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Citation	JPS Conference Proceedings,33,p.011071_1-011071_6
Text Version	Published Journal Article
URL	https://jopss.jaea.go.jp/search/servlet/search?5067097
DOI	https://doi.org/10.7566/JPSCP.33.011071
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Proc. 3rd J-PARC Symposium (J-PARC2019)
JPS Conf. Proc. **33**, 011071 (2021)
https://doi.org/10.7566/JPSCP.33.011071

Mode Distribution Analysis for Superionic Melt of CuI by Coherent Quasielastic Neutron Scattering

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(Received January 14, 2020)

Mode distribution analysis was performed for coherent quasielastic neutron scattering data for molten CuI. Three relaxation modes were distinguished, (1) a slow relaxation mode that locates spot-like around the structural maxima in the I-I partial structure factor, (2) an intermediate relaxation mode that shows the de Gennes narrowing at the structural maximum in the Cu-Cu partial structure factor, and (3) a fast relaxation mode that does not show Q dependence of relaxation time. These features can be interpreted consistently from a structural model of molten CuI proposed in earlier work where cuprous ions exhibit inhomogeneous distribution and form a chain-like fragment while iodine ions are more uniformly distributed.

KEYWORDS: QENS, CuI, superionic, dynamics, neutron, liquid

1. Introduction

CuI is a well-known superionic conductor in a high-temperature solid-phase where the mobile cations migrate between interstitial sites in the face-centered-cubic (f.c.c.) sublattice formed by immobile iodine ions [1]. At room temperature, CuI is in γ-phase with a zinc blende structure where iodine and copper sublattices also show an f.c.c. shifting (1/4, 1/4, 1/4) with each other. The superionic α-phase is a partial melting phenomenon of copper sublattice since iodine sublattice have the same structure between γ- and α-phases. In between, a β-phase with a wurtzite structure appears in a temperature region from 369 to 407 ºC [2]. It is closely related to the zinc blende structure such as that between the f.c.c. and h.c.p. although the atomic layer is doubled with an alternative arrangement of Cu and I. The local atomic arrangements in the γ- and β-phases are based on a tetrahedral structure. Such a tetrahedral local structure is preserved in α-phase to some extent because mobile cations exhibit a higher occupation probability in a tetrahedral site than an octahedral site [3]. Focusing on the mobile ions in the superionic matters involving mobile noble-metal ions, Yokota proposed the caterpillar mechanism from the deviation of ionic conductivity from the Einstein relation where one jump of an ion in the diffusion process, induced jumps of several adjacent ions [4]. Such a property of cooperative motion is detected by cation-cation

partial pair correlation from the diffuse scattering analysis of AgI [5].

Even in the molten state, it shows several features suggesting the collective or cooperative motion of cations. For example, cations show a much faster diffusion than anions as empirical and ab-initio molecular dynamics simulations revealed [6,7,8], the static structure factors have a first sharp diffraction peak. This is contributed by the cation-cation correlation indicating that the distribution of cations has a medium-range structure [9]. The cation-cation partial pair correlation function (ppcf) deeply penetrates the first neighboring shell forming the cation-anion ppcf [10].

Our previous study on the reversed Monte Carlo (RMC) structural modeling of molten CuI based on experimental diffraction data revealed that cation distribution extracted from the RMC structural model exhibits the existence of chain-like fragments consisting of around ten cations. These cations connect with an atomic distance within the first neighboring shell. This strongly suggests that the collective or cooperative motion of cations exists even in the liquid state [10,11].

To study the ion dynamics in molten CuI, quasielastic neutron scattering (QENS) measurements were conducted by the cold neutron disk chopper spectrometer AMATERAS at the Materials and Life Science Experimental Facility (MLF), Japan Proton Accelerator Research Complex (J-PARC). Since CuI is an almost coherent scatterer for neutrons, QENS involves information on dynamic pair correlation. In this paper, we will report the analysis of the shape of the QENS spectra with the association of the partial pair correlation functions.

2. Experiment and Analysis Procedures

2.1 QENS experiment

The QENS experiments of molten CuI were performed with the time-of-flight technique using the cold neutron disk chopper spectrometer AMATERAS installed at MLF, J-PARC, Tokai, Japan [12]. The scattering horizontal angles of 4.7° ~ 111.7° and vertical angles of −16° ~ 22° were covered. To access dynamics in different time scales easily, the multi-E_i technique [13] was applied. Since the monochromating chopper, operating at 150 Hz, was six times faster than the neutron pulse emerging at 25Hz, the band chopper at 25 Hz yielded incident energies (E_i's) of 94.2, 23.6, 10.5, and 5.9 meV

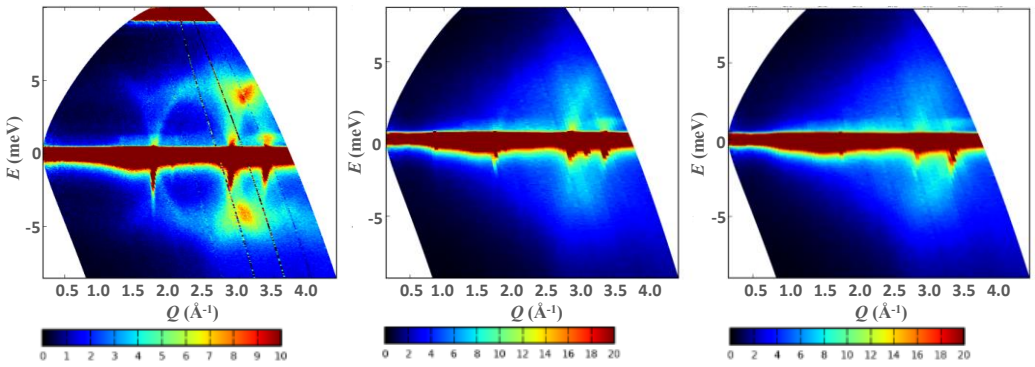

Fig. 1. Intensity map $I_{S+C}(Q,E)$ of quasielastic neutron scattering of cuprous iodide (powder sample) contained in a silica cell with E_i = 10.5 meV. The left: γ-phase at 270ºC, the middle: β-phase at 380ºC, the right: α-phase at 470ºC

simultaneously with energy resolutions of 8.4, 1.1, 0.4, and 0.15 meV for elastic scattering, respectively.

The bulk sample was sealed in a cylindrical silica cell with an inner diameter of 5.8 mm and a wall thickness of 0.5 mm. The measurements were conducted at 25 and 270 ºC for the γ-phase, 380 ºC for the β-phase, and 470 ºC for α-phase, 620, 670, and 720 ºC for the liquid phase by using an ILL 1800C furnace with Nb foil heater element. An oscillating radial collimator was used to eliminate unfavorable scattering contributions from the heater element, the radiation shields made from Nb foil and the Al outer-case of the furnace [14]. The Q-E maps of the scattering intensity were calculated by the software suite Utsusemi [15] from the scattering event data of the time-of-flight.

Figure 1 shows the scattering intensity of the crystalline (powder) CuI contained in the silica cell at several temperatures with E_i = 10.5 meV. In the γ-phase, several phonon branches are observed. In the β-phase, ionic conductivity is already high and in the order of 10^{-1} Ω^{-1} cm^{-1} [16]. A QENS-like component broadens in the energy-transfer axis and is superimposed to the phonon excitations. In the α-phase, phonon excitations are almost smeared out and only the QENS contribution remains.

To deduce quantitative dynamical structure factors of liquid CuI, we applied conventional corrections such as subtracting the scattering contributions from the instrument background with the setup of the furnace and the cell and absorption corrections of the cell and sample. Fig. 2 shows the obtained dynamical structure factors, $S(Q,E)$.

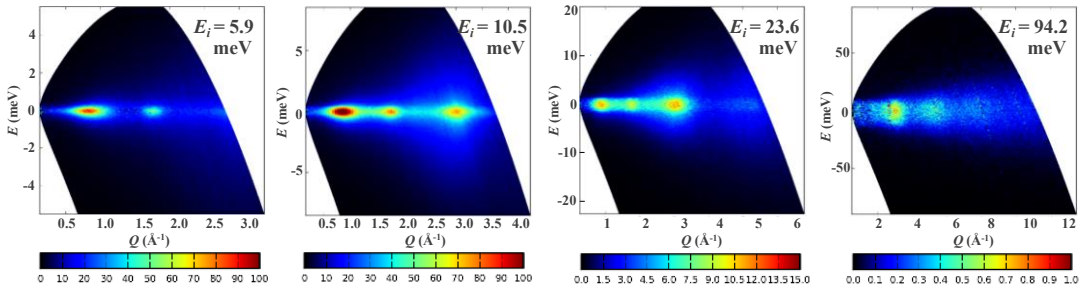

Fig. 2. Dynamic structure factors of molten CuI at 620ºC obtained by multi-E_i technique at AMATERAS (BL14) in MLF, J-PARC.

2.2 Mode distribution analysis

For the QENS spectra of liquid CuI, we performed the mode distribution analysis (MDA) developed by one of the co-authors (T. K.) [17], which is a model-free analysis. In this method, an observed $S(Q,\omega)$ is described as a superposition of elemental dynamical modes that are represented by a Lorentzian function as:

$$S(Q,\omega) = \left(A(Q)\delta(\omega) + \int B(Q,\Gamma)\frac{1}{\pi}\left[\frac{\Gamma}{\omega^2+\Gamma^2}\right]d\Gamma \right) \otimes R(Q,\omega) \quad (1)$$

where $E = \hbar\omega$, $\delta(\omega)$ is an elastic component whose magnitude $A(Q)$ should be zero at this measurement, $B(Q, \Gamma)$ is a mode distribution function, which means a magnitude of the elemental Lorentzian function with the energy width of Γ, and $R(Q, \omega)$ is an

instrument resolution function. Assuming the elemental mode could be written as a Lorentzian function is reasonable for incoherent scattering because the fact that self-diffusion must show the same relaxation (time evolution) from any time gives an exponential decay in time and, therefore, a Lorentzian shape in energy. From Eq. (1), when we know $B(Q, \Gamma)$, we can calculate $S(Q,\omega)$ and compare it to the experimentally obtained $S(Q,\omega)$. To reduce $B(Q, \Gamma)$ from the experimental $S(Q,\omega)$ is a type of inverse problem that can be solved by the regularization method. The maximum entropy method is one of the regularization methods to reduce $B(Q, \Gamma)$ and not to make finer signals than instrument resolution. In this procedure, a unique $B(Q, \Gamma)$ that reproduces all the experimental data with different energy resolution by the multi-E_i method can be obtained.

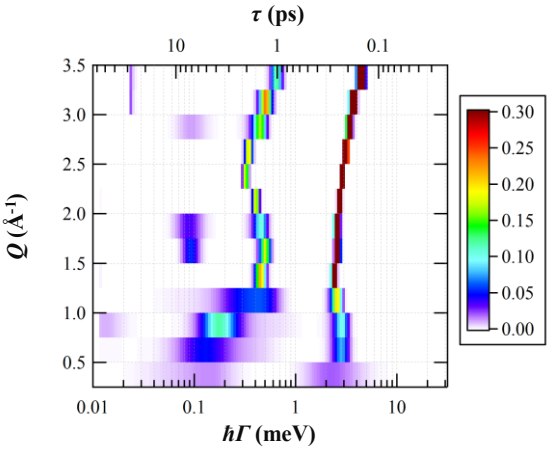

Fig. 3. Mode distribution of molten CuI at 620ºC

In the case of coherent scattering, memory loss owing to collision causes faster decay than the exponential and, therefore, the shape of QENS on the energy axis usually falls intermediate between Lorentzian and Gaussian shapes, highly depending on the system. We cannot give any evidence that the elemental dynamic mode in molten CuI can be reasonably described as Lorentzian. However, when we can reduce a simple $B(Q, \Gamma)$, the assumption might not be so far from reality. The obtained $B(Q, \Gamma)$ of molten CuI is shown in Fig. 3.

3. Results and Discussion

We observed three types of dynamic modes. One is a slow mode showing a strong twin-peaks structure located at 7 ps at around 1.75 and 2.9 Å^{-1}. Next is an intermediate mode showing an undulation from 4 ps at Q = 0.7 Å^{-1} to 1 ps at Q = 3.5 Å^{-1}. Last is a fast mode that is located in the sub-picosecond region and does not show Q dependence so much.

To understand these dynamical modes, it is noteworthy to see partial structures, $S_{ij}(Q)$ shown in Fig. 4. Experimental data of X-ray and neutron diffractions were analyzed using the RMC simulation in earlier work [10, 11]. The slow mode is located at the prominent first peak and a second peak in the I-I partial structure factor, $S_{\text{I-I}}(Q)$, suggesting that the slow mode is related to iodine dynamics. The discrete two peaks of the slow mode look like diffuse scattering at around Bragg peaks in the solid crystalline phase. This is far from a liquid property since the diffusive property in a liquid usually causes a successive contribution on the Q-axis. Iodine could show diffusive oscillation in a limited space when the arrangement survives for a while like a lattice in a solid.

On the other hand, the intermediate mode successively distributed with the undulation, as shown in Fig. 3, looks like a liquid property. A slowing down appears at Q = 2.5 Å^{-1}, where $S_{\text{Cu-Cu}}(Q)$ shows a maximum, as shown by a full line in Fig. 4. For

coherent QENS of liquid matter, we can frequently observe this kind of slowing down at a structure factor maximum, namely the de Gennes narrowing [18], which is interpreted to mean that stronger correlation survives for a longer time. Notably, the partial dynamics of cuprous ions in molten CuI exhibits de Gennes narrowing. Even at the pre-peak of the Cu-Cu partial at around Q = 0.7 Å^{-1}, a small deviation from the linear relation could be seen in Fig. 3. This is the first example where the partial dynamics shows de Gennes narrowing.

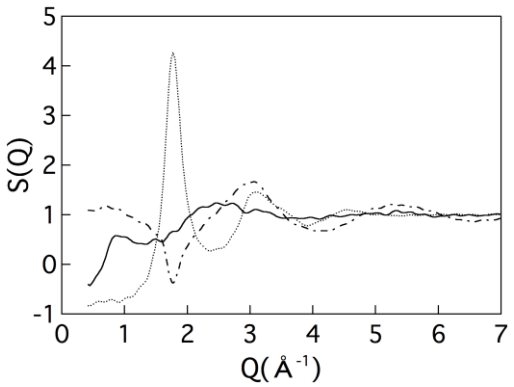

Fig. 4. Partial structure factors, $S_{ij}(Q)$, of molten CuI at 620 ºC [10,11]. Cu-Cu, I-I, and Cu-I partials are depicted by a full line, a dotted line, and chain line, respectively

The fast mode does not show any Q dependence, especially in a low Q region below 2.0 Å^{-1}, which looks like a property of local rattling motion in a confined space. This motion exhibits one-order faster dynamics than the Cu diffusive motion. This could be interpreted as a fast rattling motion of a cuprous ion in a cage surrounded by slow iodine ions.

The obtained pictures of ion dynamics in molten CuI from MDA analysis and the physical interpretation with the aid of partial structures are consistent with our insight obtained from the previous static structure analysis [10, 11]. As shown schematically in Fig. 5, after a cuprous ion (C1) jumps to an adjacent vacant site, the surrounding iodine ions (I1, I2, and I3) are structurally relaxed as per the new charge balance, which could make the central vacant expand slightly due to the repulsion force among iodine ions with a missing central cuprous ion. Such a relaxation of the iodine ions could be slow because it must extend to a further region (for example, it could induce I4, I5, and I6 motions) due to the expansion. The expanded vacant site, however, easily becomes a target for another cuprous ion (C2) to jump in. Such a jumping-in process of the cuprous ion could induce the surrounding iodine ions approaching the cuprous ion again. In this picture, iodine ions behave like a slow breathing oscillator and the cuprous ions make a stream along the preserved pathway. This difference in motion between cuprous and iodine ions results in extremely different mode distributions between the slow mode (the iodine breathing motion like a lattice vibration) and the intermediate mode (the diffusive and cooperative motion of cuprous ions). In this sense, ions in molten CuI almost

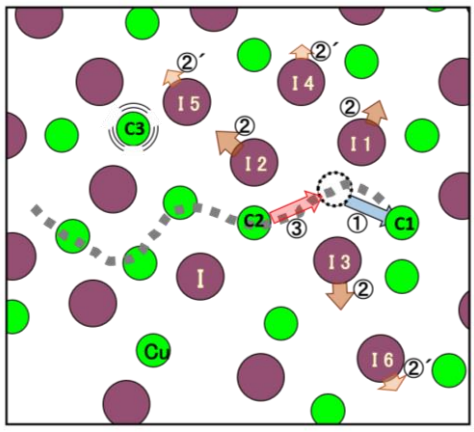

Fig. 5. Schematic motions of cuprous ions (small circles) and iodine ions (large circles) in molten CuI. The circled numbers show successive motions induced by a jump motion of the cuprous ion denoted as C1. The ion C3 shows a fast rattling motion.

behave like a superionic conductor.

4. Summary

This study investigated the ion dynamics in molten CuI using the QENS analysis. MDA revealed that three types of dynamic modes exist in this liquid. One is the slow relaxation mode relating to the iodine breathing motion. Next is the intermediate relaxation mode relating to the cuprous diffusive motion, and last is the fast relaxation mode relating to the fast rattling motion of a cuprous ion in a cage surrounding slow iodine ions. Notably, superionic behavior exists even in the molten state.

Acknowledgment

QENS experiments were conducted in the framework of “Project Research on structure and dynamics in proton, superionic and amorphous materials” approved by J-PARC (the proposal number, 2012P0906).

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