, at least in a sense of the necessary condition, at best for explaining the experimental result of Fig. 4, although this might not be the sufficient condition.

Figure 5 shows the resultant ion-electron radial distribution function $4\pi r^2\rho_0g_{ee}(r)$ of amorphous Se. The radial distribution function for ion-ion pairs of $4\pi r^2\rho_{AA}g_{AA}(r)$ is also drawn by broken line in this figure. It is found that $4\pi r^2\rho_0g_{ee}(r)$ of amorphous Se has mainly two peaks at around 0.080 nm and 0.125 nm. The second peak position is about half of the nearest neighbor Se–Se distance of 0.235 nm. The theoretical study of the electron density distribution for trigonal Se consisting of helical chains of Se atoms\(^{9}\) shows that the charge density maxima of two non-bonding $4p$ electrons (lone pair) and of remaining two bonding $4p$ electrons ($\sigma$-bond) are located at distances of 0.086 nm and 0.120 nm around a central atom, respectively. The number of electrons around a central Se\(^{2+}\) ion estimated from $4\pi r^2\rho_0g_{ee}(r)$ data in the $r$ range up to 0.22 nm is 6.4, which is close to the value of 6 electrons occupied in bonding and lone pair states around a central ion. Thus, it may be reasonably said that the first peak of $4\pi r^2\rho_0g_{ee}(r)$ for amorphous Se obtained in this work cor-
including three Se ions, which are marked by A, B and C in Fig. 3. The electron density deviates from the uniform distribution and the high electron density occurs in the region where two Se ions are close to each other. Then, the present authors maintain the view that this map of valence electron density distribution reveals clearly a structural feature with covalently bonded chains in amorphous Se.

4. Concluding Remarks

The RMC simulation has been carried out in order to obtain more quantitative electron distribution of amorphous Se from ion-electron structure factor estimated from the AXS measurements. The present results show good capability of the RMC simulation coupled with the AXS data for facilitating the understanding of particular structures in disordered materials by visualizing the spatial electron distribution in real space. Then it would be interesting to extend the present approach to other amorphous or liquid materials. Nevertheless, the present authors would rather stress that the reliability of the RMC results significantly depends on how we can accumulate highly accurate experimental data as an input for simulation.

REFERENCES