Acoustic Phonons in Molten NaI

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Received January 16, 2009; Accepted June 18, 2009

In order to investigate the phonon dynamics of molten NaI, inelastic X-ray scattering measurements were performed near the melting point at the beamline BL35XU of the SPring-8. A fast sound mode exceeding the ultrasonic velocity of sound by about 45% was observed as in other molten alkali halides, which is in fairly good agreement with a scaling formula using the effective mass of the salt constituents.

Key Words: Alkali Halides, Inelastic X-ray Scattering, Phonons, Dispersion Relation

1 Introduction

Molten salts are applied in many technologically relevant areas. Traditionally they are used in many electrochemical processes as, e.g., in high temperature fuel cells. Nowadays, further applications, such as fuel and coolant in next generation reactors, fission product recycling, or storage medium for solar power plants, etc., are emerging due to their interesting thermophysical properties as, e.g., large range of the liquid state, high specific heat, low vapor pressure, and high critical points. All these applications require thermodynamic parameters, like specific heat, thermal conductivity, viscosity, etc. Thus, it is important to investigate the microscopic origin of these thermodynamic quantities.

About thirty years ago, Hansen and McDonald carried out a pioneering molecular dynamics (MD) simulation on liquid alkali halides. The simulation revealed the existence of propagating short wavelength charge fluctuations (optic phonons) as in the solid state. Further simulations using more advanced potentials and including mass effects and ion polarization asserted this prediction. The computer studies motivated neutron scattering groups to investigate the ion dynamics experimentally. However, the experiments were subject to a serious kinematic constraint of the energy-momentum relation of neutrons. Hence, the available experimental data have been taken at the momentum transfer (Q) values beyond 10 nm⁻¹. We used inelastic X-ray scattering (IXS) which has no kinematic limitations.

In general, the measured scattering intensity of a two-component liquid can be written as a combination of three partial structure factors. An appropriate choice for the partial structure factors in ionic liquids may be based on density and charge fluctuations. In this notation, the measured scattering intensity, I(Q,ω), is expressed as

\[(f_+ f_-)^2 S_{NN}(Q,\omega) + (f_+ f_-) S_{NO}(Q,\omega) + (f_+ f_-) S_{QQ}(Q,\omega)\]

(1)

Here, f is the atomic form factor, S_{NN}(Q,\omega) describes the particle density fluctuations (acoustic modes) and S_{QQ}(Q,\omega) is determined by charge fluctuations (optic modes). S_{NO}(Q,\omega) is the cross term.

Results for the optic modes in molten NaI were already reported. In this paper, we present results of the longitudinal acoustic modes in molten NaI, and discuss the fast sound by comparing to those of other molten alkali halides.

2 Experimental

The IXS experiments were carried out by using the high energy resolution IXS spectrometer installed at the beamline BL35XU of the SPring-8. A highly resolved monochromatized X-ray beam of \(4 \times 10^9\) photons s⁻¹ emitted from an undulator insertion device, was achieved from a cryogenically cooled Si(1 1 1) double crystal followed by a Si(11 11 11) monochromator operating in an extreme backscattering geometry (about 89.98° and 21.75 keV). The same backscattering geometry was used for the energy analysis of the scattered X-rays photons with four spherically curved Si analyzers, which were located on a 10 m goniometer arm. The scattered photons were collected with CdZnTe detectors near the sample position. The overall energy resolution of the spectrometer was determined from the scattering of a Plexiglas sample, and values of 1.5-1.8 meV full-width at half-maximum were obtained. The Q resolution was set to be ±0.5 nm⁻¹. Details of the IXS spectrometer are given elsewhere.

The NaI sample was contained in a thin-walled (0.25
mm) single-crystal sapphire cell. The high X-ray absorption of molten NaI was handled by reducing the sample thickness to 0.25 mm, roughly corresponding to an 1/e absorber. The cell was placed in a vessel equipped with single-crystal Si thin windows capable of covering the scattering angles between 0° and 25°. It was applied with 1.5 bar of high purity grade He gas. The temperature of 680 °C was achieved by using a Mo resistant heater, and monitored with two W-5% Re/W-26% Re thermocouples.

3 Results and Discussion
Figure 1 shows logarithmic plots of selected \( S(Q,\omega) \) spectra for molten NaI at 680 °C normalized to \( S(Q) \). Longitudinal acoustic phonon modes are clearly observed at both the sides of the quasielastic peak as indicated by bars. The signals at larger \( \omega \) values originate from the background of the phonon modes of the sapphire cell. The excitation energy of the longitudinal acoustic modes in liquid NaI changes with increasing \( Q \).

Since the widths of the longitudinal acoustic mode are in the same range as the energy resolution, a model analysis is necessary to obtain the excitation energy, \( \omega_0 \), and its width, \( \Gamma_\omega \). For this, we used a Lorentzian for the quasielastic peak and a damped harmonic oscillator (DHO) model for the inelastic excitations. The model function was convoluted with the experimental resolution function, and fitted to the data. The solid curves represent the results of the fits, and the agreements with the experimental data are very good.

The circles in Fig. 2 show the fitted results of \( \omega_0 \). The dashed line indicates the dispersion predicted by macroscopic hydrodynamics, and its slope represents the adiabatic velocity of sound, 1150 m/s. As clearly seen in the figure, the \( \omega_0 \) values largely exceed the hydrodynamic value. The triangles in Fig. 2 show the fitted results of \( \Gamma_\omega \). It is interesting to note that two ranges are seen where the widths of the modes vary in different characteristic ways. There is a strong increase up to about 7 nm\(^{-1}\). Beyond this value, however, the lines broaden considerably slower with \( Q \) indicating a weaker lifetime dependence of the collective excitations.

Figure 3 shows the dynamical velocity of sound, \( \omega_0/Q \). It increases rapidly with \( Q \) in the low \( Q \), range up to about 5 nm\(^{-1}\), and shows the so-called positive dispersion of about 45%, which is similar to those in other molten alkali halides or molecular liquids, but much larger than those in simple liquid metals.

Demmel et al. discussed the dispersion results of...
moltan NaCl and found that the fast sound observed in this moltan NaCl is similar to the dispersion relation of pure liquid Na. From this, it was suggested that the phonon dynamics in this moltan binary system is governed by that of the lighter atom; Na atom in the case of moltan NaCl. Since the velocity of the fast sound in liquid Na is about 3000 m/s. This speculation does not explain the fast sound in the present moltan NaI 1650 m/s.

Inui et al.\textsuperscript{15} proposed an alternative model to explain the fast sound in moltan CsCl by taking the mass of the constituent atoms into account. When the velocity is in inverse proportion to the square-root of particle mass, the ratio of the sound velocity may follow the equation given by

\[ \frac{c_{\text{salt}}}{c_{\text{metal}}} = \sqrt{\frac{M_j}{2m_j}}, \]

where \( c_{\text{salt}} \), \( c_{\text{metal}} \), \( M_j \), and \( 2m_j \) denote the sound velocities of a moltan salt and a liquid metal, the cation mass, and the effective mass, respectively.\textsuperscript{21} Table 1 shows the parameters for moltan NaCl, NaI, and CsCl. The scaling factor deduced by Eq. (2), 0.77, for moltan NaI is relative-ly good agreement with the experimentally obtained ratio of the fast sound velocity, 0.55.

The physical picture behind Eq. (2) is that quasi-particles with effective mass move collectively in the moltan salts as if they were atoms in the corresponding liquid metal. A cooperative motion of the cations and anions is inferred from this picture. We may not need to assume a plasmon-type mode of the cations on a uniform anion background to explain the fast dispersion in moltan NaCl\textsuperscript{6} and KCl\textsuperscript{7}.

### 4 Conclusion

In order to investigate the phonon dynamics of moltan NaI, IXS measurements were preformed near the melting point at BL35XU/SPring-8. A fast sound exceeding the ultrasonic velocity of sound by about 45% was observed as in other moltan alkali halides, which is in fairly good agreement with a scaling formula using the effective mass of the salt constituents.

### Acknowledgement

The IXS experiment was performed at the beamline BL35XU in the SPring-8 with the approval of Japan Synchrotron Radiation Institute (JASRI) (Proposal No. 2002B0179).

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