Neutron Scatterting Analysis of Liquid Structure of Sn and Ge in Wide Temperature Range.

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Abstract

The structure factors of liquid tin were obtained in 2000 by neutron scattering experiments at temperatures of 1373K, 1473K, 1673K and 1873K in addition to 573K, 773K and 1073K in 1999. Glassy(vitreous) carbon is revealed to be a good material for neutron scattering experiment at high temperatures. The absorption of neutron due to glassy carbon is as small as the case of silica glass container. Corrections of absorption and multiple scattering were performed. As a result, high temperature structure factors of liquid Sn were obtained accurately. In addition, by using this glassy carbon cell, the structure factor at 1273K and 1673K of liquid germanium was also obtained.

Introduction

It is considered that the diffusion in liquid states deeply relates to its liquid structure. Ideally dynamic structures measured by the inelastic neutron scattering experiments give us the direct information of the atomic motion related to the diffusion phenomena. Moreover, it is important to obtain also the static structure which provides the average environment of moving atom. Therefore, in this project, the static structures of liquids are studied directly from the X-ray and neutron scattering experiments. Neutron scattering experiments up to the high temperatures are being performed by the high temperature furnace up to 2100K installed in the JRR-3M reactor at Japan Atomic Energy Research Institute (JAERI).

In this project, the molecular dynamics simulation is also performed to obtain detailed

information of liquid structures and atomic motions. In some liquid metals, reliable inter-ionic potentials, which are required for molecular dynamics simulation, are not always available from the theoretical basis. For such cases, the inverse method is essential to obtain the inter-ionic potentials from the accurate structure factors. For such purposes, it is important to obtain the exact structure factor in the wide temperature range. In this project, the brief description is given for the liquid structure studies in the wide temperature range for liquid Sn and liquid Ge.

Experiment and data correction

The neutron scattering experiments were performed at the TAS-1 spectrometer in the JRR-3M reactor of JAERI. The incident and the scattered beam were collimated by the solar slits. The wave length of the neutron beam is determined by the angle of the monochrometer. The measured Q-range is from 0.5 $Å^{-1}$ to 10.5 $Å^{-1}$, which corresponds to the scattering angle from 5° and 120° with the neutron wavelength of about 1 Å.

The measurements were performed with the use of the high temperature furnace(A.S. Scientific Company). The heater material is niobium whose melting point is 2741K. The heater was surrounded by the radiation shields which were composed of 8 niobium co-axial cylinders. The furnace can be evacuated less than 10^{-3}Pa. The high temperature up to 2100K is available by these specifications. The experimental temperature was 573K , 773K, 1073K, 1373K, 1673K, 1873K in the case of liquid Sn and 1273K and 1873K in the case of liquid Ge. For the low temperature experiments up to 1073K, the sample was enclosed in the cylindrical silica glass cell under vacuum. Glassy(vitreous) carbon was used in the higher temperature experiments. The scattered neutron intensity was accumulated more than a few ten thousands counts at the high scattering angle region. Intensity data were obtained with every 0.05 or 0.1 $Å^{-1}$.

Absorption correction and multiple scattering correction were performed by using the intensity data of the blank cell, $I_{Cell}(Q)$, and the sample in the cell, $I_{Sample+Cell}(Q)$, and finally the static structure factors were obtained.

At first, the absorption correction was performed by the method of Paalman and Pings[1)] . The details are shown as follows:

$$I_{sample}(Q)=\frac{1}{A_{S,SC}(Q)}I_{Sample+Cell}(Q)-\frac{A_{C,SC}(Q)}{A_{S,SC}(Q)A_{C,C}(Q)}I_{Cell}(Q) \qquad (1);$$

$$A_{S,SC}(Q)=\frac{1}{\pi R_{Sample}^2}\int_0^{R_{Sample}}\int_0^{2\pi}\exp[-\mu_S l_S(r,\theta;Q)-\mu_C l_C(r,\theta;Q)]rdrd\theta \qquad (2);$$

$$A_{C,SC}(Q)=\frac{1}{\pi(R_{Cell}^2-R_{Sample}^2)}\int_{R_{Sample}}^{R_{Cell}}\int_0^{2\pi}\exp[-\mu_S l_S(r,\theta;Q)-\mu_C l_C(r,\theta;Q)]rdrd\theta \qquad (3);$$

$$A_{C,C}(Q)=\frac{1}{\pi(R_{Cell}^2-R_{Sample}^2)}\int_{R_{Sample}}^{R_{Cell}}\int_0^{2\pi}\exp[-\mu_C l_C(r,\theta;Q)]rdrd\theta \qquad (4);$$

l_S : neutron path length in the sample; μ_S : absorption coefficient of the sample;

l_C : neutron path length in the cell; μ_C : absorption coefficient of the cell

Absorption factors, $A_{S,SC}$, $A_{C,SC}$ and $A_{C,C}$ are numerically calculated from the present cell dimension, the number density and neutron cross-sections of both the sample and the cell. $A_{S,SC}$ is the neutron absorption factor where neutron is scattered at the sample. $A_{C,SC}$ is the absorption factor where neutron is scattered at the cell and pass through the sample and container. $A_{C,C}$ is the absorption factor where neutron is scattered at the cell and pass through the container.

R_{Sample} and R_{Cell} are outer radii of sample and cell respectively. The inner diameter was 8.0mm and wall thickness was 0.3mm for the silica glass cell, and for the glassy carbon cell the inner diameter was 10.0mm and wall thickness was 0.3mm or 0.5mm.

Then, the correction of multiple scattering was performed by means of the method due to Blech and Averbach[2]. Neutrons of multiple scattering were the scattered neutrons more than twice, which are not related to the liquid structure. Therefore it must be subtracted from the whole intensity. In the manner of Blech and Averbach, the raito of the intensity of multiple scattering to the whole intensity is function of the sample dimension R/h(R: sample radius, h: sample height) and μ R(μ : absorption coefficient(cm^{-1})). This correction in the original paper is assuming that the scattering process is isotropic. However, the differential cross section actually depends on the scattering angle. Therefore the secondary scattering intensity was calculated and then it was compared with the primary scattering which have a scattering angle dependence such as structure factor. As a result, it is recognized that secondary intensity is constant with respect to the scattering angle. It is revealed that the multiple scattering intensity was about 6% of the whole intensity for Sn under the present experimental condition.

After the incoherent scattering intensity was subtracted from the corrected intensity, then the coherent intensity which is related to the liquid structure was obtained. The coherent intensity was normalized at large-Q region, then the liquid structure factor, S(Q), was derived as shown in Fig.1. The liquid structure factors of Ge were also obtained as shown in Fig.2.

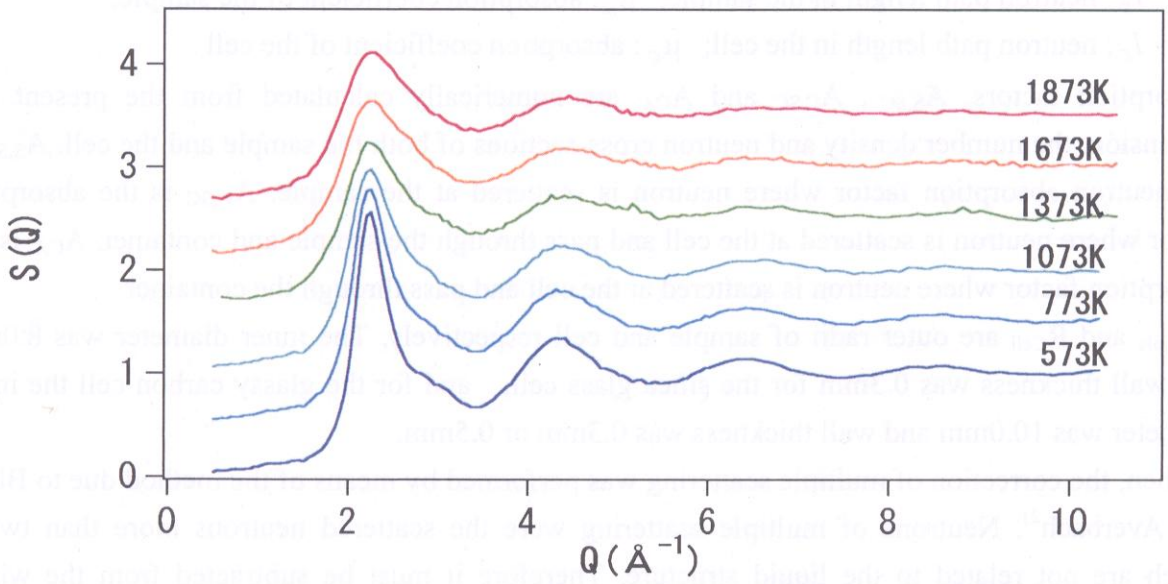

Fig.1 The structure factor of liquid tin.

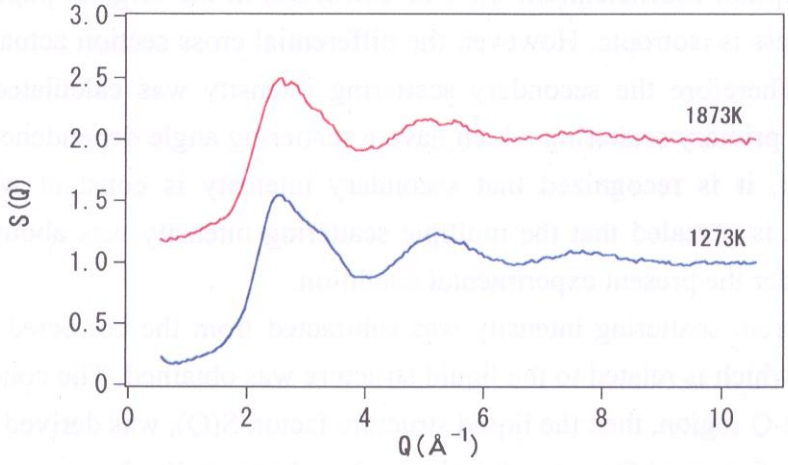

Fig.2 The structure factor of liquid germanium.

Because of the low neutron absorption of silica glass, the obtained structure factor of liquid Sn at the low temperatures has only a small error. As for the high temperature data, an error seems to be so small if the glassy carbon is adopted as the container. Therefore, it can be considered that glassy carbon is a good material for neutron scattering experiments at high temperatures.

Results & Discussions

For the first time, the high temperature structure factors of liquid Sn at 1373K, 1673K and 1873K were obtained. As for the S(Q) at lower temperatures up to 1073K, the obtained structure factor are, to some extent, different from the previous X-ray structure data[3]. Especially as for the first peak, present data is larger than that of the previous X-ray data at 573K. With the increase of the temperature, the difference of first peak is smaller. At the small-Q range just before the first

peak, the present data are larger than the previous data. It can be considered that there remains the intensity of 'inelasticity' at small-Q range in the present experiment data. We are now obtaining the correct structure data in the small-Q region from the X-ray small angle experiment. We are now planning to determine the correct g(r) both from the present neutron structure data and the X-ray small angle experiment in small-Q region. The obtained structure factors of liquid Ge, shows also larger background in the small-Q region.

There is a distinct 'shoulder' in the large-Q side of the first peak for the structure factor of liquid tin at 573K. The shoulder becomes smaller with the increase of the temperature, and finally at the temperature of 1873K it seems to disappear at a first look. However, it seems to be present even in this high temperature range judging from the fact that the intensity in this Q range remains to be constant. On the other hand, as for the structure factor of liquid Ge, there remains a distinct shoulder even at 1873K far from the melting point.

Summary

For the neutron scattering experiments at high temperatures, the glassy carbon was tested for the container material. As a result, it proved to be effective for such experiments because of its low absorption of neutron and no Bragg peaks. In addition, it is available for the high temperature experiments up to 1873K. The obtained raw data of liquid Sn and Ge by using this glassy carbon container were corrected by means of the standard procedures, which are the absorption correction of Paalman and Pings and multiple scattering correction of Blech and Averbach. The program code was developed for the corrections of the absorption and the multiple scattering. The results of these analysis will be described elsewhere in near future.

References

1 Paalman H H and Pings C J, J. Appl. Phys., 33(1962)2635

2 Blech I A and Averbach B L, Phy. Rev. A, 137(1965)1113

3 Waseda Y, "The Structure of Non-Crystalline Materials, Liquid and Amorphous Solid" (Mcgraw-Hill, New York 1980)