

Neutron diffraction study of liquid Ge in wide temperature range

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Abstract

Neutron diffraction measurements have been carried out for liquid Ge over a wide temperature range from 1000°C to 1550°C. The structure factor of liquid Ge just above the melting point has a pronounced shoulder in the high momentum transfer region of the first peak. With increasing temperature, the position of the first peak moves slightly to a higher value of Q and the shoulder becomes inconspicuous at high temperature.

1. Introduction

There are several single-element liquids with anomalous static structure factors that have a shoulder in the high momentum transfer region of the first peak of the structure factor. Among such liquids, Ge and Si have attracted attention because of the semiconductor-metal transition which occurs on melting accompanied with volume contraction¹⁾. Moreover, the tetrahedral unit in the crystalline and amorphous phases²⁾ and the relatively low coordination number (~ 6.8 , as reported in the literature³⁾) in the liquid phase around the melting point are in contrast with simple liquid metals where the coordination number is 10-12.

Many researchers have attempted to interpret the structure of Ge as a mixture between tetrahedral units and the metallic phase, and tend to emphasize the persistence of the covalent bonding even in the liquid state. On the other hand, theoretical studies have pointed out a metallic character in the bonding⁴⁾. The ion-ion potential suggested by Silbert and Young, which has a hard-sphere core with a positive step, reproduced the shoulder in the structure factor,⁵⁾ and integral equation calculations of liquid Zn, Cd and Hg which have a shoulder or asymmetry of the first peak showed that the deduced effective pair interactions have a similar small positive step⁶⁾. This suggests the existence of two characteristic lengths in liquid metals. From the viewpoint of the homogeneous metallic phase with loose packing, it is suggested that the shoulder appears at $Q = 2k_F$ corresponding to the diameter of the free-electron Fermi surface, and the atomic configuration is modulated by the Friedel oscillations. Recent molecular dynamics simulations⁷⁾ by Kulkarni et al. showed that the bond-angle distribution, with cut-off

at a relatively short distance, has a broad peak around 100° vaguely suggesting the existence of tetrahedral units, and they suggest that the liquid becomes more homogeneous at 2000K.

It is therefore important to obtain precise information on the structure factor of liquid Ge over a wide temperature range. So far, the structure factor of liquid Ge has been measured by X-ray and neutron diffraction by several researchers^{3,8-10)} just above the melting point. There are some differences in the low- Q region, as well as in terms of the height of the first peak and the position of the second peak. In this paper, we report the temperature dependence of the structure factor of liquid Ge over the range from 1000°C to 1550°C , as measured by the neutron diffraction method.

2. Experimental

Neutron diffraction of liquid Ge was carried out at 1000, 1100, 1250, 1500 and 1550°C and at atmospheric pressure utilizing the high-efficiency and high-resolution powder diffractometer HERMES¹¹⁾ of the Institute for Materials Research, Tohoku University, installed at the JRR-3M reactor. The spectrometer has 150 ^3He detectors for every 1° and a counter table that can be rotated around the axis of the sample table. The spectra were accumulated with two initial angles of 3.0° and 3.5° . The series of solar slits at the front of the counters is suitable for reducing the scattering intensity from the background. The neutron beam wavelength was 1.8196 \AA .

The germanium sample was obtained commercially with a purity of 99.9999 wt%. A bulk sample was inserted into the cylindrical cell made of glassy carbon provided by Nisshinbo Industries Inc. The diameter of the cell was 9.8 mm and its wall thickness was 0.2 mm. The furnace was a 1800°C -Furnace constructed by A S Science Products, Ltd. The heater consists of two concentric cylinders made of 0.05-mm -thick niobium foils and has 8 thermal shields around the radiative heater element. Typical voltage and current were 10V and 240A at 1500°C . The temperature of the sample was measured by a tungsten-rhenium thermocouple. He gas was introduced to keep the liquid sample stable in the carbon cell. Our experimental procedures are described in detail elsewhere¹²⁾. Glassy carbon is known to absorb hydrogen, which considerably increases the inelasticity of the neutron scattering. The scattering intensity from the carbon cell at room temperature is compared with that at 1000°C after being normalized by the monitor counts. A large amount of incoherent contribution is observed in the room-temperature spectrum. Assuming that all incoherent contributions come from hydrogen, the quantity of hydrogen absorbed into glassy carbon at room temperature can be estimated to be 3.0 at.%. The observed spectrum at 1000°C fortunately does not appear to include the large inelastic contribution which tends to incline the centroid of the interference function. Nevertheless, a large scattering intensity can be observed in the low- Q region which may be due to the grain structure of the glassy carbon. This suggests that almost all of absorbed hydrogen

was released from the carbon cell below 1000°C. In addition, from the systematic temperature dependence of the obtained structure factors at low Q , we conclude that the cell contributions do not change in the temperature range from 1000°C to 1550°C.

3. Results

In Fig. 1 the scattering intensity of liquid Ge at 1000°C contained in the glassy carbon cell is shown together with that for the empty cell, the background of the furnace and the vanadium rod. Since vanadium is almost incoherent in the neutron scattering process, the spectrum of vanadium represents counter efficiency. The detectors of the HERMES spectrometer are well adjusted in terms of counter efficiency except for the small hump at 113.3° and the steep valley at 149.0°. Three small but spiky peaks at 50.5, 73.9 and 94.9° are diffraction peaks from the vanadium rod which gives a small contribution to coherent scattering, guaranteeing the high resolution of the diffractometer. Moreover, the low background noise increases the accuracy of the deduced structure factors.

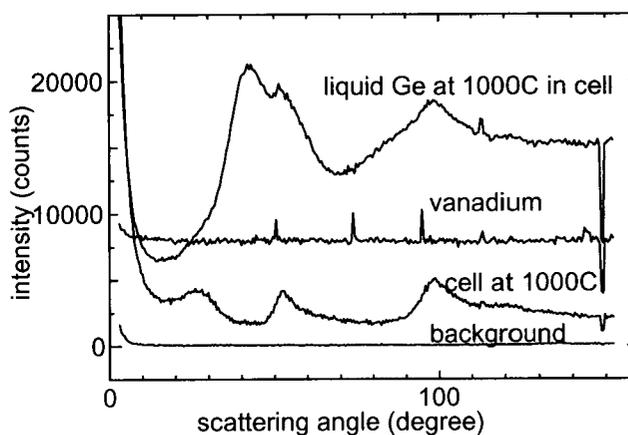


Fig. 1 Spectra of scattering intensity for liquid germanium in the glassy carbon cell, and for the glassy carbon cell, the background of the furnace filled with He 1atm gas and the vanadium rod. The counts for the cell and the background are scaled to the intensity of liquid Ge.

The structure factors, $S(Q)$, in the range of momentum transfer Q up to 6.7 \AA^{-1} were deduced by a standard procedure which includes absorption correction, subtraction of scattering from the cell, normalization using the spectra for vanadium and reduction of multiple scattering contributions. The absorption coefficients were calculated by the method proposed by Paalman and Pings¹³⁾. The cross section of multiple scattering was taken from the table formulated by Blech and Averbach¹⁴⁾. The scattering cross section was taken from the table by Sears¹⁵⁾. The number density appropriate for each temperature was estimated from the literature.¹⁶⁾

The structure factors, $S(Q)$, of liquid Ge are shown in Fig. 2. The accumulated monitor counts are 16.6×10^6 , 2.0×10^6 , 8.8×10^6 , 16.6×10^6 and 2×10^6 at 1000, 1100, 1250, 1500 and 1550°C, respectively. Several researchers have previously measured $S(Q)$ of liquid Ge within 100°C above the melting point ($\sim 937^\circ\text{C}$) and their structure factors also exhibit the characteristic shoulder in the high- Q region of the first peak^{3,8-10)}. On the other hand, there were some differences between earlier X-ray data and neutron data in the low- Q region, with regard to the height of the first peak, and the height and position of the second peak. In our data at 1000°C, the first peak is located at 2.53 \AA^{-1} and its peak height is about 1.42, which is consistent

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with the data of Bellissent-Funel and Bellissent.⁸⁾ and Alteholz and Hoyer¹⁰⁾, but slightly smaller when compared with the data of Waseda and Suzuki³⁾ and Salmon⁹⁾. The shoulder appears at around 3.3 \AA^{-1} in accordance with data in the literature^{3, 8-10)}. The second peak is located around 5.1 \AA^{-1} , similar to the data in refs. 3, 8 and 9, but the peak height is rather low compared with the results of these studies.

The temperature dependence of the structure factor is not large, but a clear tendency is evident as shown in Fig. 3. The height of the first peak decreases slightly with increasing temperature and the position moves to the high- Q side. At the highest temperature, the peak position becomes 2.60 \AA^{-1} . The shoulder becomes inconspicuous and almost disappears at 1550°C . This temperature dependence seems to follow the prediction of the MD simulation at 2000 K ⁷⁾ where the structure factor resembles that of a simple liquid metal and the first peak is located around 2.7 \AA^{-1} .

Strictly speaking, the neutron diffraction data presented in this work are expected to include both the density and temperature dependences of $S(Q)$. Both the position of the principal peak and

that of k_F , the Fermi momentum, are roughly proportional to $n^{1/3}$, where n denotes the density of the liquid. Given that the density decreases as the temperature increases, and taking into account

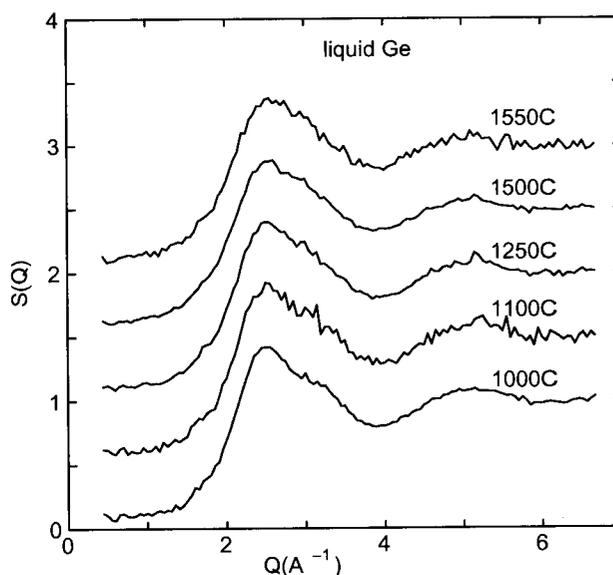


Fig. 2 Structure factors of liquid germanium at 1000, 1100, 1250, 1500, and 1550°C . The spectra are shifted vertically with respect to each other. The accumulated monitor counts were 16.6×10^6 , 2.0×10^6 , 8.8×10^6 , 16.6×10^6 , and 2×10^6 , respectively.

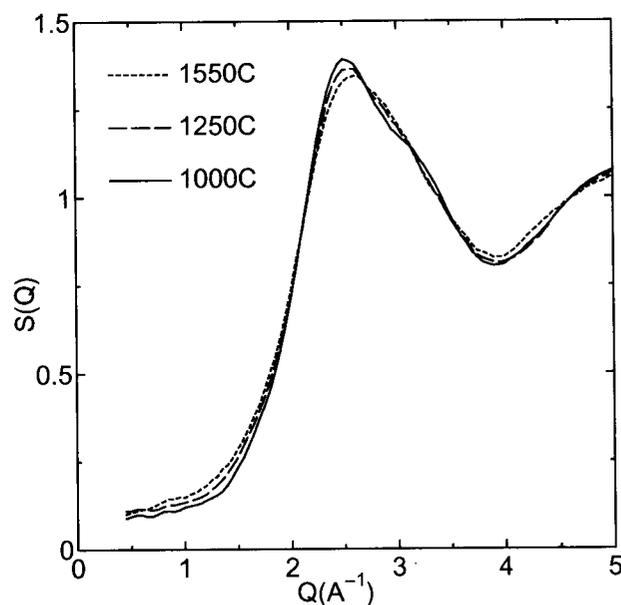


Fig. 3 Structure factors of liquid germanium at 1000, 1250, and 1550°C . The spectra have been smoothed out by averaging over 3 successive points.

the results shown in Fig.3, we can postulate that our results are dominated by the temperature dependence of $S(Q)$.

Our data confirm that the structural change proceeds gradually as the temperature is increased from 1000°C to 1550°C. It is difficult to explain that this gradual change is due to the disappearance of tetrahedral units with covalent bonds, because the disappearance of covalent bonds usually causes a significant structural change affecting the medium-range order including the second-neighbour distribution and the bond angle distribution. Recently, it was reported that a molecular dynamics simulation of liquid gallium, which has a similar shoulder in the $S(Q)$, using a potential including the induced polarization effects, reproduces a feature of the shoulder located at the high- Q region of the first peak in $S(Q)$ ¹⁷. Such polarization effects may be affect in liquid Ge just above the melting point where the coordination number of nearest neighbouring atoms is relatively small. With increasing temperature, thermal agitation may make the atomic configuration of the local structure homogeneous with increasing mean atomic distance, which obscures the polarization effects.

Although our results confirm the metallic character of liquid Ge over the range of temperatures studied, it is still an open question whether or not, on further increasing the temperature, liquid Ge will undergo a metal-semiconductor transition well before the liquid-gas transition.

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