Inelastic Neutron Scattering of Liquid Sn - Nature of Coherent Quasielastic Neutron Scattering

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Abstract

For the purpose to evaluate atomic diffusive dynamics in liquid Sn the inelastic neutron scattering measurement has been carried out. The quasielastic neutron scattering in a part of the inelastic scattering results from the diffusion or structure relaxational motion. The obtained width of the quasielastic line versus momentum transfer Q deviates from Fick's law and close to the jump-diffusion model corresponding to water. As Sn is the almost coherent scatterer, this width is considered to be derived from the existence of the correlated motion of particles. The quasielastic line behavior in liquid Sn may represent the slow structural relaxation of the particle shell around the new site after the jump motion of a Sn atom in diffusion process.

1. Introduction

The properties of liquids are important in a wide range of scientific and technical areas, from its role as a transport medium, a solvent, a material processing and so on. However, the study of the dynamical properties of liquids has still remaining problems even in the simple liquids. This is caused by the difficulty of making a simple and correct model for liquids from a microscopic view. In the last decade computer simulations have progressed in this field, but the appropriate model, which should explain the bulk and microscopic natures simultaneously, does not yet exist.

The diffusion in liquids is very sensitive to the structure. In liquid IVB group (Si,

Ge, Sn and Pb) the structure varies between simple one and complex one, and their diffusive motions must be changed with this variation. Solid state Si and Ge with lighter atomic masses have the diamond type covalent bonds and show the semiconductor character. On the other hand Pb with heaviest atomic mass has the metallic character. The solid state Sn shows an intermediate character between the metallic and the semiconductor one. It is metallic at the high temperatures while it is semiconductor like with a diamond structure at the low temperatures. The structure of liquid group IVB elements reflects this systematic variation of the chemical bond in the solid states. Then, a systematic investigation of diffusion in liquid group IVB elements essentially relates to the study of microscopic dynamical structures with this systematic variation of complexity. Therefore, it is very important to study the variation of dynamical structure factor $S(Q,E)$ among group IVB liquids.

This study has done in this point of view. The main objectives of our project are to clarify the diffusion mechanism deduced by several methods and to establish a diffusion model for simple metal and complex semiconductor melts such as Si or GaAs in future. The research activities contained in our project consist of the theoretical analysis using the hard sphere model, the classical and ab inito molecular dynamics and mode coupling theory, liquid structure measurements by X-ray and neutron diffractions, and macroscopic diffusion coefficient measurement under microgravity. This neutron inelastic scattering measurement of liquid Sn started as a part of the "diffusion project".

The neutron inelastic scattering is a powerful tool to investigate the microscopic dynamics of atoms in liquids. The neutron energy, whose wavelength becomes same order as interatomic distances in the condensed matters, is comparable to the energy of thermal motions of atoms. This is an important merit for the study of liquids from microscopic dynamical and structural aspects. The inelastic neutron scattering is a useful method for such purpose. The quasielastic scattering in the part of the inelastic neutron scattering comes from the diffusion or structural relaxation phenomena of the matters. Such phenomena show the broadening of the elastic peak. From this broadening we can deduce the information of the diffusive motion in the real matters by comparison with the theoretical models. In this study we have carried out the $S(Q,E)$ measurement for liquid Sn near its melting point. At such a temperature the liquid Sn may still have the residue of the crystal structure. Then the diffusion dynamics may be influenced by the structural relaxation relating to this residue.

2. Experimental

The inelastic scattering measurements were carried out by using the direct-geometry type spectrometer INC installed in KENS at High Energy Accelerator Research Organization (KEK) in Japan. Figure 1 shows the schematic layout of INC. INC is set up at the thermal source port and its incident flight path length, from the neutron source to the sample, is 8.2 m. The incident neutron is made to be monochromatic by Fermi chopper, then the high energy monochromatic neutron can be used for the experiment. The energy transfer between the neutron and the sample can be calculated by the time-of-flight method. INC has a large number of detectors which cover the wide scattering angle from 5.5 to 131 degree continuously. The lower angle counter bank (< 40.5 degree) is arranged at the final flight path length of 2.5 m to measure the $S(Q,E)$ in the region of small momentum transfers efficiently. The higher angle counter bank (> 48.6 degree) is set at 1.3 m position from the sample. Figure 2 shows a typical Q-E region covered with INC. INC can cover the wide Q-E space, which is calculated from the incident neutron energy we chose and the scattering angle of the detectors. Normally the quasielastic line becomes broader with increasing Q, then we choose 100 meV as incident neutron energy to cover the wide spectra of $S(Q,E)$, as shown in Figure 2.

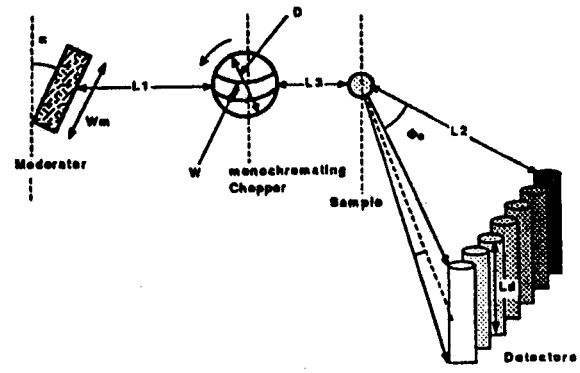

Fig. 1. Schematic layout of INC spectrometer.

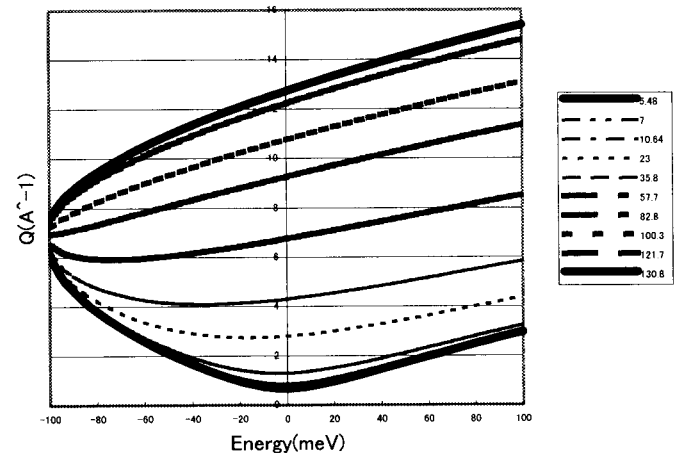

Fig. 2. Example of searched momentum-energy (Q-E) space by INC(incident neutron energy = 100 meV). The numbers near various lines indicate the scattering angle.

The liquid Sn sample had a cylindrical shape of 8 mm diameter and 50 mm height. The shape was decided from the estimation to decrease the multiple scattering of scattered neutron. The sample cell was made by quartz with wall thickness of 0.3 mm. The sample was enclosed in the cell and set into the furnace. For the data accumulation, the sample was kept at 573K during 3 days.

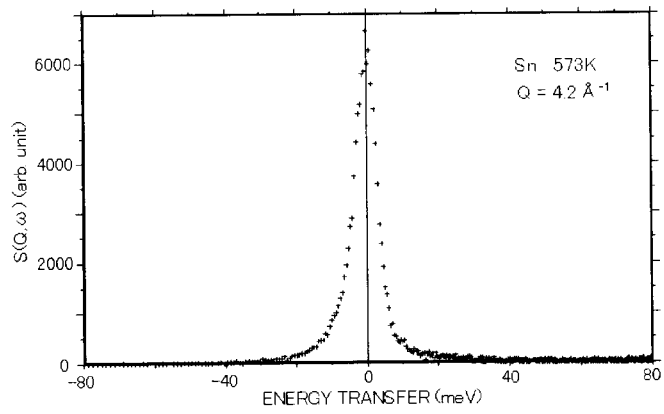

Fig.3. An example of quasielastic spectrum of liquid Sn (573 K).(Q= 4.2 Å^{-1})

The example of the obtained spectrum is shown in figure 3. The evaluation of the width of the quasielastic peak have been performed under the assumption that the spectrum is composed of the single Lorentzian component. This assumption may be plausible because the liquids like Sn are composed of a single particle and it is sufficient for the analysis of the quasielastic line to take account of the long range translational motion.

3. Results and Discussions

The Q^2 dependence of the half width at half maximum (HWHM) of the quasielastic peaks is shown in figure 4. The experimental results are indicated by circles. The HWHM becomes smaller with decreasing Q, while it has a trend to go to a specific value asymptotically at large Q. Under the assumption of the continuous diffusion behavior in simple liquids the HWHM of the incoherent quasielastic line should be in proportion to Q^2, which can be deduced from Fick's law [1].

If the quasielastic peak contains the coherent scattering component, the HWHM oscillates around the Q^2 law, such as the case of liquid Ar [2]. The result of liquid Sn deviates from such continuous diffusion model and resembles the diffusive motion in light water [3]. For the analysis of the water spectrum Singwi and Sjölander assumed a residence time τ_0, which indicates the oscillatory motion of molecules on their equilibrium positions [4]. The water molecules are bound each other by hydrogen bonds. The movement of a molecule to the next position for diffusion requires a large jump and reforming its shell around the new position. The long-range diffusive motion is a pile of such jumps. This jump-diffusion model leads

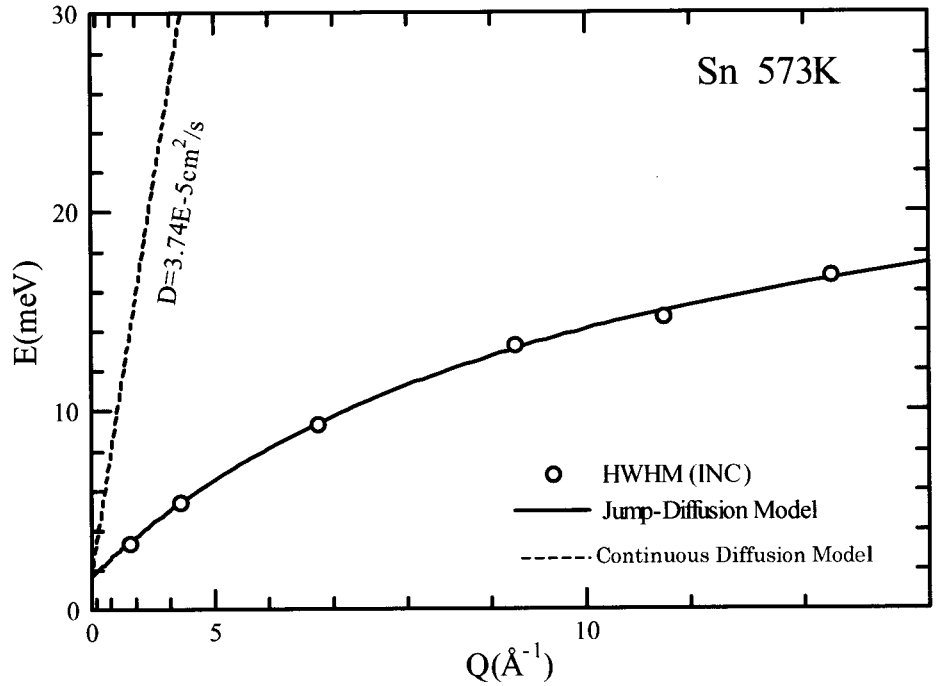

Fig. 4. Half width at half maximum, E, of quasielastic line (Circles are obtained by INC. Solid line is calculated with the jump-diffusion model. Broken line indicates the model of continuous diffusion).

to the equation for the HWHM of quasielastic line,

$$\mathrm{HWHM} = \frac{1}{\tau_0}\left[1 - \frac{\exp(-2W)}{1+Q^2 D\tau_0}\right], \tag{1}$$

where W corresponds to the Debye-Waller factor and D indicates the diffusion coefficient. Equation (1) is deduced by an assumption that the particle oscillates in its equilibrium position for a much longer time than the time for its diffusive motion.

The fitted line of eq. (1) to experimental HWHM is shown as a solid line in Fig. 4. The fitting results are τ_0 = 0.16 ps, $D = 0.68\times10^{-5}$ cm²/s and mean square displacement $\langle l^2\rangle$ = 0.065 Å² for W. The agreement between the fitted line and the experimental HWHM is good. This means that, on the whole, the particle dynamics in liquid Sn shows the similar behavior to that of the water molecule. The different point between Sn and light water is that the former is a coherent scatterer and the latter is almost an incoherent scatterer due to extremely large inelastic scattering cross section of H nuclei. The interpretation of the coherent quasielastic scattering is a little bit complex, but this case could be explained with the jump-diffusion model. In the case of the liquid Sn at low temperature the residential time τ_0 is longer than the diffusion time to the next site. The coherent quasielastic line width

reflects the structural relaxation time of the surrounding particle shell around the new site. The shell is reconstructed by correlated slow motion of particles in the small region. In contrast the diffusive motion is the rapid jump to the outside of the surrounding shell. The Sn atom stays in the shell with relaxation time τ_0, then jumps out to another shell. The latter process corresponds to the diffusive motion. In Fig.4 the broken line shows the continuous diffusion model in which the macroscopic diffusion coefficient of liquid Sn at 573 K was inserted. The diffusion coefficient deduced from the jump-diffusion model is smaller compared with this macroscopic value. As mentioned above this may be caused by the difference between the single particle motion and the coherent motion of particles which reflects the slow surrounding shell motion.

Figure 5 shows the whole quasielastic line reproduced by the experimental

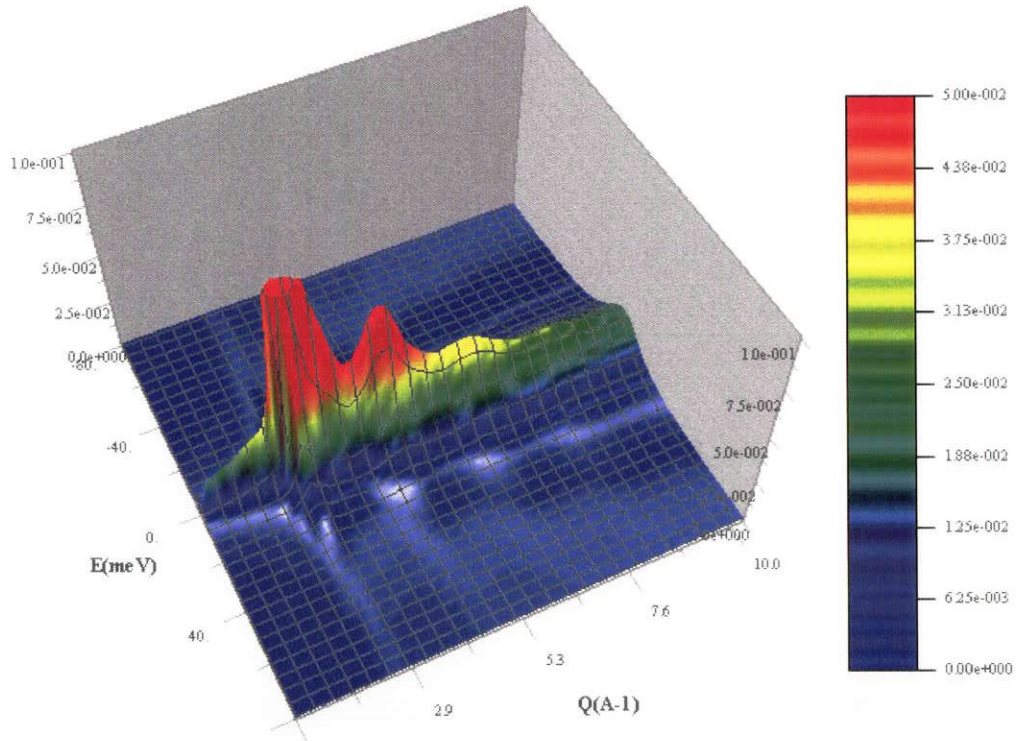

Fig. 5. Quasielastic line of liquid Sn at 573 K reproduced from experimental $S(Q)$ and the jump-diffusion model. The numbers attached to colors indicate the magnitude of $S(Q, E)$ in unit of meV^{-1}.

structure factor $S(Q)$ [5] and the jump-diffusion model. The characteristic oscillation is shown on the all Q-E space. This complex feature is caused by the coherent scattering effect, that is, the microscopic structure of the liquid. For the precise analysis of the coherent quasielastic scattering it needs the information of $S(Q,E)$ on the wide Q-E space. The high-resolution inelastic neutron scattering experiment with direct-geometry spectrometer is useful for this purpose.

4. Conclusion

We have measured the inelastic neutron scattering of liquid Sn near melting point on the wide Q-E region. By the analysis of the coherent quasielastic width the Q dependence of the HWHM is similar to the incoherent quasielastic scattering of light water. By applying the jump-diffusion model of water, the HWHM behavior could be explained. In the liquid Sn at low temperature, the particle motion could become the water-like diffusion behavior with repetition of oscillation and jump. The continuous diffusion appears as a result of the long time progress of such repetition. The Sn quasielastic line may show the slow structural relaxation of the surrounding particle shell around the new site after the jump motion of the diffusing particle.

For the precise analysis of this microscopic diffusion phenomena we need to measure the incoherent single particle motion and coherent motion by neutron quasielastic scattering separately. We have a plan to make a new measurement of liquid Sn by using some isotope. Table 1 shows the neutron scattering cross sections of various Sn isotopes. Almost all isotopes are coherent scatterers. However, by combining measurements of the isotope which have the incoherent cross section and the completely coherent isotope, we may analyze the incoherent and coherent $S(Q,E)$ separately. For this kind of experiment we need the more intense neutron source and high-resolution spectrometer. We will try this kind of experiment on the other neutron facility.

Table. 1. Cross sections of Sn isotopes. ($1fm=1\times10^{-15}m$, $1barn=1\times10^{-24}cm^2$)

Isotope	Abundance	b_{coh}(fm)	b_{inc}(fm)	σ_{coh}(barn)	σ_{inc}(barn)	σ_S(barn)	σ_A(barn)
Sn	–	6.225	–	4.871	0.022	4.892	0.626
^{112}Sn	1	6.(1.)	0	4.5(1.5)	0	4.5(1.5)	1
^{114}Sn	0.7	6.2	0	4.8	0	4.8	0.114
^{115}Sn	0.4	6.(1.)	–	4.5(1.5)	0.3	4.8(1.5)	30.(7.)
^{116}Sn	14.7	5.93	0	4.42	0	4.42	0.14
^{117}Sn	7.7	6.48	–	5.28	0.3	5.6	2.3
^{118}Sn	24.3	6.07	0	4.63	0	4.63	0.22
^{119}Sn	8.6	6.12	–	4.71	0.3	5	2.2
^{120}Sn	32.4	6.49	0	5.29	0	5.29	0.14
^{122}Sn	4.6	5.74	0	4.14	0	4.14	0.18
^{124}Sn	5.6	5.97	0	4.48	0	4.48	0.133

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