Full Multiple-Scattering Approach to L_3 XANES of Germanium

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Abstract The observed L_3 XANES spectra for crystalline and amorphous germanium are analysed by use of the full multiple scattering calculations. The prominent peaks found in the crystalline spectra are smeared out in the amorphous spectra. The difference of the observed XANES spectra is explained by the bond-angle fluctuation in the amorphous Ge where the Ge-Ge bond distance is fixed.

1. INTRODUCTION

For an amorphous state of Ge the structural parameters is best illustrated by the second shell, which is more sensitive to changes in disorder than the first shell. Second-shell disorder can occur by variations in bonding angle; these variations take much less energy than changes in first-neighbor distance which require bond stretching. A neutron diffraction study for these systems gives high resolution distribution function, and the structure of a-Ge is described in terms of a tetrahedrally bonded random network [1]. Previous EXAFS analyses showed that nearest Ge-Ge distance in a-Ge is sharply distributed at the same distance in crystal. The second-shell peak in Fourier transformed EXAFS spectra was not found for a-Ge [2,3]. Stern *et al.* estimated σ^2 for second shell in a-Ge as $0.08 \pm 0.02 \text{ \AA}^2$ [2]; from which we can estimate the angular fluctuation $\sim 7^\circ$ around the tetrahedral angle assuming that Ge-Ge nearest distance is fixed. However EXAFS data analysis is difficult for second shell.

Naoe *et al.* measured Ge- L_3 near edge spectra of crystalline and amorphous thin film and compared them with that of single crystal Ge [4]. They also observed small temperature effects on the XANES spectrum of crystalline film. The prominent peaks found in the XANES spectrum of crystalline film are smeared out in the spectrum of amorphous film. To understand the observed behavior we apply a full multiple scattering approach [5,6].

2. METHOD OF CALCULATION

To calculate XANES spectra a set of phase shifts are important, and they are usually sensitive to electronic structure of each atom. We use the $Z+1$ potential for phase shift calculation of central Ge atom because the core hole potential is imperfectly screened by other electrons in the X-ray absorbing atom.

3. RESULTS AND DISCUSSION

At first we calculate the XANES spectra of Ge crystal in order to check the convergence in regard to cluster size. A cluster including 55 Ge atoms is the largest cluster considered here, and a good convergence is found for a cluster with 29 Ge atoms. From now on all clusters are the same size clusters.

Next we investigate the sensitivity to the scattering potential for XANES electrons. In

Figure 1 Calculated and experimental Ge L_3 XANES spectra for crystalline Ge.

solid Ge each germanium atom has $4s^1 4p^3$ hybridized electronic structure, and two different potentials are constructed for the above electronic configuration and $4s^2 4p^2$ configuration. The calculated result shows that Ge L_3 XANES spectra are insensitive to the outer electron configuration. We also study the importance of $Z+1$ -potential; the core hole potential plays a minor role in this case. Regardless of the above results $4s^1 4p^3$ configuration and $Z+1$ -potential are used throughout this work.

Keeping these results in mind we study the spectral change from crystalline to amorphous structural transformation. Figure 1 shows the calculated and experimental Ge L_3 XANES spectra for crystalline Ge. The calculated result shows rather prominent first peak as observed in the experimental XANES spectrum.

Figure 2 shows the calculated and experimental Ge L_3 XANES spectra for amorphous Ge. Here four different models are used to calculate the XANES spectra. In all of these models Ge-Ge distances between a central atom and four atoms in the first shell are fixed as that in crystalline Ge, whereas some atoms are displaced from the equilibrium positions at tetrahedral sites keeping atoms in second and higher order shells fixed for their equilibrium positions for simplicity. Though these models yield different Ge-Ge distances between Ge atoms in the first shell and those in the second shell, the calculated spectra are most sensitive to the nearest neighbor distortion and we have no problem even in these simple models.

When we consider a crystalline model, one Ge atom (atom 1) in the first shell is in the z-axis, and other three Ge atoms (2~4) occupy T_d symmetry sites in equilibrium. In model 1 only atom 2 is rotated around z-axis with 10° , in model 2 atoms 2, 3 and 4 are all rotated around z-axis with 10° , in model 3 atom 2 is rotated around z-axis with 10° whereas atoms 3 and 4 are rotated with 10° in opposite direction and in model 4 atoms 2 and 4 are rotated around z-axis with 10° whereas atom 3 is rotated with 10° in opposite direction. The calculated results for these models well explain the peak reduction of the first peak region observed in Fig. 1. As the distortion from T_d symmetry increases as in models 3 and 4, the peak reduction is pronounced. We have investigated other models with small distortion, and we find the small peak reduction in those cases. Of course we can consider many other models taking account the distortion in higher order shells. However it would be impossible to consider all possible models and estimate their statistical weight.

4. CONCLUSION

The observed peak reduction at the first peak region for amorphous Ge is successfully explained by use of the angular distortion, though Ge-Ge distances are fixed.

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Figure 2 Calculated (model 1~4) and experimental Ge L_3 XANES spectra for amorphous Ge.