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## XANES study of the electronic structure of molten germanium

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Based on measured XANES spectra of crystalline and liquid germanium (*c*-Ge and *l*-Ge), multiple scattering (MS) simulation and density of states (DOS) self-consistent calculation using the configurations generated with reverse Monte Carlo (RMC) simulation for *l*-Ge have been carried out to study the electronic structures near the Fermi level  $E_f$  of *l*-Ge. The strong white line for *l*-Ge is attributed to the high DOS in the conduction band and partially to the excitonic effect. The DOS of *l*-Ge is quite high around  $E_f$ , as in a metal, while that for *c*-Ge opens a gap there. Taking the core hole effect into account, the *p*-like partial DOS of the absorbing atom shows a DOS "piling up".

**Keywords:** XANES, multiple scattering, solid-liquid transition, semiconductor-metal transition, electronic structure

### 1. Introduction

Upon melting of covalent semiconductors, such as Si, Ge, GaSb etc, a semiconductor-metal transition occurs, and the coordination number increases to 6–7 which is, however, less than the 10–12 found in normal liquid metals (Salmon 1988, Petkov et al 1994). The phenomena have attracted considerable research interest in both the technological and basic sciences. To understand the mechanism it is necessary to study both the atomic and the electronic structures of the liquids in comparison with the solids. Some reliable results on the atomic structure have been obtained in recent years (Salmon 1988). However, experimental studies on the electronic structure are still scarce due to the practical difficulties. XANES spectroscopy provides information on the electronic structure of unoccupied states above the Fermi level  $E_f$  (Bianconi 1988). Studies on the electronic structures of melts with XANES are still lacking due to the difficulties both in measuring at high temperature and in analyzing the data for which the atomic configuration is not well defined. We present the measured K-edge XANES of *l*-Ge and a theoretical analysis to understand the electronic pictures of the unoccupied states near  $E_f$  by solving the atomic configuration. The results of *c*-Ge is given as a comparison.

### 2. Experiment

The XANES and EXAFS measurements were performed in a transmission mode at the beam line 10B equipped with a Si(311) channel-cut monochromator at the Photon Factory (PF) in Japan. A special sample cell was made of two sapphire tubes with thin closed ends inserted into an open tube in such a way that the closed ends of the inner tubes faced each other with a uniform narrow gap of about 20  $\mu\text{m}$  between them. The closed ends were polished to a thickness of 250  $\mu\text{m}$  in order to improve

the efficiency of X-ray transmission. Special care was taken when filling the gap with Ge melt to keep a uniform thin liquid film vertically in vacuum (Hosokawa et al 1993). In this arrangement, the effect of the sample surface is negligible and the oxidization has not been observed.

The XANES spectra of *c*-Ge and *l*-Ge measured at room temperature and 1303K are shown in the upper panels of Fig.1 and Fig.2 respectively. The white line of *l*-Ge is more intense without shoulder features and is quite smooth on the high energy side due to disorder, unlike that of *c*-Ge which is full of features. The threshold of the *l*-Ge edge is shifted towards the lower

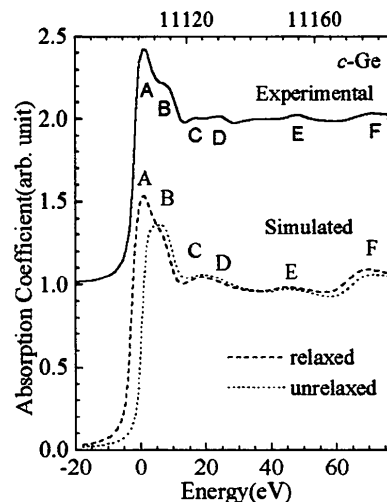


Fig.1 K-edge XANES spectra of *c*-Ge: upper panel: measured; lower panel: simulated with fully relaxed and unrelaxed potential

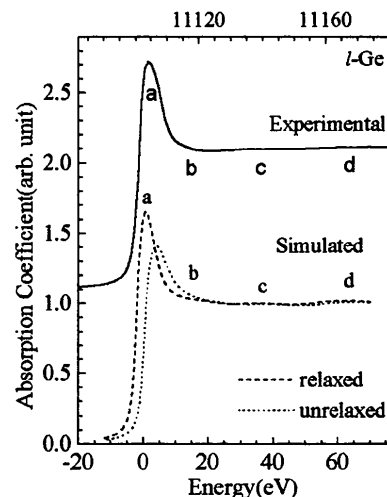


Fig.2 K-edge XANES spectra of *l*-Ge: upper panel: measured at 1303K; lower panel: simulated with fully relaxed and unrelaxed potential

energy by about 1.3–1.4 eV related to that of *c*-Ge.

### 3. *ab initio* Calculation of XANES

*ab initio* one electron full multiple scattering (MS) (Durham 1988, Natoli et al 1986, Rehr et al 1991) simulations of the XANES for *c*-Ge and *l*-Ge have been carried out. The real Hedin-Lundqvist self-energy was included as exchange-correlation potential (Chou 1987). The muffin-tin radii were chosen according to the Norman criterion (Norman 1974). The

calculated spectra were convoluted with a Lorentzian to account for the core hole lifetime chosen to have a width of 2.35 eV (Rahkonen et al 1974).

Using XANES to determine the unoccupied electronic structure near  $E_f$ , core hole effect has to be considered. According to the final state rule this effect can be reduced to the one electron approximation. In this work, the absorption cross sections were calculated in an unperturbed potential describing the ground state, and in a fully relaxed potential including the core hole effect by the  $Z+1$  approximation (Lee et al 1977).

### 3.1. Calculation for *c*-Ge

The lower panel of Fig.1 shows the calculated XANES in a relaxed and unrelaxed potential for a cluster of 99 atoms of *c*-Ge. Empty spheres are placed in the tetrahedral holes with respect to the diamond lattice. The spectra show a nearly rigid shift of about 3.15eV towards low energy and an increase of the white line intensity due to the core hole effect. The agreement with the experiment is improved by the relaxed potential. All features of the XANES are well reproduced indicating that the potential used here is acceptable. The white line (feature A) with a shoulder (feature B) arises from projected *p*-like

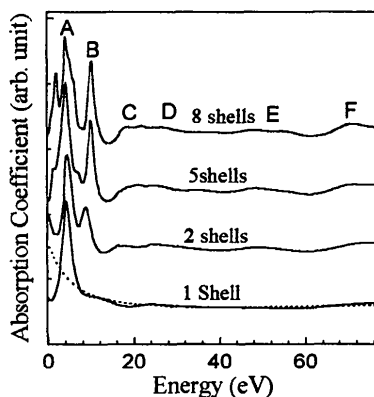


Fig.3 Calculated *c*-Ge XANES by using different cluster sizes without taking any broadening effects into account

unoccupied DOS near  $E_f$ , and the peaks at higher energy arise from *sp*-like derived bands. Fig.3 shows the calculated *c*-Ge XANES using different atomic cluster sizes around the absorbing atom. In order to see the fine structure, these spectra have not included any broadening effect. A sharp feature A is predicted for a small cluster with only four neighbouring atoms located at the four apices of the tetrahedron, and the change in intensity of peak A with cluster size is negligible. Hence the final states of this feature show the character of the  $sp^3$  hybrid orbital antibonding states. The peak B is well defined when the second shell including 12 atoms is added. It can be seen that the electronic states in the conduction bands are determined over a large number of atoms and the XANES can not be interpreted with molecular orbitals of a simple cluster formed by the absorber and its nearest neighbours.

### 3.2. Calculation for *l*-Ge

We have to know the atomic configuration first for calculation of the XANES spectra of *l*-Ge. RMC simulation (Mcgreevy 1988) with 1000 atoms based on the EXAFS and neutron diffraction data (Salmon 1988) has been performed to create configuration models of *l*-Ge. After  $10^5$  steps, a series of independent

configurations are obtained. The pair distribution function  $g(r)$  and the K-edge EXAFS of *l*-Ge have been well reproduced from these models as shown in Fig.4. The simulations predict a broad, homogeneous distribution of the local bonding configurations which is in agreement with MD simulations (Kresse et al 1994).

Based on the independent configurations, K-edge XANES of *l*-Ge have been calculated with an *ab initio* full MS approach

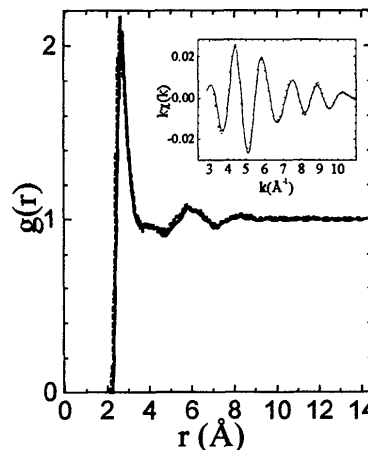


Fig.4 Pair distribution function of *l*-Ge: solid line - measured (Salmon 1988); dashed line - simulation. Inset: EXAFS: solid line - experimental; dotted line - simulation

using clusters with radii of about 9Å covering three coordination shells in the  $g(r)$  function. The calculated spectra averaged over 16 configurations are shown in the lower panel of Fig.2 which compare quite well with the experiment. Calculations with small clusters with radii of about 3.6Å covering the main peak in  $g(r)$  can give almost the same results. Hence, for disordered systems like *l*-Ge, in contrast with crystals, the general character of the electronic states can be described by the short-range properties with the long-range coordinates as an averaged background in a series of independent configurations. By averaging the spectra in more configurations, the consistency with experiment should be improved.

The final-state effect on the *l*-Ge K-edge XANES is shown in the lower panel of Fig.2. The white line is shifted by the electron-hole interaction of about 2.75 eV towards lower energy, while the peaks b, c and d in the continuum show only a nearly rigid shift of about 2 eV. The excitonic shift of the white line is less than that for *c*-Ge, indicating that the core-hole is more screened in *l*-Ge and, therefore, that *l*-Ge is more metallic. The relaxed potential improves the agreement of the calculated XANES of *l*-Ge with the measured data, especially for the white line intensity, indicating the incomplete screening. Hence, the molten Ge is not so metallic as normal metals.

## 4. DOS Calculation

In order to check the electronic structure near  $E_f$ , DOS calculations were performed by using the self-consistent linear muffin-tin orbital method in the atomic sphere approximation (LMTO-ASA) (Anderson et al 1984, Skriver et al 1984). Spare empty spheres were used for the *c*-Ge calculation, and 60-atom super-cells from independent atomic configurations which can produce almost the same pair distribution function as that derived from a large ensemble for *l*-Ge DOS calculation.

The *l*-Ge DOS attributed to *s*-like and *p*-like bands averaged over 16 configurations is presented in Fig.5 compared with that

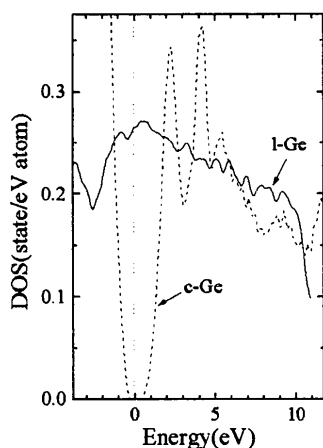


Fig.5 The  $p$ -like+ $s$ -like partial DOS of  $c$ -Ge (dotted line) and  $l$ -Ge averaged over 16 configurations (solid line).

of  $c$ -Ge. The energy origin is at the calculated  $E_f$ . There is a pseudo gap between a predominantly  $s$ -like lower energy part and a  $p$ -like higher energy part of the band for  $l$ -Ge. This is consistent with MD calculations (Jank et al 1990, Kresse et al 1993, Takeuchi et al 1994, Kulkarni et al 1997) and a photoemission measurement (Indlekofer 1988) (which can only reflect the electronic states below  $E_f$ ). The DOS of  $l$ -Ge remains high around  $E_f$ , as in a metal, while that for  $c$ -Ge opens a gap there. Above  $E_f$  the DOS both for  $l$ -Ge and  $c$ -Ge are quite high contributing to the high white lines in XANES spectra. The peak value of the unoccupied DOS for  $l$ -Ge is not very much higher than that for  $c$ -Ge as measured white line due to the core-hole effect as seen in the XANES calculation.

The  $p$ -like projected DOS in the conduction band of  $c$ -Ge contributes to features A and B while the  $p$ -like partial DOS of  $l$ -Ge only contributes to feature A, therefore, the unoccupied  $p$ -like band for  $l$ -Ge is much narrower than that for  $c$ -Ge. This is consistent with the fact that  $l$ -Ge has long-range disorder.

Taking the core hole effect into account by using the  $Z+1$  approximation to simulate the potential of excited atom, the  $p$ -like DOS in the vicinity of the absorbing atom shown in Fig.6 indicates that there is a DOS "piling up" caused by the core hole-electron interaction. This enhanced  $p$ -like DOS is compatible with the high white line of the  $l$ -Ge K-edge XANES. This is consistent with above XANES calculations.

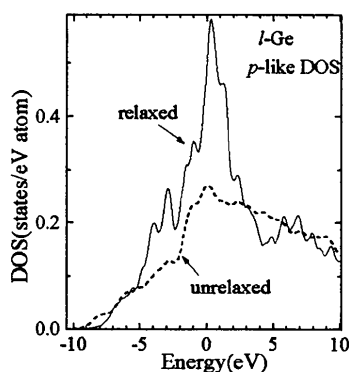


Fig.6 Calculated  $p$ -like DOS in the vicinity of the absorbing atom with ground state (dashed line) and  $Z+1$  approximation (solid line) potential for the absorbing atom.

## 5. Conclusion

Based on our measured XANES spectra of  $c$ -Ge and  $l$ -Ge, MS and DOS calculation have been carried out to obtain the electronic structures near  $E_f$ . In the case of  $l$ -Ge, the configurations needed for the calculations were generated by RMC simulation. The calculated spectra are in good agreement with the measurement. The strong white line of  $l$ -Ge shows high DOS near  $E_f$  and is partially due to the core hole final state effect.  $l$ -Ge is not so metallic as normal metals. The DOS of  $l$ -Ge is quite high around  $E_f$  as for a metal, while that for  $c$ -Ge opens a gap there. There is a  $p$ -like DOS "piling up" in the vicinity of the absorbing atom caused by the core hole-electron interaction. The MS XANES calculation could be improved by self-consistent-field potential, however the self-consistent LMTO-ASA results show that the potential used here is quite reasonable.

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