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# The electronic and structural changes in the supercooled liquid and glassy $\text{As}_2\text{Se}_3$

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## Abstract

We have measured extended X-ray absorption fine structure (EXAFS) and dc conductivity  $\sigma$  of the liquid and glassy  $\text{As}_2\text{Se}_3$ . Each  $|F(r)|$ , the magnitude of the Fourier transform of EXAFS oscillations around As and Se atoms, has a symmetric peak around 2.5 Å. The curve fitting analysis indicates the presence of chemical order and no homopolar As–As and Se–Se bonds. When liquid  $\text{As}_2\text{Se}_3$  is cooled to the glassy state through the supercooled state, the inter-layer correlation increases and the two-dimensional (2D)  $\text{As}_2\text{Se}_3$  network structure transforms to a three-dimensional (3D) one. This transformation is the reason for the change in the temperature variation of the coordination number  $N$  around 300°C whose temperature is higher than  $T_g (= 181^\circ\text{C})$ . The change in the slope of  $\log \sigma$  versus  $1/T$  around 300°C is assumed to be associated with the appearance of broadened and localized charged defect states near the band tail. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Crystalline  $\text{As}_2\text{Se}_3$  has a covalent network structure which contains threefold coordinated As atoms and twofold coordinated Se atoms [1]. This network forms stacked layers which are held together by the van der Waals force. The X-ray and neutron diffraction (ND) experiments [2,3] reveal that the local structures of liquid and glassy  $\text{As}_2\text{Se}_3$  are similar to the fundamental structural units of the crystal. The first peak at 2.4 Å in the radial distribution corresponding to As–Se bond length in liquid  $\text{As}_2\text{Se}_3$  is well resolved from subsequent

features which implies that the intra-layer correlation is dominant [4]. There are few diffraction experiments on liquid  $\text{As}_2\text{Se}_3$  which cover the temperature range from the liquid to glass through the supercooled state. Furthermore, the difficulty of the analysis of the experimental data for diffraction lies in the fact that it is almost impossible to separate the partial structure factor  $S_{\alpha\beta}(Q)$ , from the total structure factor  $S(Q)$ . This difficulty is because X-ray form factors and neutron scattering lengths of the two atoms in  $\text{As}_2\text{Se}_3$  are similar and the As–As, Se–Se and As–Se bond lengths are not very different. The reason for the limited partial structural information is because of a lack of suitable isotopes for ND to separate  $S_{\alpha\beta}(Q)$ . The extended X-ray absorption fine structure (EXAFS) technique is complementary to ND

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since it can provide selective information concerning the local structure of the liquid and glassy  $\text{As}_2\text{Se}_3$ . The highest filled electronic band, the valence band of  $\text{As}_2\text{Se}_3$ , is formed by the overlap between lone pair (LP) orbitals and As–Se bonding  $\sigma$  orbitals. The band gap depends on the interaction between LP orbitals. It should be noticed that structural modifications are associated with the difference in the bonding energies and the transfer of LP electrons to the neighboring sites due to the large electronic polarizability of the chalcogen [5]. Disorder produces a tail of localized states extending from the valence band and also from the conduction band formed by the anti-bonding orbitals into the energy gap between these two bands. The localization favors the response of atoms to the trapped charges to form a valence alternation defect pair [5]. Recently Hosokawa et al. have reported that the diffraction pattern of liquid  $\text{As}_2\text{Se}_3$  contains a first sharp diffraction peak (FSDP) in  $S(Q)$  [2], which gives the evidence for the medium range order (MRO) [6]. The FSDP remains up to 900°C where liquid  $\text{As}_2\text{Se}_3$  changes from the semiconducting to the metallic state [7]. We have also found [8] that liquid  $\text{As}_2\text{Te}_3$  transforms from the two-dimensional (2D) network structure to the one-dimensional (1D) chain structure with metallic properties around 500°C accompanied by volume contraction.

In this paper, we report the results for the EXAFS and dc conductivity  $\sigma$ , measurements for liquid  $\text{As}_2\text{Se}_3$  and discuss how the network configurations and the electronic states change when liquid  $\text{As}_2\text{Se}_3$  is cooled below the glass transition temperature,  $T_g (=181^\circ\text{C})$ , through supercooled liquid state.

## 2. Experimental

The mixture was prepared in the same way as described elsewhere [7]. The electrical conductivity  $\sigma$ , of the  $\text{As}_2\text{Se}_3$  has been measured by the dc four probe method using a Pyrex glass cell with tungsten electrodes in the temperature range between 145°C and 500°C. The EXAFS experiments for the  $\text{As}_2\text{Se}_3$  were carried out on As and Se K-edges using the spectrometer installed at BL-10B station

of the Photon Factory at the National Laboratory for High Energy Physics (KEK) in the temperature range between 110°C and 500°C. A quartz cell with the sample space (50  $\mu\text{m}$  in thickness) was employed. The liquid  $\text{As}_2\text{Se}_3$  was pushed into the sample space by He gas. Further experimental details are described elsewhere [7–9].

## 3. Results

Fig. 1 shows the EXAFS oscillations  $\chi(k)$ , up to 14  $\text{\AA}^{-1}$  for As and Se K-edges. The oscillations are detectable in high  $k$  region (4  $\sim$  12  $\text{\AA}^{-1}$ ) where the signal-to-noise ratio is smaller. Such a good quality of the spectra was obtained even at high temperature. Fig. 2 shows the magnitude of the Fourier transform of  $\chi(k)$ ,  $|F(r)|$ , obtained around the central As and Se atoms for liquid  $\text{As}_2\text{Se}_3$  at different temperatures including temperatures for which the samples were in supercooled and glassy

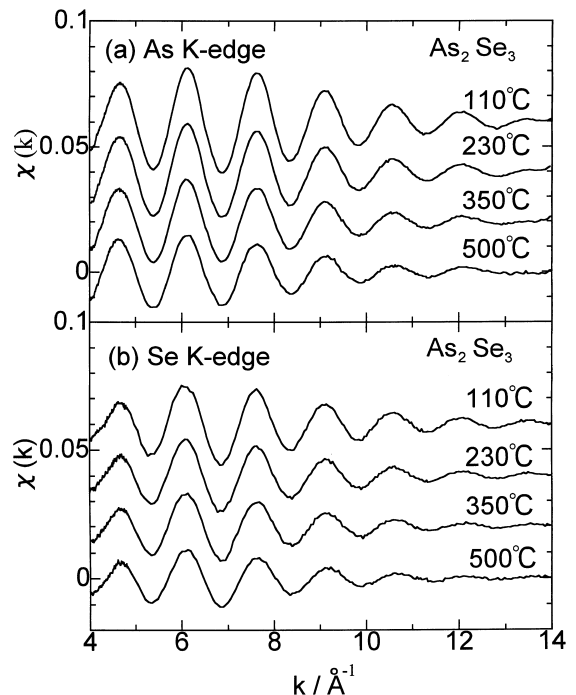


Fig. 1. EXAFS oscillations  $\chi(k)$ , obtained around the As K-edge (a) and Se K-edge (b) for  $\text{As}_2\text{Se}_3$  at various temperatures between 110°C and 500°C.

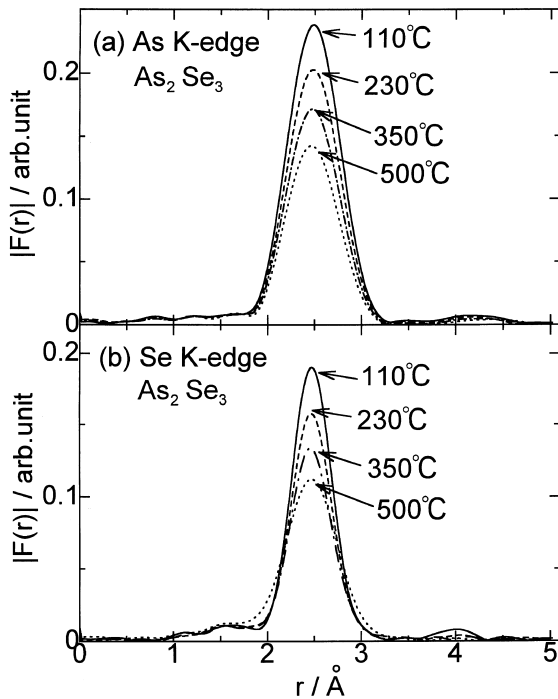


Fig. 2. The magnitudes of the Fourier transform of  $k\chi(k)$ ,  $|F(r)|$ , obtained around the As K-edge (a) and Se K-edge (b) for  $\text{As}_2\text{Se}_3$  at various temperatures between 110°C and 500°C.

states. Of particular interest, each  $|F(r)|$  has a symmetric peak around 2.5 Å and the amplitude of peak increases with decreasing temperature. The one-shell curve fitting analysis which is enough to derive the structural parameters has been carried out in  $k$  ranging from 3 to 12 Å<sup>-1</sup> by using the theoretical parameters calculated by the FEFF code [10,11]. The As–Se bond length is deduced to be  $2.41 \pm 0.01$  Å which is independent of temperature. The important findings derived from one-shell curve fitting analysis are presence of the chemical order, so that there exist no homopolar bonds, i.e., As–As and Se–Se. The chemical order is preserved at least up to 500°C. This preservation is in contrast to liquid  $\text{As}_2\text{Te}_3$  in which  $|F(r)|$  curves are asymmetric which may be due to homopolar bonds As–As and Te–Te [8]. Fig. 3 shows the temperature variations of the coordination number  $N$ , around the central As and Se atoms, respectively. The  $N$  around the As atoms changes from  $2.6 \pm 0.1$  at 500°C to  $3.0 \pm 0.1$  near  $T_g$  with decreasing temperature. Around the Se atoms  $N$

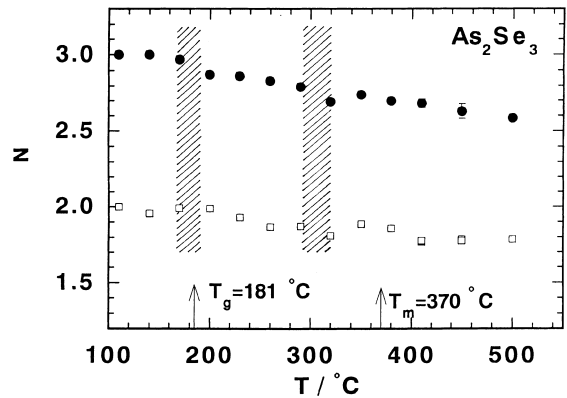


Fig. 3. Temperature variations of the coordination number  $N$  for neighboring atoms. Solid circles indicate  $N$  for Se atoms around a central As atom. Squares indicate  $N$  for As atoms around a central Se atom. The bars indicate the limit of errors. The hatched lines represent the regions where the difference in the temperature variations of  $N$  appears.

changes from  $1.8 \pm 0.1$  at 500°C to  $2.0 \pm 0.1$  near  $T_g$ . Our results for glassy state below  $T_g$  agree with previous results [9], that is, at the stoichiometric  $\text{As}_2\text{Se}_3$  composition As atoms are threefold coordinated while Se atoms are twofold coordinated. It is interesting to note that differences in temperature dependence of  $N$  are observed near  $T_g$  and 300°C which are denoted by hatched lines in Fig. 3. Fig. 4 shows the temperature variations of the mean square displacement  $\sigma^2$ , for neighboring

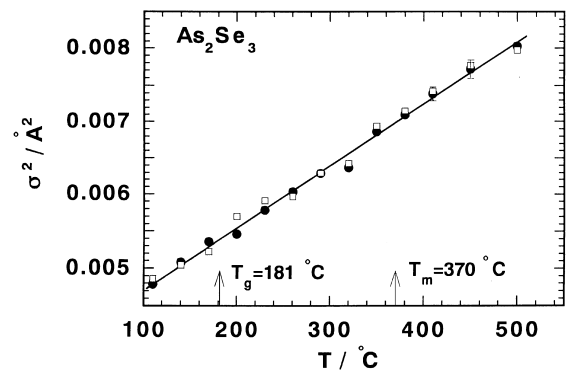


Fig. 4. Temperature variations of the mean square displacement  $\sigma^2$  for neighboring atoms. Solid circles indicate  $\sigma^2$  for Se atoms around a central As atom. Squares indicate  $\sigma^2$  for As atoms around a central Se atom. The bars indicate the limit of errors. The solid line is drawn as guide for the eye.

atoms around As and Se atoms. A linear function is fitted to the  $\sigma^2$  data. It is noteworthy that  $\sigma^2$ s are the same for the As–Se and Se–As pairs. In Fig. 5 the d.c. conductivity  $\sigma$ , for  $\text{As}_2\text{Se}_3$  is plotted as a function of  $1/T$  in the temperature range between 145°C and 500°C. A slight change in the slope of  $\log \sigma$  versus  $1/T$  curve is observed around 300°C, where a rapid increase in  $N$  around As and Se is observed, as seen in Fig. 3. The activation energy of the conductivity  $E_\sigma$ , deduced from the slope of  $\log \sigma$  versus  $1/T$  is  $1.07 \pm 0.03$  eV above 300°C and  $0.99 \pm 0.03$  eV below 300°C, which are in fairly good agreement with data by Edmond [12] and those by Hurst and Davis [13,14]. They reported that  $E_\sigma$  above 300°C is 1.06 eV and 0.906 eV below 300°C [15].

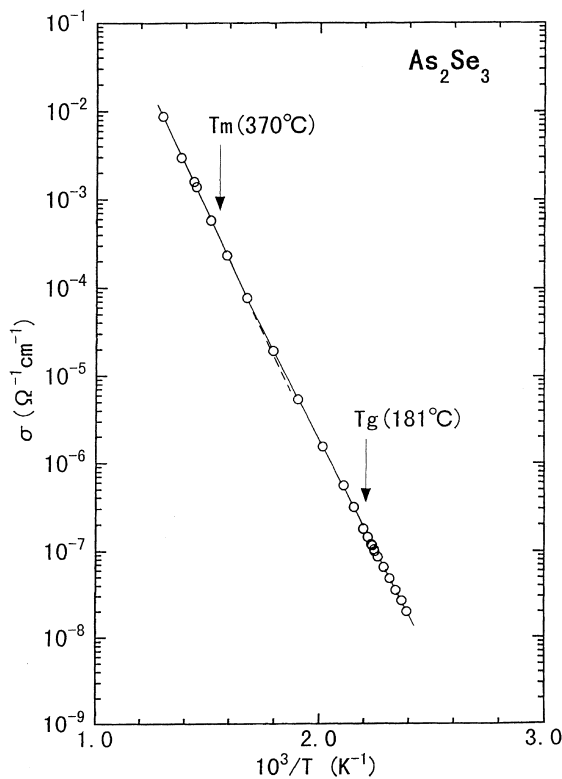


Fig. 5. Temperature variations of the d.c. conductivity  $\sigma$  for  $\text{As}_2\text{Se}_3$  as a function of the reciprocal absolute temperature in the range between 145°C and 500°C. Error bars are within circles. The solid and dashed lines are drawn as guides for the eye.

#### 4. Discussion

The analysis of  $|F(r)|$  derived from EXAFS data reveals that the chemical order of the As–Se network is at least preserved to 500°C for liquid  $\text{As}_2\text{Se}_3$ . The bonding energies reported in the literature [13] are 52 kcal/mol for As–Se, 49 kcal/mol for Se–Se and 46 kcal/mol for As–As bond. Thus, the differences in these energies show that As–Se bonds are more favored, resulting in the chemical order. The X-ray diffraction pattern of liquid  $\text{As}_2\text{Se}_3$  [2] provides that the Se–Se separation corresponding to the second peak of the radial distribution function,  $g(r)$  is around 3.6 Å at 500°C and the bond length of the As–Se pairs derived from the present EXAFS analysis is 2.4 Å at 500°C. Since the building unit in liquid  $\text{As}_2\text{Se}_3$  is considered to be an  $\text{AsSe}_{2/3}$  shallow pyramid with a triangular base [4], the bond angle of bonded Se–As–Se or As–Se–As units in the liquid  $\text{As}_2\text{Se}_3$  is estimated to be around 100°, which is close to that in the crystalline and amorphous states [1,4]. In spite of difference between the local environments around the threefold coordinated As atom and those around the twofold coordinated Se atom, the mean square displacement  $\sigma^2$ , are the same for As–Se and Se–As pairs at various temperatures, as shown in Fig. 4. We suggest that this is due to a ring arrangement within the layer which is a favorable configuration to stabilize the chemically ordered network structure. The  $S(Q)$  curve for liquid  $\text{As}_2\text{Se}_3$  deduced from the X-ray diffraction measurement contains the FSDP up to 900°C [9], which is evidence for the existence of MRO for temperatures below 900°C. It is instructive to note that the FSDP in  $S(Q)$  for liquid and glassy  $\text{As}_2\text{Se}_3$  arises from the MRO within layer, judging from the similarity of  $\sigma^2$ s for the As–Se and Se–As pairs. The  $N$  around As and Se in the liquid state at temperatures higher than  $T_g$  decreases by thermal breaking of bonds between As and Se. Around 300°C, the network may begin to stack in layers with increase of inter-layer correlation and extend to the 3D space with decreasing temperature, and is consequently frozen at  $T_g$ . There appear nearly half filled p-like nonbonding (LP) states around the twofold coordinated As atoms caused by breaking of bonds between As and Se. The charged pair defects ( $\text{D}^+$  and  $\text{D}^-$ ) due

to charge transfer and bond rearrangement between Se and As create the localized states near the band tail. The behavior of  $\sigma$  below 300°C is associated with hopping conduction in the localized states near the band tail and that of  $\sigma$  above 300°C is due to the conduction at a mobility edge, as discussed by Mott and Davis [16].

## 5. Conclusion

In liquid As<sub>2</sub>Se<sub>3</sub> the chemically ordered As–Se network over the distances characteristic of MRO is preserved. The physically reasonable assumption is that there appears a 2D like network structure in liquid As<sub>2</sub>Se<sub>3</sub> to satisfy the simple covalency requirements of As and Se. With decreasing temperature through supercooling, the 2D like network stacks in layers and transforms to the 3D structure. The charged defects (D<sup>+</sup> and D<sup>-</sup>) caused by bond breaking create the localized states near the band tail. This explains the change in the temperature variations of  $N$  and  $\sigma$ .

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