Propagating particle density fluctuations in molten NaCl

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In this paper we present the observation of acoustic modes in the spectra of molten NaCl measured over a large momentum transfer range using synchrotron radiation. A surprisingly large positive dispersion was deduced with a mode velocity exceeding the adiabatic value by nearly 70%. The large effect seems to be describable as a viscoelastic reaction of the liquid. Additionally, the derived dispersion resembles the Q-ω relation of the acoustic modes in liquid sodium. As an explanation for the large positive dispersion we propose that the density fluctuations in molten NaCl can be interpreted as a decoupled motion of the lighter and smaller cations on a nearly resting anionic background. These molten alkali halide measurements are the first experimental evidences for the so-called fast sound in a binary ionic liquid.

After a lot of experimental and theoretical studies in the field of collective dynamics of liquids a common understanding of some effects seems to emerge. A variety of inelastic-scattering experiments have been carried out on so-called simple liquids, as e.g., liquid (l-) alkali metals[1-4] or l-noble gases,[5] but also on more complex systems like liquid ammonia or o-therphenyl and in particular on water.[6] Despite the diverse nature of these liquids, the measured data revealed as one common feature a positive dispersion in the Q-ω relation of the collective modes, i.e., in the lower Q range, the frequencies of the short wavelength excitations increase faster with rising momentum transfer than expected from the adiabatic speed of sound. This finding was interpreted as a viscoelastic response of the liquid to high-frequency perturbations.[7,8] In l-alkali metals the excitations are clearly separated from the quasielastic line and the positive dispersion is found to be about 20%. In more complex substances, in particular water, shoulderlike excitations are observed in the spectra and the ratio of the high-frequency mode velocity to the adiabatic speed of sound reaches a factor of more than two.[9]

Less is known about the dynamics of binary liquids. Stimulated by molecular dynamics (MD) simulations a prediction has been made that in binary liquids a "fast sound" mode can exist.[10] The interpretation of this mode suggests a decoupled movement of the lighter subsystem on the heavier background at high frequencies. Neutron-scattering experiments on the simulated Li_4Pb liquid could not verify the appearance of this mode in a convincing manner.[11,12] On the other side measurements on noble gas mixtures have been interpreted in this view.[13] Particular binary liquids are the molten salts and as prototypes of them the molten alkali halides. From the viewpoint of complexity binary ionic liquids are between alkali metals and molecular liquids and much theoretical effort has been spent in this field.[14] Molten salts were first investigated by molecular dynamics simulations over 25 years ago by Hansen and McDonald.[15] Besides the prediction of collective opticlike modes no indications for acousticlike excitations could be found in the spectra. Later MD simulations took into account the different masses, but could also not reveal any sign of acousticlike modes in

the spectra.[16,17] With inclusion of polarization effects, as was shown for molten NaI, indications for propagating density fluctuations were found as shoulders at the smallest attainable Q vectors.[18] This result was interpreted as the "liquid state analogue of the longitudinal acoustic phonon in the melt."

The computer based studies motivated neutron-scattering groups to investigate the ion dynamics in molten salts (for a review see Ref. 19). However, all the experiments were subject to one serious constraint, the energy-momentum relation of the neutron, which restricts the allowed regions of momentum and energy transfer. Hence most of the available experimental data have been taken at momentum transfers beyond 10 nm^{-1}.[19,20] No direct evidence of acousticlike modes could be observed in the spectra due to a too short lifetime of the modes and/or interference with optic-type modes. To avoid the difficulties associated with neutrons we decided to use high resolution inelastic x-ray scattering (IXS) for our experiments. IXS has no kinematic restrictions hence it allows to measure large energy transfers of the scattered photons even at low-Q values. In molten salts the predicted optic and acoustic modes are well separated in the low-Q range. For measurements of the microscopic dynamics in a molten salt this method has not yet been used, which might be associated to the technical challenges with the design of appropriate sample environments. The main problem is to keep the molten salt in a closed container which endures the required high temperatures and resists the corrosive nature of the sample. Here we report the direct observation of acoustic modes in the dynamic scattering law $S(Q,\omega)$ of a molten salt. The measured results can be interpreted as the first experimental evidences for the celebrate fast sound phenomenon in a molten alkali halide.

The experiment was carried out at the inelastic beamline ID28 of the European Synchrotron Radiation facility ESRF in Grenoble. X-rays were monochromatized to 17.794 keV using the combination of a cryogenically cooled Si(111) pre-monochromator and a main monochromator in extreme backscattering geometry [Si(999), $\theta=89.975°$]. The energy resolution of the spectrometer was determined from the scattering of a Plexiglas sample to 3.2 meV (full width at half-
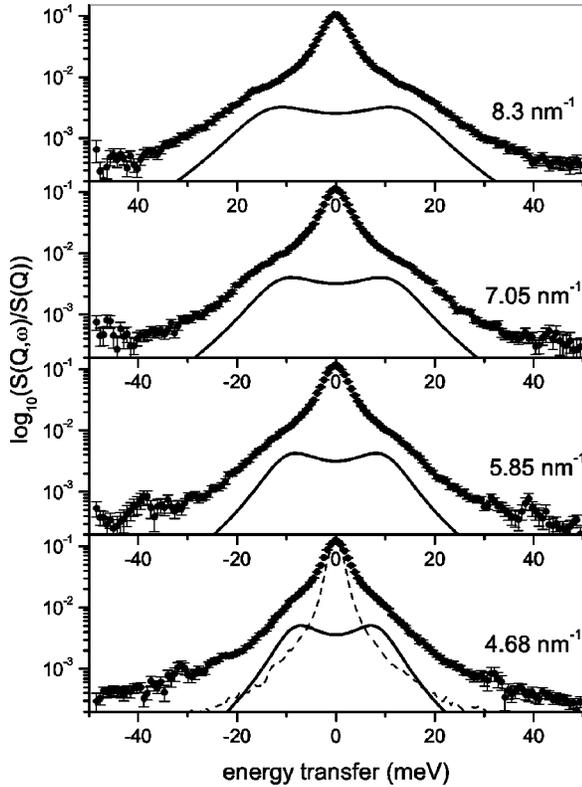
FIG. 1. $S(Q,\omega)$ spectra normalized to $S(Q)$ are shown in a logarithmic scale. Experimental data are given by dots with error bars, solid lines represent fits of the DHO model convoluted with the resolution function. The resolution function is shown as a dashed line.

FIG. 2. The fit results from the DHO fit of the spectra are shown (squares) and the peak positions from the fit of the current functions (triangles). Furthermore the widths Γ of the DHO fits are plotted in the same scale. Results from MD simulations are depicted as circles and the adiabatic sound velocity of molten NaCl as a line.

maxima). Four analyzers were used simultaneously. The l-NaCl sample was contained in a single crystal sapphire cell with a wall thickness of 0.25 mm. The sample thickness was adjusted to about 1 mm, corresponding to the optimum ratio of absorption to transmission for the used x-ray energy. The sample environment consisted of an internally heated vessel equipped with Be windows which cover a scattering angle range up to 25°. High temperatures were generated with a tungsten resistance heater.[21] Empty cell measurements were carried out separately using the same cell at the same temperature (1170 K). $S(Q,\omega)$ was measured at 1170 K (melting temperature of NaCl= 1070 K) for 20 different Q values between 2 nm^{-1} and 29 nm^{-1}. In the interesting low-momentum transfer region up to ten scans were performed to obtain data with high statistical quality.

The empty cell contribution was subtracted from the data using an appropriate absorption factor, which was calculated from the sample thickness and which agrees well with the measured transmission of the sample. Data were normalized to the integrated intensity and a detailed balance correction was carried out. As an example, four spectra are shown in Fig. 1 on a base 10 logarithmic scale. The acousticlike collective excitations are visible as shoulders. At larger energy transfer some statistical noise remains, in particular, in the spectra at $Q=4.68$ nm^{-1} and $Q=5.85$ nm^{-1} resulting from the sapphire phonons subtraction of the container. However, due to the high sound velocity in sapphire ($c=11\,000$ m/s)

these modes lie far outside the interesting energy range and do not influence the reported results. To extract the properties of the collective excitations the data were fitted to a model function. We chose a Lorentzian for the quasielastic line and a damped harmonic oscillator (DHO) model for the inelastic excitations

$$I(Q,\omega)=\frac{A_0}{\pi}\frac{\Gamma_0}{\omega^2+\Gamma_0^2}+\frac{A}{\pi}\frac{4\Omega\Gamma}{(\omega^2-\omega_p^2)^2+4\Gamma^2\omega^2}, \quad (1)$$

A_0 and Γ_0 are amplitude and half-width (half-width at half maxima) of the central line and A, Γ, and ω_p are amplitude, width, and frequency of the inelastic excitation. Ω is related with ω_p by $\Omega=\sqrt{\omega_p^2-\Gamma^2}$. The fitting procedure also included a convolution with the spectrometer resolution function which was represented by a Voigt function. For the fit the Matlab based program package "MFIT" was used (ILL, Grenoble). The fitted DHO functions convoluted with the resolution are included in Fig. 1. Clearly visible is the dispersing character of the inelastic excitations. Furthermore current spectra $j(Q,\omega)=\omega^2 I(Q,\omega)$ were calculated and the inelastic peak positions were determined. The results of both fit procedures are shown in Fig. 2. The error bars represent three standard deviations of the respective fit error. Also shown are the widths of the inelastic excitations Γ. The widths are at least two to three times smaller than the excitation frequencies. This fact can be interpreted that propagating modes exist up to about 9 nm^{-1}. At larger momentum transfer values the modes are overdampped and are probably overlaped by optic modes. For comparison the peak positions from the current correlation functions are included. These values are naturally shifted to slightly larger energy values compared to the corresponding $S(Q,\omega)$ data. Also given in the figure are peak positions from current spectra of two MD simulations.[16,17] The agreement between our experimental data and the simulation results is surprisingly excellent, al-

though no acousticlike excitations could be found directly in the $S(Q,\omega)$ spectra of the MD simulations. The slope of the line in Fig. 2 is given by the adiabatic sound velocity of l-NaCl [c_{ad}(NaCl) = 1750 m/s] and represents the expected hydrodynamic dispersion of sound modes.[22] The peak positions of the measured inelastic excitations lie clearly above this line. For l-NaCl our data indicate a positive dispersion of up to 70% compared to the adiabatic value.

The large value for the positive dispersion and the damping of the modes seem to fit quite reasonably between the above mentioned results for the alkali metals with distinct inelastic modes and water with damped shoulderlike modes and larger positive dispersion. For these liquids the upward bending of the dispersion was explained within the framework of generalized hydrodynamics. In this theoretical approach a transition from low-frequency dynamics with viscous relaxation of the liquid to a high-frequency elastic response describes the positive dispersion. To test whether the particle dynamics in l-NaCl can be understood within this view we have calculated the upper limit for the high-frequency sound velocity $c_\infty(Q)$, which is related to the normalized fourth frequency moment.[7] In Ref. 16 a formula for the fourth frequency moment of a binary ionic liquid is given. We expanded this formula to the $Q \to 0$ limit and then we got the following expression, which is quite similar to the one for monoatomic liquids:[7]

$$c_\infty(Q \to 0) = \left(\frac{\sqrt{m_{Na}^* m_{Cl}}}{m_{Na} + m_{Cl}} \frac{3 k_B T}{\mu} + \frac{3}{10} \omega_E^2 \sigma^2 \right)^{1/2}, \quad (2)$$

where μ is the reduced mass, k_B is the Boltzmann constant, and T is the temperature. The hard sphere parameter σ was approximated by the mean nearest-neighbor distance between the ions in molten NaCl $\sigma = 0.28$ nm.[22] For the Einstein frequency ω_E we used the results of an instantaneous normal mode analysis for l-NaCl.[23] The maximum of the derived frequency distribution is a reliable estimate for the Einstein frequency, as it was shown, e.g., for liquid Cs.[24] As an approximation we took the mean value of the two ions $\omega_E = 90 \pm 15$ cm$^{-1} = 17 \pm 3 \times 10^{12}$ s^{-1}. Using these values Eq. (2) gives a high-frequency mode velocity of $c_\infty = 2720$ m/s, surprisingly near to our findings despite all the approximations (see Fig. 3). Hence the observed positive dispersion in l-NaCl seems to be understandable as a viscoelastic effect of the liquid. This explanation has been applied successfully to alkali metals and in particular to water.[9] In this sense molten NaCl appears to be a typical liquid with no surprises.

But we would like to point out a surprising feature of the collective particle dynamics in molten NaCl. Figure 3 shows the phase velocities of the acoustic modes calculated from the peak positions of our spectra. Also included is the phase velocity of the collective acoustic modes of l-Na close to melting obtained from IXS measurements.[3] The Q dependence of both is surprisingly similar. At the lowest Q values they depart and each one seems to converge towards its corresponding hydrodynamic sound velocity: c_{ad}(Na) = 2500 m/s and c_{ad}(NaCl) = 1750 m/s. On the other hand, the agreement between the l-NaCl and the l-Na phase veloci-
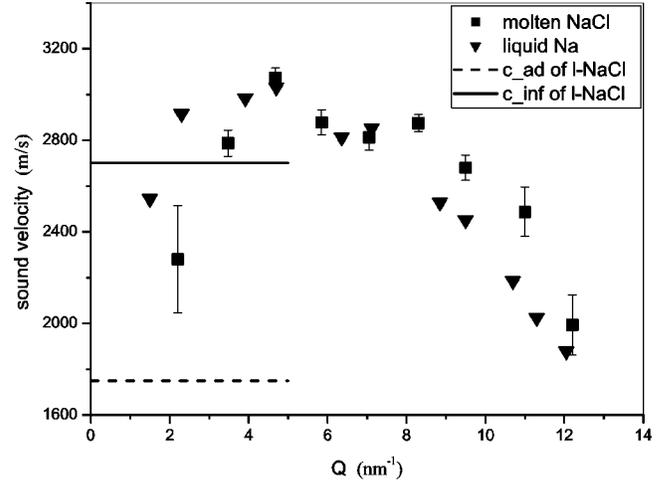
FIG. 3. The phase velocity from the peak positions of molten NaCl is plotted in combination with values of liquid Na. The solid line shows the calculated high-frequency sound velocity $c_\infty(Q = 0)$ and the dashed line shows the adiabatic sound velocity for molten NaCl.

ties suggests that in the acousticlike excitations of l-NaCl only the motion of the sodium subsystem is visible in the spectra. Such a phenomenon that one component is moving decoupled from the other component in a binary liquid was already deduced from MD simulations on molten Li$_4$Pb and called "fast sound."[10] It should be noted that the liquid Li$_4$Pb was described in the simulations by a potential with an ionic contribution. From the remarkable agreement between the two dispersion relations we suppose that the fast sound phenomenon is a possible explanation for our results. It seems to be that the mass difference between the ions cannot be the essential part for this effect in molten alkali halides. Which physical mechanism behind this collective movement may be and which role the necessity of ion polarization plays is an open field for speculation, e.g., one can suppose that the Na ions are moving between breathing shells of the chlorine ions. The necessity of inclusion of ion polarization to describe the acousticlike dynamics was already shown in the case of l-NaJ.[18] MD simulations with more advanced potentials than in the past could be quite helpful to unravel this question.

In conclusion we have shown that in l-NaCl propagating particle density fluctuations could be observed directly in the spectra. This result rules out the formerly often used rigid ion potentials for MD simulations to describe acousticlike dynamics of molten alkali halides. A large positive dispersion was measured, which seems to be understandable in the context of viscoelastic theory. Yet the collective dynamics of molten NaCl shows an additional surprising feature that the dispersion is quite similar to the corresponding excitations in liquid sodium. An interpretation is proposed that the Na$^+$ subsystem is moving independent on the anionic background at high frequencies. Our measurements are the first experimental evidences for the so-called fast sound in a binary ionic liquid.

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