Measurement of Low Q Region of S(Q) of Liquid Metals due to the Small Angle X-ray Scattering Method.

Tadahiko Masaki[1], Shuji Munejiri[2] and Toshio Itami[2]

1:Space Utilization Research Center, National Space Development Agency of Japan (NASDA), 2-1-1 Sengen, Tsukuba, 305-8505 Japan.
2:Space Utilization Research Program, National Space Development Agency of Japan (NASDA), 2-1-1 Sengen, Tsukuba, 305-8505 Japan.

Abstract

For the evaluation of effective interatomic potentials due to the inverse problem method coupled with the molecular dynamics simulation, the low wave number region of static structure factor is necessary with high accuracy. The small angle X-ray scattering with liquid slab sample is one of the methods to obtain it, though the intensity of small angle scattering is much smaller than that of usually measured angle. The sample holder of liquid slab sample between thin graphite crystals is developed for the laboratory base small angle X-ray scattering facilities which is 18 kW Mo rotation target. The obtained scattering data of liquid tin and germanium are reported.

1. Introduction

The evaluation of actual interatomic potentials and its temperature dependence in liquid metals is one of the most difficult problems in condensed matter physics because the many body interaction and the electron states should be take into account. In the case of group IVB elements such as Pb, Sn, Ge and Si, the ambiguity is inherent in the evaluation of interatomic potential based on the liquid theory and the nearly free electron model. This is derived from the fact that the electron-ion interaction in group IVB liquid metals induces the complicated interatomic forces and liquid structures. For example, it is well known that the shoulder or hump can be observed at the higher wave number side of the first peak of the static structure factor, S(Q) (Q: wave number) of group IVB liquids.

Recently, the evaluation scheme of effective pair interatomic potential directly from the static structure factors is proposed by Reatto et.al [1]. This method solves the inverse problem by the predictor-corrector method with the application of molecular dynamics simulation. Munejiri et.al [2] reported that the effective pair interatomic potential can be obtained from static structure factors with a high accuracy with the combination between the large scale molecular dynamics simulation and the accurate experimental S(Q). It should be remembered that it is not always successful for group IVB liquids to obtain the pair interatomic potentials from the conventional pseudo potential NFE approach. This predictor-corrector scheme is applicable to the non-simple liquid metals such as group IVB liquids because the effective pair interatomic potential can be directly evaluated from the experimental static structure without approximation and the obtained effective interatomic potential reproduces the static structure self-consistently. In addition to this merit, it is expected that the physicochemical properties, such as diffusion coefficient, could be obtained simultaneously with high accuracy in terms of the molecular dynamics simulation because the applied pair potential exactly reflects the static structure factor of actual liquid.

For this evaluation scheme, the static structure factor S(Q) must be given with high accuracy in the low wave number (low Q) region. The symmetrical transmission method is typically applied for the small angle scattering, however it is difficult to obtain it with high accuracy in the case of liquid metals because the X-ray is well absorbed by metals. Moreover, the scattering intensities of low Q region of S(Q) are rather small compared with the higher Q region.

This report describes the newly developed sample holder of slab liquid sample with graphite crystals. Due to this sample holder, the thickness of liquid sample can be reduced down to 100 micro meters and this reduction of sample thickness enables us to perform the laboratory base small angle X-ray scattering experiments. This holder was able to be also supplied for the recycle use. As the results, the efficiency of measurements of blank cell is improved.

2. Sample holder for laboratory base small angle X-ray scattering

On the experiments of liquid metals at the high temperature, necessary conditions for the crucible materials are high melting point, stability, no chemical reactivity and non-wettability to liquid samples, etc. Especially, in the case of X-ray scattering experiment due to the transparency method, the lighter element should be selected because of small X-ray absorption coefficient. For this purpose, graphite is one of the best materials judging from above factors. Additionally, in the case of single crystal of graphite, the diffusive scattering from liquids can be clearly observed through the windows between the sharp Bragg peaks of graphite crystal.

In this research, the thin graphite crystal was applied to the container wall of liquid slab sample. The holder was specially designed for the recycling use of graphite crystals.

The highly oriented pyrorytic graphite crystal, HOPG was sliced into the thin plate whose thickness was around 100-200 micro meter. In the case of liquid tin, the thickness of sample is required to be less than 100 micro meter for the data acquisition during the feasible experimental time. Fig. 1 shows the sample holders with the casting channel and syringe. The sample was injected into the thin space between HOPG plates through the cannel and the small hole of HOPG plate. The sample casting was performed after the setting of holder in the furnace. For the preparation of such thin liquid sample, the so-called *in-situ* casting was necessary.

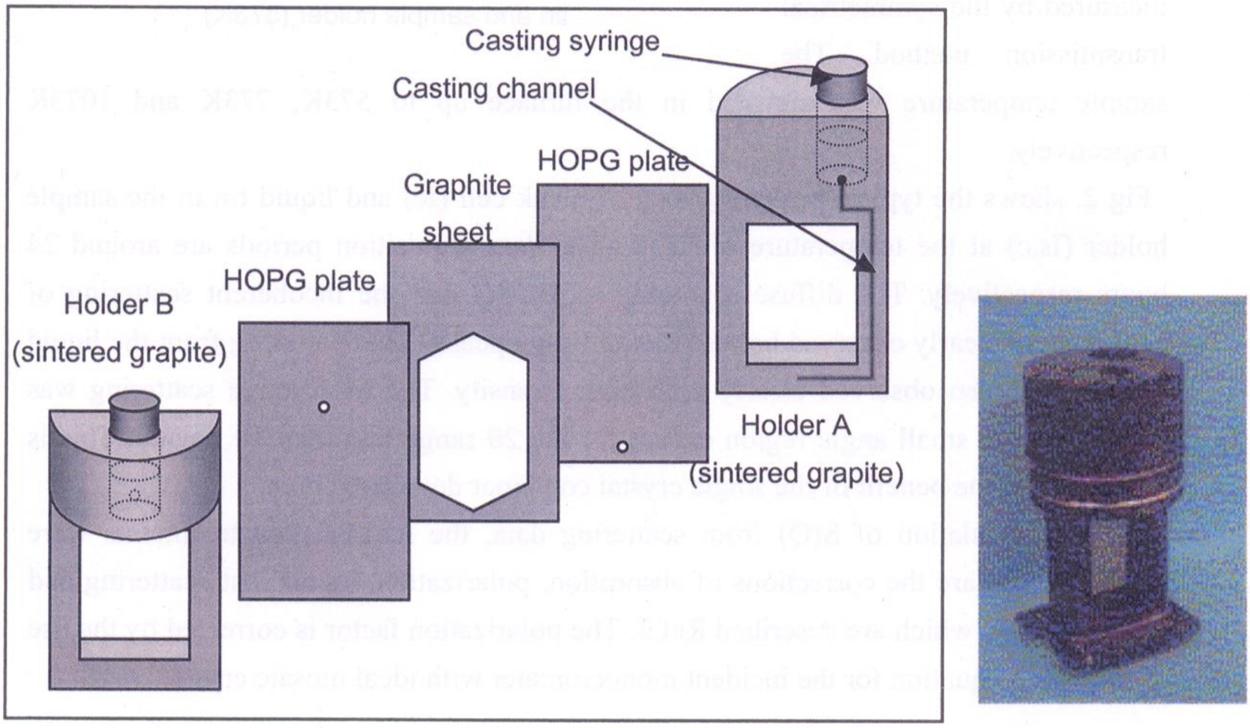

Fig.1 Schematic figure and photo of sample holder with casting channel and syringe

3. Data treatment

The static structure of liquid tin was measured with the use of small angle X-ray scattering. The low wave number region of S(Q), which is less than 1Å^{-1}, is important to evaluate the effective pair interatomic potential because the inverse of S(Q) is dominant to determine the direct correlation function, as already described. Therefore, the low Q region (0.4 Å^{-1} – 2.0 Å^{-1}) of S(Q) was measured carefully by the small angle X-ray scattering. The monochromatic Mo Kα X-ray by the graphite crystal was collimated through the three slits system. The X-ray source, the goniometer and the proportional counter were installed in the grove box which was filled with high purity Ar gas in order to prevent the oxidation of liquid tin and sample holder at high temperature. The angular dependence of the scattering intensity was measured by the symmetrical transmission method. The sample temperature was elevated in the furnace up to 573K, 773K and 1073K respectively.

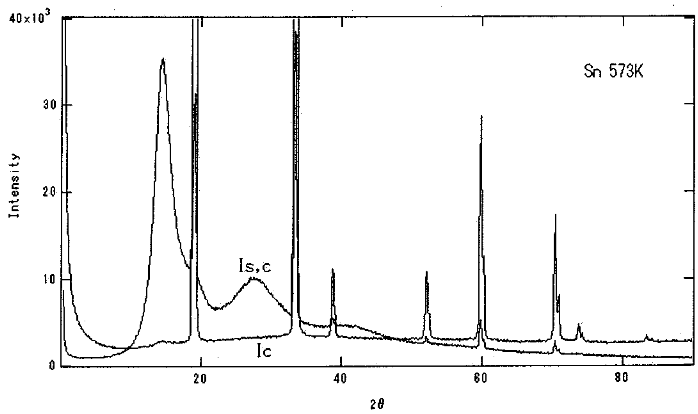

Fig.2 Typical scattering intensities of molten tin and sample holder (573K)

Fig 2. shows the typical scattering data of blank cell (Ic) and liquid tin in the sample holder (Is,c) at the temperature of 573K. The data acquisition periods are around 24 hours respectively. The diffuse scattering of HOPG and the incoherent scattering of carbon were clearly observed between large Bragg peaks. The scattering from the liquid sample was also observed clearly with high intensity. The obstructive scattering was avoided in the small angle region except for the 2θ range less than 10 degree. This is derived from the benefit of the single crystal container developed here.

For the calculation of S(Q) from scattering data, the normal data treatments were applied; those are the corrections of absorption, polarization, incoherent scattering and cell scattering, which are described Ref.3. The polarization factor is corrected by the use of following equation for the incident monocromater with ideal mosaic crystal.

$$P(2\theta) = \left(1 + x\cos^2 2\theta\right)/\left(1 + x\right), \qquad (1)$$

where $x=\cos^2 2\alpha_c$ and $2\alpha_c$ is twice of the Bragg angle of HOPG. The absorption and subtraction of cell scattering was performed by the use of following equation.

$$I_s = \frac{1}{A_{S,SC}}\left[I_{S,C} - \frac{A_{C,SC}}{A_{C,C}} I_C\right]. \qquad (2)$$

$$A_{S,SC} = t_S \sec\theta \exp\left[-\left(\mu_C t_C + \mu_S t_S\right)\sec\theta\right]. \qquad (3)$$

$$A_{C,SC} = t_C \sec\theta \exp\left[-\left(\mu_C t_C + \mu_S t_S\right)\sec\theta\right]. \qquad (4)$$

$$A_{C,C} = t_C \sec\theta \exp\left[-\mu_C t_C \sec\theta\right]. \qquad (5)$$

In these equation, I_C is the scattering intensity of blank cell, $I_{S,C}$ is the scattering intensity of the sample with the cell and I_S is the corrected intensity of the sample. t_S and t_C are the thickness of sample and HOPG plates respectively. μ_S and μ_C are the mass absorption coefficient of the sample and the carbon cell respectively.

The scattering intensity of sample is normalized to the static structure factor due to the following normalization constant α,

$$\alpha I^{cor} = I^{coh} + I^{inc} \qquad (6)$$

,where I^{coh} is the intensity of coherent scattering, I^{inc} is the intensity of incoherent scattering. Strictly, the multiple scattering should be incorporated for the correction. Since the multiple scattering is neglected in the conventional case of X-ray scattering, we also neglected it. The normalization constant is evaluated by the use of following equation, which is so-called Generalized Krogh-Moe-Norman mathod.

$$\alpha = \frac{\int_{Q_{\min}}^{Q_{\max}} Q^2\left[\langle f^2\rangle + I^{inc}\right]dQ - 2\pi^2\rho_0}{\int_{Q_{\min}}^{Q_{\max}} Q^2 I^{cor} dQ} \qquad (7)$$

, where ρ_0 is the average number density of sample and f is the atomic scattering factor. The dumping factor is introduced to this equation in the conventional case. In our calculation, the dumping factor is adopted to be zero.

4. Results and discussions

Fig.3 shows the static structure factor of molten tin, which was obtained from coupling of the data of the present X-ray small angle scattering and that of neutron scattering[4]. The data of small angle scattering of X-ray and neutron scattering can be connected smoothly around Q = 2 A^{-1}. In the case of germanium, the scattering intensities are extremely

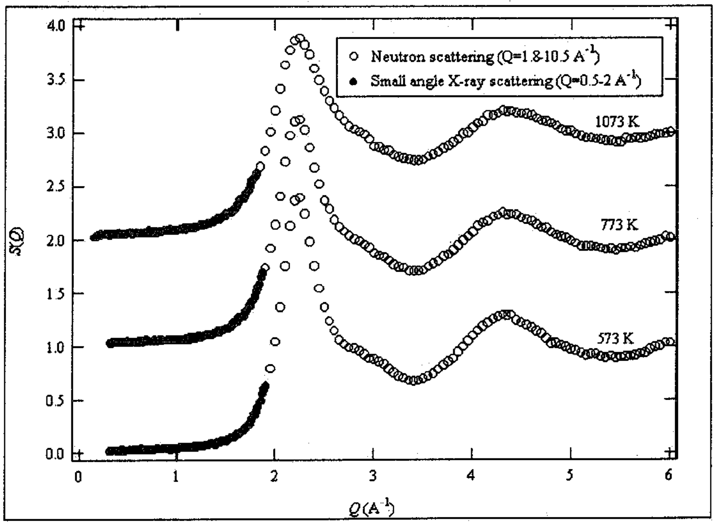

Fig.3 Static structure factors of molten tin.
closed circle: X-ray small angle scattering
open circle: neutron scattering

small compared to the case of tin because the mass absorption coefficient of germanium is twice higher than that of tin. Therefore the experiment of germanium with high accuracy is much more difficult. For the improvement of data accuracy, the position sensitive proportional counter, PSPC, will be introduced in further experiments.

References

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