

The Structural Study of Liquid SnSe₂ Alloys

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The structure of liquid SnSe₂ alloy was investigated to study the chemical short-range order by pulsed neutron scattering method. The structure factor, $S(Q)$, for this alloy has a hump on the lower Q value of the first peak and shoulders on the higher Q values of the first and second peaks. The analysis of the total correlation function, $GT(r)$ by a gauss-function fitting method suggests that the chemical short-range order of SnSe₂ in the solid state is partly preserved after melting.

Keyword: structure, liquid semiconductor, liquid Sn-Se system, neutron scattering, intermediate-range order

1. Introduction

Liquid Se-rich Sn-Se alloys are typical semiconducting materials and show significant characteristics in their electronic properties [1]. With increasing temperature, these alloys exhibit a nonmetal-metal transition. The concentration dependence of the electrical conductivity for liquid Sn-Se alloys exhibits a minimum at the composition of SnSe and a maximum at around the composition of SnSe₂ [2]. While the electrical conductivity for liquid SnSe alloy shows small temperature variation, those of liquid SnSe₂ alloy exhibits distinct temperature dependence.

It is well known that the chemical short-range order in the solid state still remains after melting in several liquid metal-selenium alloys [3,4]. For the Sn-Se system, the results of the electrical conductivity and the viscosity measurements [2,5] suggest that the chemical short-range order would be preserved in the liquid state. In the solid state, the Sn-Se system has two intermetallic compounds such as SnSe and SnSe₂ [6]. The SnSe₂ compound has a layered structure [7]. The structure of the SnSe compound is a distorted NaCl type[8]. Liquid structures of Sn-Se are expected to exhibit continuous transformation from Se-like to SnSe₂- or SnSe-like one with a change of composition. The interesting behaviour of the electrical conductivity might be related to the liquid structure of these alloys.

Neutron diffraction is one of the useful method for the direct observation of structural changes. In this paper, we report the structure factor for liquid SnSe₂ alloy and discuss

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the liquid structure.

2. Experimental

Pulsed neutron scattering experiment on liquid SnSe_2 alloy was carried out using the High Intensity Total scattering spectrometer (HIT II) installed at the pulsed neutron source for High Energy Physics (KEK) at Tsukuba. The sample was sealed in a thin walled quartz glass cell (8 mm inner diameter and 0.4 mm wall thickness) in vacuum. In this experiment, the sample was melted with a specially designed infrared furnace installed in the instrument. The structure factor, $S(Q)$, was obtained from the scattered intensity after the usual corrections, such as subtraction of the cell intensity, absorption and normalization with a vanadium standard. The details of the data analysis procedure have been described in ref.[9].

3. Results and analysis

Figure 1 shows the total structure factor, $S(Q)$, for the liquid SnSe_2 alloy at 700 °C together with the data of liquid Sn and Se taken from a reference book [10]. Compared with the $S(Q)$ of liquid Se, the characteristic features have been observed on the $S(Q)$ of liquid SnSe_2 . The $S(Q)$ of liquid SnSe_2 has a hump on the lower Q value of the first peak, and has shoulders on the higher Q values of the first and second peaks. The height of the first peak become larger than that of liquid Se.

While the position of the first peak shifts towards higher Q values, the positions of second and third peaks and second minimum shift to the lower Q values. The amplitude of the high- Q oscillations is reduced.

The total pair distribution function, $g(r)$, may be written as

$$g(r) = 1 + \frac{1}{2\pi^2\rho r} \int_0^\infty [S(Q) - 1] \sin(Qr) Q dQ \quad (1)$$

where ρ is the average number density of atoms. The sample densities were measured using a γ -ray absorption method. Figure 2 shows the total pair distribution functions for SnSe_2 alloy together with the results for pure elements taken from a ref-

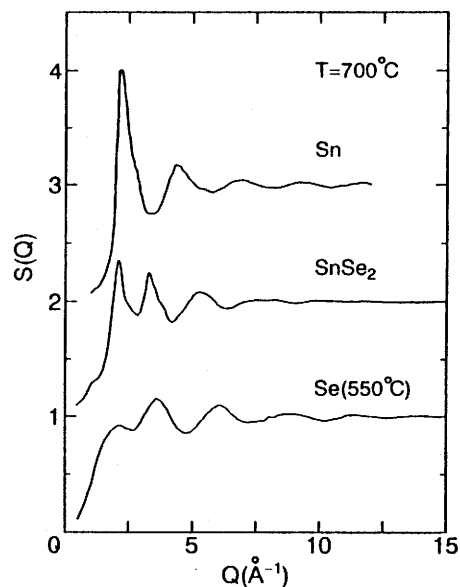


Fig.1 Total structure factor, $S(Q)$, for liquid SnSe_2 alloy at 700 °C and the data of liquid Sn and Se [10].

erence book [10]. The position of first peak in $g(R)$ for SnSe₂ shifts towards higher R value and its height decreases. The height of second peak is comparative to that of first peak and its width is broadened.

The coordination number, n_1 , of the first shell for liquid SnSe₂ was evaluated by the integrals of in the radial distribution function, $\text{rdf}(r) = 4\pi r^2 g(r)$, up to the first minimum. The result for liquid SnSe₂ is 2.3.

4. Discussion

It is well known that liquid Se consists of a chain-like structure. The introduction of Sn in the liquid Se may modify the covalently bonded chain-like structure. As

show in Fig.1, a profile of $S(Q)$ shows that there is a substantial change among the topology of liquid SnSe₂, Se and Sn. Addition of Sn to liquid Se causes the broadening of the first peak in $g(r)$ as shown in Figs. 2. This suggests that the contributions of Sn-Se and/or Sn-Sn correlation are added to the first peak in $g(r)$.

To proceed with the analysis of structure for the liquid SnSe₂, we attempt to decompose the total atomic correlation functions $GT(r) = 4\pi r p g(r)$ because of $GT(r)$ has the properties that instrumental resolution enter as a symmetric function. Then $GT(r)$ can be expressed as a sum of gaussian functions as follows:

$$GT(r) = \sum_i A_i \exp\left[-\frac{4 \ln 2 (r - r_i)^2}{w^2}\right] \quad (2)$$

The decomposition of the $GT(r)$ is performed with a three-peak fitting routine. The peak height A_i , full width half maximum w and peak position of Gaussfunction r_i are used as fitting parameters. In the fitting routine, these parameters are free to take on optimal values. The weighted average coordination number n_i for the shell i by

$$n_i = A_i r_i \left(\frac{\pi w^2}{4 \ln 2} \right)^{\frac{1}{2}} \quad (3)$$

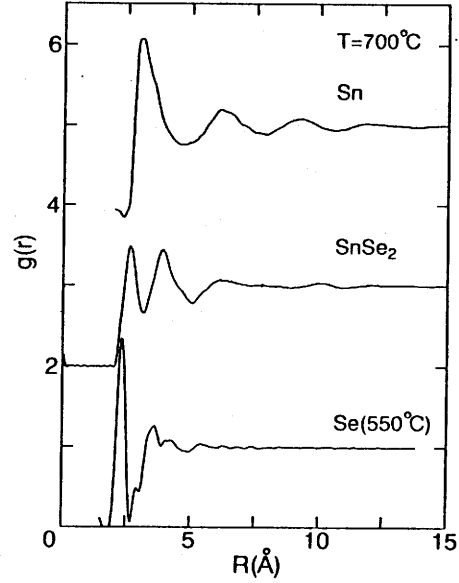


Figure 2 Total pair distribution functions for liquid Sn-Se alloys at 700 °C and the data of liquid Sn and Se [10].

Figure 3 shows the fitting results of $GT(r)$ for SnSe_2 . Although there is an overlap of the peak at higher R values, the first peak in $GT(r)$ of liquid SnSe_2 looks like symmetric and is well fitted by a single gauss function which peak is located at 2.64 Å. The Pauling covalent bonding distance of Sn and Se atoms are 1.4 Å and 1.17 Å, respectively [11]. Since the first peak positions are close to the sum of the covalent radii of elemental Sn and Se, it seems reasonable to interpret the first peak as being largely due to the Sn-Se correlation.

Since the Se-Se bond length in liquid and amorphous Se is 2.33 Å and 2.34 Å, respectively [10,12,13], the profile of $GT(r)$ indicates that the contribution of the chain-like Se-Se correlation to the first peak becomes negligible and then the structure of liquid SnSe_2 changes from the chain-like structure of liquid Se. The crystal SnSe_2 has layered structure, which is made up of chains of corner-sharing $\text{Sn}(\text{Se}_4)_{1/2}$ tetrahedra linked into layers by edge-sharing tetrahedra. The average coordination number of $\text{Sn}(\text{Se}_4)_{1/2}$ tetrahedra is 2.67 assuming that the coordination number of Sn is four and that of Se is two. The experimental result for liquid SnSe_2 is 2.30. The hump in the first peak of $S(Q)$ indicates that an intermediate-range order exists in liquid SnSe_2 . There are many defect states such as dangling bonds in the liquid state. These facts leads to a reasonable inference that the SnSe_2 -like short-range order preserved after melting. Hence the present analysis suggests that the Sn atoms introduced into liquid Se may act as a terminator, which may be associated with the strengthening of the inter-chain interaction and com-

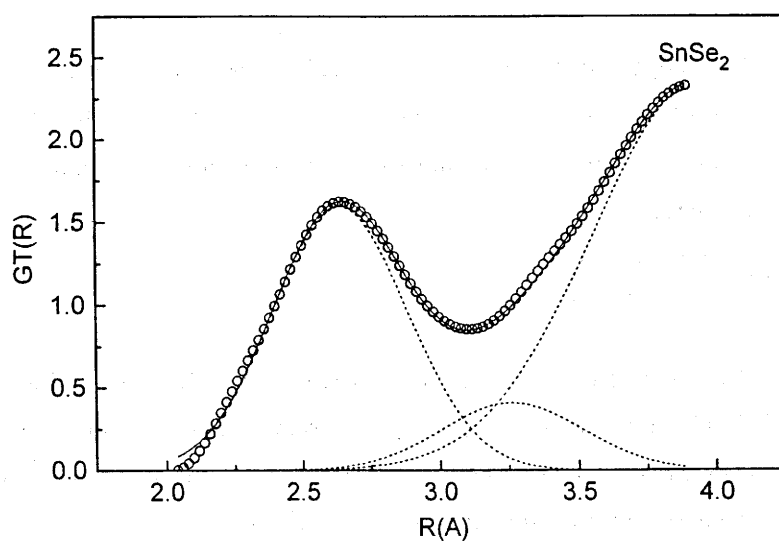


Figure 3 Total correlation function, $GT(R)$, for liquid SnSe_2 at 700 °C. Solid circles shows the experimental values, broken curves show subpeaks obtained by deconvolution and a solid curve indicates the sum of the subpeaks.

posed of the SnSe₂-like short-range order.

The electronic properties of liquid Sn-Se alloys gradually changes from semiconducting to metallic one with increasing Sn concentration. A metal-nonmetal transition takes place in the middle of concentration. The electrical conductivity, σ , for the liquid SnSe₂ is 150 ohm⁻¹cm⁻¹ at 700 °C. From the values of σ and their temperature dependence, the liquid SnSe₂ is classified to the semimetallic one based on the criterion introduced by Enderby et al. [3]. While the oscillation of the $S(Q)$ at high- Q is clearly visible for liquid Se, the amplitude of oscillation for liquid SnSe₂ is reduced and that for liquid Sn is strongly damped. These features indicate that there is a substantial change in the liquid structure, and also show that there is an alteration to the character of the bonding. The second peak around 3.3 Å⁻¹ in the $S(Q)$ curve for SnSe₂ seems to be associated with covalent bonds in liquid Se and SnSe₂[10]. The Se-Se bonds in liquid Se is highly covalent. The profile of $S(Q)$ and the analysis of $GT(R)$ suggest that the covalent Sn-Se bond in liquid SnSe₂ has partly metallic character. The semimetallic properties of SnSe₂ is closely related to the change in the local structure such as the disappearance of the chain-like Se-Se correlation.

5. Conclusion

The structure of the liquid SnSe₂ alloy at 700 °C was investigated. The hump, observed in the structure factor, indicates that the intermediate-range order still remains after melting. The chain-like Se-Se correlation disappears in SnSe₂. The change in the electronic properties from semiconducting to semimetallic ones can be attributed to the change in the chemical short-range order or local structure in the SnSe₂ alloy.

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