ELSEVIER

Journal of Alloys and Compounds 452 (2008) 136–139

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Ionic dynamics of molten cuprous iodide

Yukinobu Kawakita [a,*], Yasuhiko Kato [b], Hiroyuki Shigeta [b], Kaoru Shibata [c], Shin'ichi Takeda [a]

[a] *Department of Physics, Faculty of Sciences, Kyushu University, 810-8560 Fukuoka, Japan*
[b] *Department of Condensed Matter Chemistry and Physics, Graduate School of Sciences, Kyushu University, 810-8560 Fukuoka, Japan*
[c] *Pulsed Neutron Instrumentation Research Group, Neutron Technology Development Research Center, Quantum Beam Science Directorate, Japan Atomic Energy Agency (JAEA), Tokai-mura, Naka-gun, 319-1195 Ibaraki-pref, Japan*

Received 15 September 2006; received in revised form 17 December 2006; accepted 29 January 2007
Available online 3 March 2007

Abstract

Quasi-elastic neutron scattering measurements have been performed in order to investigate ionic dynamics in molten CuI at 650 °C. The prominent elastic contribution was observed at around 0.85 $Å^{-1}$, where the partial structure factor of the Cu–Cu correlation has the first sharp diffraction peak. The analysis of the relaxation time in the intermediate scattering functions deduced from the quasi-elastic scattering spectra reveals that molten CuI exhibits extremely slow dynamics with the characteristic relaxation time over 1 ps in this *Q*-region, which is much longer than the self-diffusion of Cu ions.

Keywords: Dynamics; Cuprous iodide; CuI; Molten salt; Neutron

1. Introduction

CuI is well known to exhibit super-ionic behavior in the high temperature solid state where the mobile Cu ions migrate between the sites in the sublattice of immobile I ions [1]. As for the static structure factors of molten cuprous halides, several workers have reported interesting structural properties [2–6]. The most significant feature in the partial structure factors of molten CuCl [2,3] and CuBr [5] is that Cu–Cu pairs shows a structureless profile, which is different from the cation–cation correlations in molten alkali halides which show perfect charge transfer. As for the molten CuBr and CuI, Waseda et al. [6] deduced the partial structures from anomalous X-ray scattering measurements with aid of the Reverse Monte Carlo (RMC) simulation. Although they have not mentioned it, the partial pair correlation of Cu–Cu pairs for molten CuI deduced by them has more structure than that of molten CuCl.

Recently we have performed neutron and X-ray diffractions up to a high wave number region beyond 20 $Å^{-1}$ and deduced three partial structure factors of Cu–Cu, Cu–I and I–I correlations of molten CuI with the aid of RMC simulation [7]. That of Cu–Cu pairs has a broad peak around 2.70 Å, which means that like-ion Cu–Cu correlation penetrates into the first unlike-ion coordination shell. This characteristic penetration may be interpreted as a decrease in Coulomb repulsion force interacting between Cu ions arising from the reduced charge transfer between unlike ions and a possible indicator of partial covalent nature in Cu–Cu bond. The large density fluctuations of Cu ions make the first sharp diffraction peak (FSDP) at 0.85 $Å^{-1}$ in the Cu–Cu partial structure factor. When Cu ions are bonded with each other within the distance of 3.4 Å, one-dimensional streams appear in the structure model which can possibly be explained by cooperative motion of Cu–Cu pairs.

Several theoretical attempts have been reported to interpret such characteristic structural properties of molten copper halides. Recently, from *ab initio* molecular-dynamic simulations Shimojo et al. [8] concluded that there is some possibility of covalent character between Cu–Cu pairs in molten CuI.

The purpose of this research is to search the indication of such cooperative motions and the existence of covalently bonded Cu–Cu pairs from the dynamical point of view. Since Cu atoms have a coherent scattering cross section larger than I one (Cu 7.49 b, I 3.50 b), quasi-elastic neutron scattering measurements have been performed on molten CuI at 650 °C to see the Cu–Cu coherent dynamics.

* Corresponding author. Tel.: +81 92 726 4734; fax: +81 92 726 4734.
E-mail address: kawakita@rc.kyushu-u.ac.jp (Y. Kawakita).

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2007.01.179

2. Experimental procedure

Quasi-elastic neutron scattering (QENS) experiments of molten CuI were performed using a LAM-40 spectrometer [9] connected to the cold source at the spallation pulse neutron scattering facility, KENS, in High Energy Accelerator Research Organization, KEK, Tsukuba, Japan. The spectrometer was an inverted-geometry time-of-flight spectrometer consisting of seven sets of assemblies of pyrolytic graphite (PG) analyzer mirrors and detectors with the angle interval of 16°. By Bragg reflection with pyrolytic graphite (0 0 2 plane) mirrors after the scattering events the scattered neutrons with the energy of 4.59 meV were counted by the ^{3}He detectors as time series data from the spallation event. With the knowledge of the flight length, the arrival time of the scattered neutron gives information of the velocity and the energy of the incident neutron. Therefore the energy transfer from the neutron to the sample material could be analyzed. The analyzer- and detector assemblies were located on a movable table so that the accessible scattering angle ranged from 8° to 120°. Thus it was possible to measure dynamic structure factors in the range of wavenumbers from 0.2 to 2.6 Å^{-1} and energy transfers from −4 to 10 meV with the energy resolution of about 0.2 meV.

The sample was sealed in a thin-walled quartz glass tube with an inner diameter of 1 cm, a coaxial length of 10 cm and a wall thickness of 0.3 mm. The neutron beam was collimated by boron nitride and cadmium neutron-absorbers to irradiate samples of about 6 cm length. The sample cell, which was put into a thin niobium sample holder so as to reduce the temperature gradient, was located in a chamber filled with pure Ar-gas under a pressure of about 130 mbar. High temperature of 650 °C was achieved by using an inner radiation heater with a thin niobium foil as heater element.

To extract the dynamic structure factor, $S(Q, E)$, from the time-of-flight (TOF) spectra, the background contribution was carefully removed and the scattering contribution from the container material was subtracted with taking into account the absorption by the sample and the container. The counter efficiency was determined using the spectrum of a vanadium standard sample. The obtained spectra were symmetrized with respect to the energy transfer by multiplication of the detailed balance factors. Each spectrum was normalized to the incident intensity. Since the TOF spectrum under the measuring condition of constant scattering angle is not on the constant Q trajectory, we usually interpolate values on a Q–E lattice by using a surface spline technique. At present, this interpolation has not been carried out yet, therefore in this paper the $S(2\theta, E)$ spectra will be presented with the representative Q-values being referred to the energy transfer of zero ($E = 0$). The spectra include multiple scattering contributions from the sample geometry and the final neutron energy which are estimated by Sears' method [10] to be 15%. The spectra obtained by the forth detector were omitted because of contamination by white electrical noise.

3. Results

The obtained dynamic structure factors are shown in Fig. 1. The most prominent elastic peak is observed at around 0.85 Å^{-1}

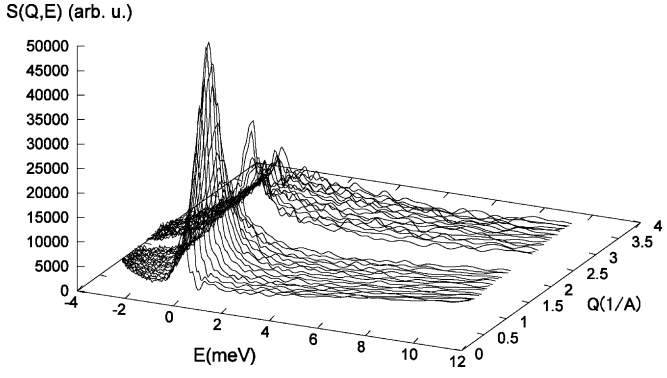

Fig. 1. Dynamic structure factors of molten CuI at 650 °C.

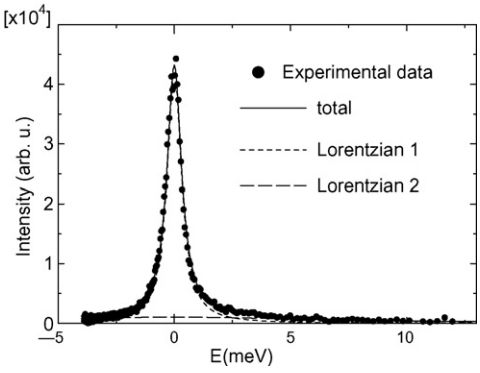

Fig. 2. Quasi-elastic neutron scattering spectrum of molten CuI at 0.795 Å^{-1} and 650 °C fitted with the sum of two Lorentzian functions. (●) Experimental data; short-dashed line, Lorentzian 1 (narrower); dashed line, Lorentzian 2 (broader); full line, sum of both Lorentzian functions.

where the partial structure factor of the Cu–Cu correlation has the first sharp diffraction peak [6,7]. Due to the lack of data from 1.4 to 2 Å^{-1} an exact assignment is not possible, but the spectrum at 2 Å^{-1} reflects the I–I correlation which has a sharp peak at 1.775 Å^{-1} in the static partial structure.

In order to investigate the shape of the QENS spectra, curve fittings with several typical functions such as Lorentzian and Gaussian have been tried. It was found that the spectra in the low Q-region below 1.4 Å^{-1} were well reproduced by the sum of two Lorentzian functions as shown in Fig. 2 for the typical spectrum near the FSDP.

The fitted curve was not convoluted by the energy resolution function which has an asymmetrical shape based on the pulse shape of the neutron source. Although the energy resolution functions under the elastic condition were determined by measuring the standard vanadium sample, those at non-zero energy transfers are unknown. Since the deforming of the pulse shape depends on flight time, the energy resolution function should depend on energy transfers. The convolution of the fitted curve by such an energy transfer-dependent resolution function or the de-coupling of the experimental quasi-elastic scattering data by the resolution function is a problem which has to be solved in near future. Nevertheless, it is plausible that the relatively steep shape of the resolution function of the spectrometer, which has no wide tails such as Lorentzian and Gaussian functions have, does not leave a large influence on the scattering intensity of liquid materials.

The narrow Lorentzian reproduces the overall shape of the QENS spectra whereas the broad Lorentzian serves to fit the tail region. The magnitudes of two Lorentzian functions are plotted in Fig. 3. That of the narrow function traces the total structure factor obtained by neutron diffraction, while that of the broad one exhibits an almost constant Q-dependence. The spike around 1.3 Å^{-1} is a residual background contribution from the heater element and thermal shields made of niobium. From the knowledge of the partial structure factors [6,7] and the diffusion constants of the ions ($D_{Cu} = 3.0 \times 10^{-4}$ cm^2/s, $D_I = 0.9 \times 10^{-4}$ cm^2/s, obtained by *ab initio* MD simulation [11]), the Cu–Cu correlation is found to be dominant in the narrow function. The broad function is neglected in the following

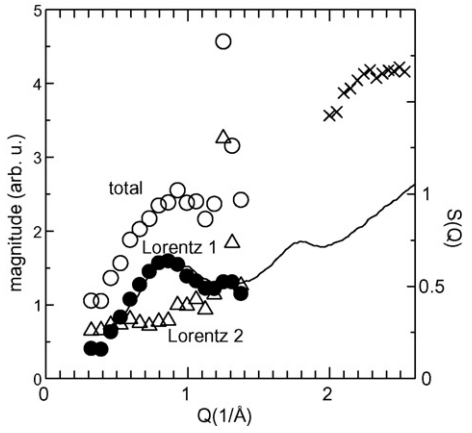

Fig. 3. The magnitude of the Lorentzian functions used below 1.4 Å^{-1} to fit the experimental quasi-elastic scattering spectrum. (●) Narrower Lorentzian, (△) broader Lorentzian, (◯) total magnitude. (×) Single Lorentzian used beyond 2 Å^{-1}. The full line denotes the total static structure factor obtained by neutron diffraction [7].

analysis since it is regarded as the multiple scattering contributions which should be much smeared and broadened than the single scattering law of $S(Q, E)$.

Beyond 2 Å^{-1}, the dynamic structure factor has a small center peak and a noisy background. Although these spectra seem to be too short for a discussion of the shape of the QENS, we have fitted them by single Lorentzians for reference. The magnitude is much higher than the static total structure factor which means the spectra include many error factors from the background and multiple scattering contributions. However the energy width of QENS in such a Q-region still gives us some information on the dynamics because the center peak is well distinguished and the background contribution must be much broader for the reason mentioned above.

The half width at the half maximum (HWHM) of the QENS spectra is plotted in Fig. 4 as function of Q. It is almost constant in the low Q-region below 0.8 Å^{-1}, however, it is still broader than the energy resolution of the instrument which is estimated as 0.2 meV from measurement of the vanadium standard sample. In the intermediate Q-region, the half width shows a peak around 1.3 Å^{-1}, where the total static structure exhibits the minimum between the FSDP from the Cu–Cu correlation and the first peak from the I–I correlation. Beyond 2 Å^{-1}, the width is around 3.5–4.0 meV.

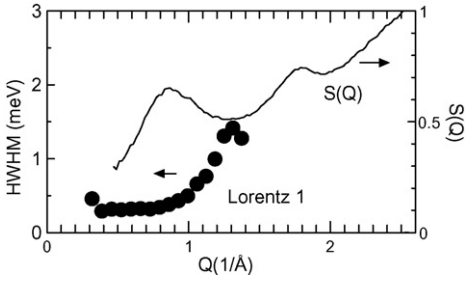

Fig. 4. Q-dependence of the half width at half maximum (HWHM) of the narrower Lorentzian in the curve fitting (denoted by ●). The total static structure factor obtained by neutron diffraction [7] is given by the full line.

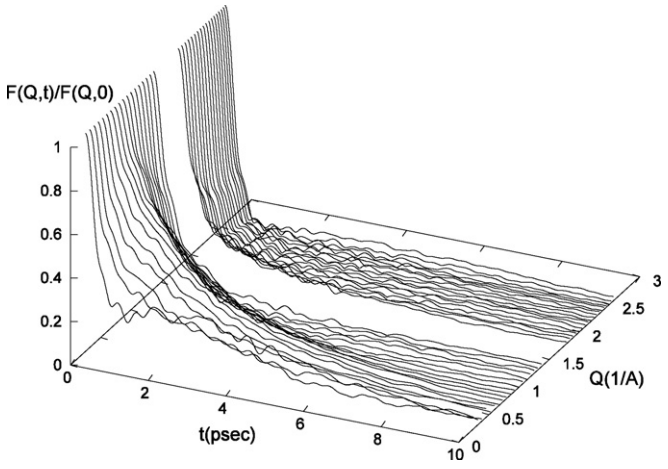

Fig. 5. Intermediate scattering functions of molten CuI as function of t and Q at 650 °C.

4. Discussion

For single particle dynamics which is obtained by incoherent quasi-elastic neutron scattering, the diffusion constant D is related to the energy width of QENS, Γ, as $\Gamma = \hbar DQ^2$. From the theoretical diffusion constant [11], the energy width of the incoherent QENS is estimated as 0.6 meV at 1 Å^{-1} and 3.7 meV at 2.5 Å^{-1} for I ions, and 2.0 meV at 1 Å^{-1} and 12 meV at 2.5 Å^{-1} for Cu ions. The coherent QENS is related to the mutual diffusion of atomic pairs. The Q-dependence of the energy width of the QENS reveals that in the low Q-region the mutual diffusion of Cu–Cu pairs is much slower than the self-diffusion of Cu ions. On the other hand, the energy width in the high Q-region beyond 2 Å^{-1} seems to match that of I ions.

The intermediate scattering function, which is deduced by Fourier transform of the QENS spectra from energy to time, is helpful to discuss on the structural relaxation as follows:

$$F(Q, t) = \int S(Q, E) \exp\left(\frac{iEt}{\hbar}\right) \mathrm{d}E. \quad (1)$$

$F(Q, t=0)$ is exactly the static total structure factor when the integration is extended over whole range of E. The $F(Q, t)$'s are normalized by $F(Q, t=0)$. They are shown in Fig. 5. The normalized intermediate scattering function, $\psi(Q, t)$, is related to the density auto-correlation as follows:

$$\psi(Q, t) = \frac{F(Q, t)}{F(Q, t=0)} = \frac{\langle \rho_Q(t)\rho_{-Q}(0)\rangle}{\langle |\rho_Q(t)|^2\rangle}, \quad (2)$$

which shows how the density–density correlation at a specific wavenumber Q relaxes in the real time space. In the Q-region where the FSDP of the Cu–Cu correlation locates, extremely slow dynamics is observed. The relaxation exhibits exponential decay in this Q-region, which corresponds to the Lorentzian shape of the QENS. The characteristic relaxation time is estimated as 1.606 ps at 0.86 Å^{-1}. Whether the origin of the slow dynamics is the short-lived bonding of Cu–Cu pairs with covalency as suggested by Shimojo et al. [8] or not is still open to discussion, because the estimated relaxation time is much longer than the life times of such a pseudo-bonding.

5. Summary

QENS measurements were performed on molten CuI at 650 °C. The prominent elastic contribution was observed at around 0.85 $Å^{-1}$, where the partial structure factor of the Cu–Cu correlation has the first sharp diffraction peak. The analysis of the relaxation time of the density–density correlation reveals that molten CuI exhibits extremely slow dynamics with the characteristic relaxation time of 1.606 ps at 0.86 $Å^{-1}$, which is much longer than the self-diffusion of Cu ions.

Acknowledgments

The authors are thankful to Professor F. Shimojo for helpful discussions. They also thank Professor S. Hosokawa for the encouragement of this study. QENS experiments were performed at KENS with approval of KEK (Proposal Nos. 2004-B2-197 and 2004-B1-004). This work was partly supported by a Grant-in-Aid for Creative Scientific Research (No. 16GS0417) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

[1] J.B. Boyce, et al., Phys. Rev. B 23 (1981) 2876.
[2] D.I. Page, K. Mika, J. Phys. C: Solid State Phys. 4 (1971) 3034–3044.
[3] S. Eisenberg, et al., Phil. Mag. A 46 (1982) l95.
[4] Y. Shirakawa, et al., J. Phys. Soc. Jpn. 60 (1991) 2678.
[5] D.A. Allen, R.A. Howe, J. Phys.: Condens. Matter 4 (1992) 6029–6038.
[6] Y. Waseda, et al., J. Phys.: Condens. Matter 12 (2000) A195.
[7] S. Takeda, H. Fujii, Y. Kawakita, Y. Kato, S. Kohara, K. Maruyama, Physica B 385–386 (2006) 249–251.
[8] F. Shimojo, et al., J. Phys. Jpn. 73 (2004) 2148.
[9] K. Inoue, K. Kanaya, Y. Kiyanagi, K. Shibata, K. Kaji, S. Ikeda, H. Iwasa, Y. Izumi, Nucl. Instrum. Methods A 327 (1993) 433.
[10] V.F. Sears, Adv. Phys. 24 (1975) 1.
[11] F. Shimojo, private communication.