

Dispersion relations of the acoustic modes in divalent liquid metals

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Abstract. Collective dynamics in liquid Ca and liquid Cd was studied by inelastic x-ray scattering (IXS). Using our experimental technique to prepare proper sample cells and high performance of an IXS beamline (BL35XU) at SPring-8 in Japan, the dynamic structure factor with reasonable statistics was obtained for these divalent liquid metals. For both liquids, the dynamic structure factor at low Q exhibits a central peak with a shoulder or small hump clearly visible on each side, and the inelastic excitation energy determined using the model function composed of Lorentzian and the damped harmonic oscillator function disperses with increasing Q . The dispersion curves of these liquids were compared with that of the longitudinal acoustic phonon in each crystalline phase. From these results, clear difference in the interatomic interaction between liquid Ca and liquid Cd was inferred.

1 Introduction

Atomic dynamics in a liquid has intensively been investigated since inelastic neutron scattering (INS) was found to probe atomic motions in a material [1]. After an INS study on liquid Rb [2], liquid metals are known to exhibit a distinct inelastic excitation of the collective motion of atoms in the dynamic structure factor $S(Q, E)$, where Q and E are momentum and energy transfer, respectively. Since high-resolution inelastic x-ray scattering (IXS) was available at the end of last century, collective and single particle dynamics in many liquid metals have been studied using these methods [3].

Among liquid metals, sp -valent metals are classified as a simple liquid metal and they are considered typical liquids. In fact, inelastic scattering measurements of liquid alkali metals were carried out by many researchers [3]. However, those on alkaline earth metals exist only in a few studies. Although IXS results of liquid Mg [4] and INS results of liquid Ba and Liquid Ca [5] were reported, the INS results presented excitation energies only at a few Q

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points. We could not find dispersion curves of the acoustic mode in liquid alkaline earth metals besides liquid Mg.

Recent development of computer resource has made application of *ab initio* molecular dynamics (AIMD) simulations more popular. Del Rio and Gonzalez [6] reported a result of systematic studies on atomic dynamics in liquid alkaline earth metals using AIMD. Their results seem consistent with the previous experimental results. However, to compare the simulation results with the experimental ones in detail, it is needed to accumulate experimental data of divalent liquid metals.

We carried out IXS measurements of liquid Ca using synchrotron radiation at SPring-8 in Japan. Although liquid Ca has a strong chemical reactivity as well as a much higher melting point compared to alkali metals, we could obtain $S(Q, E)$ with reasonable statistics at $Q < 12 \text{ nm}^{-1}$, using a special cell made of stainless steel. A high-brilliant IXS beamline (BL35XU) at SPring-8 was also needed to obtain good data. As another type of divalent metals, we investigated atomic dynamics in liquid Cd using IXS. INS measurements for liquid Cd of natural isotopes must be very difficult because the ^{113}Cd isotope has a very high absorption coefficient for neutron. Using IXS, we could obtain reasonable $S(Q, E)$ and compare our results with AIMD ones of liquid Cd [7]. In this article, we report our IXS results of liquid Ca and liquid Cd, and discuss the interatomic interaction in these liquids.

2 Experimental procedure

The experiments were conducted at the high-resolution IXS beamline (BL35XU) at SPring-8 in Japan [8]. Backscattering at the Si (11 11 11) reflection provided a beam of approximately 10^{10} photons/sec in a 0.8 meV bandwidth onto the sample. The energy of the incident beam and the Bragg angle of the backscattering were 21.747 keV and approximately 89.98° , respectively. The spectrometer resolution was approximately 1.5 meV depending on the analyzer crystal, as was experimentally determined by scattering from polymethyl methacrylate (PMMA). The Q resolution, ΔQ , was set to be 0.45 and 1.0 nm^{-1} (full width) for $Q \leq 11$ and $Q > 11 \text{ nm}^{-1}$, respectively.

Liquid Ca of 99.99% purity was mounted in a stainless-steel cell of Tamura-type [9] that was machined to provide a 1.5 mm sample thickness. The cell was placed in the Marburg chamber [10]. IXS spectra were measured at 1128 K in pure He atmosphere at 0.1 MPa. The background spectra were measured at the same temperature using the same cell without sample. After the absorption correction, the backgrounds were subtracted from the data, and the normalized dynamic structure factor $S(Q, E)/S(Q)$ were obtained by normalizing the signal spectrum with the integration with respect to E . Because x-ray windows of the cell were made of polycrystalline foil, the background was larger than a single crystalline sapphire cell. However, the same cell was used for the empty and sample measurements, phonon excitations from stainless-steel foil were safely subtracted.

Liquid Cd of 99.999 % purity was mounted in a single crystalline sapphire cell of the Tamura type [11] that was carefully machined to provide a 0.2mm sample thickness. The cell was placed in a high pressure vessel equipped with large Be windows [12]. IXS spectra from 1.9 to 32 nm^{-1} were measured at 623 and 1173 K in pure He atmosphere at 1 MPa. The background spectra were measured at 623 K using an empty sapphire cell and $S(Q, E)/S(Q)$ were obtained by the way described in the previous paragraph.

3 Results

Figure 1 shows $S(Q, E)/S(Q)$ of liquid Ca at 1128 K. The Q maximum of 10.6 nm^{-1} was limited by the aperture of a scattering window of the cell. $S(Q, E)/S(Q)$ at 1.7 nm^{-1} exhibits

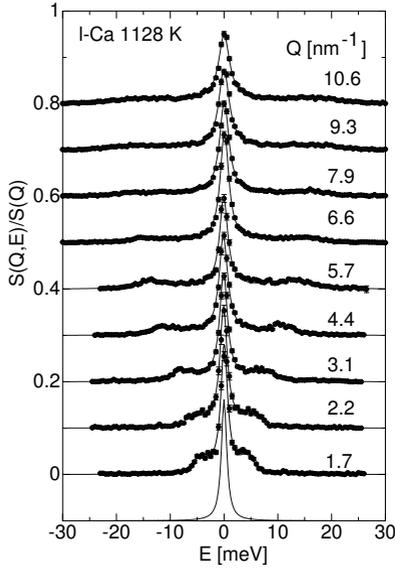


Figure 1. $S(Q, E)/S(Q)$ of liquid Ca at 1128 K. Black circles are the experimental results and lines are optimized fits. A sharp peak at the bottom is the resolution function.

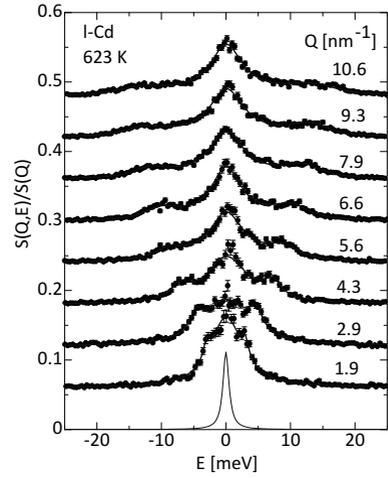


Figure 2. $S(Q, E)/S(Q)$ of liquid Cd at 623 K. Black circles are the experimental results and lines are optimized fits. A sharp peak at the bottom is the resolution function.

the inelastic excitation as a shoulder of the quasielastic peak on each side. The inelastic excitation disperses with increasing Q and an excitation peak profile is visible at 4.4 and 5.7 nm^{-1} .

Figure 2 shows $S(Q, E)/S(Q)$ of liquid Cd at 623 K at $Q \leq 10.6 \text{ nm}^{-1}$. As shown in the figure, $S(Q, E)/S(Q)$ at 1.9 nm^{-1} exhibit the inelastic excitation as a shoulder of the quasielastic peak similarly to liquid Ca. The inelastic excitation disperses with increasing Q up to 14.6 nm^{-1} . As the first peak position of $S(Q)$ in liquid Cd is approached, the inelastic excitation on each side in $S(Q, E)/S(Q)$ is merged into the central peak, and de-Gennes narrowing profile of $S(Q, E)/S(Q)$ is observed at 21.3 nm^{-1} (the data are not shown in Fig.2).

We deconvoluted the experimental $S(Q, E)/S(Q)$ of liquid Ca and liquid Cd using the resolution function $R(E)$ and a model function $F_{\text{model}}(Q, E)$ consisting of a Lorentzian for the quasi-elastic peak and a single damped harmonic oscillator (DHO) function [13] for the inelastic excitation, as following equations.

$$S(Q, E)/S(Q) = \int dE' [B(E')F_{\text{model}}(Q, E')]R(E - E'), \quad (1)$$

$$F_{\text{model}}(Q, E) = \frac{A_0}{\pi} \frac{\Gamma_L}{\Gamma_L^2 + E^2} + \frac{A_1}{\pi\beta} \frac{4\Gamma_1 \sqrt{\Omega_1^2 - \Gamma_1^2}}{(E^2 - \Omega_1^2)^2 + 4E^2\Gamma_1^2},$$

$$B(E) = \beta E / [1 - \exp(-\beta E)],$$

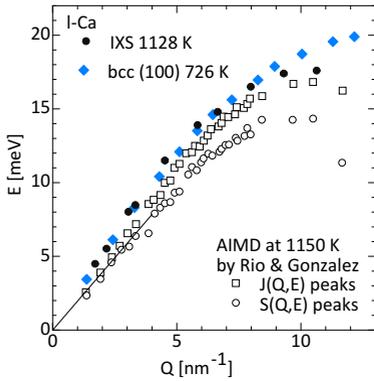


Figure 3. Dispersion relation of the acoustic mode in liquid Ca. Black circles, open squares and open circles denote the IXS results, peak positions of the current-current correlation function and the dynamic structure factor obtained by the AIMD [6], respectively. Also shown are the excitation energy of the longitudinal acoustic phonons in crystalline Ca of a bcc phase (Blue diamonds) and the ultrasonic sound speed in liquid Ca (solid line).

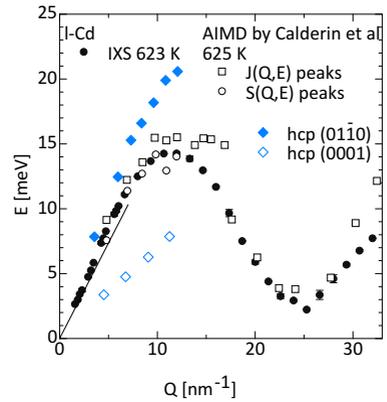


Figure 4. Dispersion relation of the acoustic mode in liquid Cd. Black circles, open squares and open circles denote the IXS results, peak positions of the current-current correlation function and the dynamic structure factor obtained by the AIMD [7], respectively. Also shown are the excitation energies of the longitudinal acoustic phonon to (0110) direction (solid blue diamonds) and (0001) direction (open blue diamonds) in crystalline Cd of a hcp phase, and the ultrasonic speed in liquid Cd (solid line).

where $\beta = (k_B T)^{-1}$. A_0 and Γ_L are the amplitude and the linewidth of Lorentzian, respectively. A_1 , Γ_1 and Ω_1 are the amplitude, the linewidth and the excitation energy for the inelastic excitation. Although a transverse acoustic excitation at lower E is often discussed in collective dynamics in a liquid, a simple model function of a Lorentzian and a DHO gave a good fit to the experimental $S(Q, E)/S(Q)$, as indicated through solid lines in Figs.1 and 2.

The excitation energy of the DHO component Ω_1 (black circles) for liquid Ca is shown in Fig. 3. It is known that Ω_1 does not coincide with the energy of the inelastic peak in $S(Q, E)/S(Q)$ but approximate the peak energy of the current-current correlation function $J(Q, E)$. The results of liquid Ca show that Ω_1 (black circles) at $Q < 5 \text{ nm}^{-1}$ disperses along with approximately 3900 m/s, which is 34 % faster than the ultrasonic sound speed of 2950 m/s [14]. This panel also depicts the excitation energy of the longitudinal acoustic mode predicted by the AIMD simulation. The simulation gave the energy of the peak positions in $S(Q, E)$ and $J(Q, E)$. As shown in the figure, the AIMD simulation slightly underestimated the IXS results. Interestingly, the IXS results are very similar to a phonon dispersion curve to (100) direction of high-temperature bcc phase of crystalline Ca [15] as indicated in the figure.

The Q dependence of Ω_1 (black circles) in liquid Cd is shown in Fig.4. Ω_1 at $Q \sim 5 \text{ nm}^{-1}$ disperses along approximately 2600 m/s, which is 19 % faster than the ultrasonic sound speed of 2200 m/s [14]. The excitation energies of the longitudinal acoustic mode predicted by the AIMD simulation are plotted in the figure, using the same symbols in Fig. 3. The AIMD results agree with the IXS ones although open squares give a slightly higher energies than black circles at the top of the dispersion curve. We plot the dispersion curve of crystalline Cd with hcp form [16]. Probably owing to directional dependence of the elastic property, the

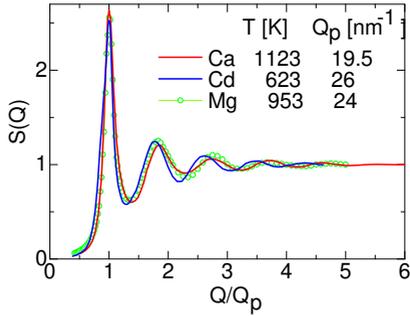


Figure 5. $S(Q)$ of liquid Mg, Ca and Cd obtained by x-ray diffraction [17] on the normalized Q scale.

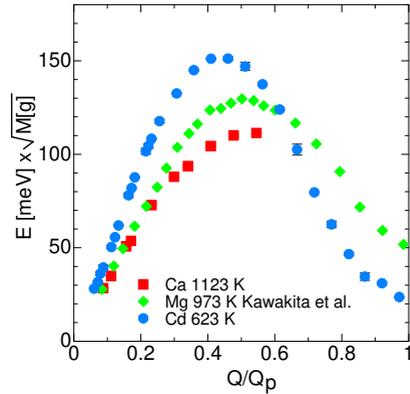


Figure 6. Excitation energies of the acoustic mode normalized by the atomic mass for liquid Ca and Cd as a function of the normalized Q scale. Also shown is that of liquid Mg [4].

excitation energy in hcp form largely depends on the crystalline axes as shown in the figure. The IXS results at $Q \leq 5 \text{ nm}^{-1}$ are located near the phonon dispersion curve to $(01\bar{1}0)$.

4 Discussion

Figure 5 shows $S(Q)$ of liquid Ca, Mg and Cd reported by Waseda [17], as a function of Q/Q_p , where Q_p is the first peak position of $S(Q)$ indicated in the figure. $S(Q)$ profiles on the normalized Q scale are similar between the alkaline earth elements but that of Cd is different from them. The oscillatory phase of liquid Cd is faster than those of liquid Ca and Mg. These results hint that the interatomic interaction may be similar between liquid Ca and liquid Mg but it is different from that of liquid Cd.

The effective pair potential of divalent liquid metals were reported by Jank and Hafner [18]. They showed that the density of states (DOS) of liquid Mg is similar to DOS of a free electron gas but DOS of liquid Ca is different from that because d -states in Ca is closer to the Fermi level compared to Mg. However, the effective pair potential of liquid Mg and Ca that they deduced is similar; the potential exhibits a clear minimum near the first nearest neighbor distance in the liquids. In contrast, the effective pair potential of liquid Cd exhibits a profile that a repulsive component is dominant when a relativistic effect is included. Their results are qualitatively consistent with the results inferred from the normalized $S(Q)$ profiles shown in Fig. 5.

We compare the dispersion curves of liquid Ca, Mg and Cd in Fig. 6 on the normalized Q and E scales, where the E is normalized by the square root of atomic mass. As shown in the figure, the dispersion curves of liquid Ca and Mg agree with each other up to $Q/Q_p = 0.2$. Although the maximum position in the dispersion curves appears at approximately $Q/Q_p = 0.5$, the maximum energy of liquid Ca is smaller than that of liquid Mg. These results indicate that the interatomic interaction of liquid Ca is slightly different from that of liquid Mg.

As shown in Fig. 6, the dispersion curve of liquid Cd is much different from those of the alkaline earth elements. The result suggests that the interatomic interaction in liquid Cd is much different from that in liquid Ca and liquid Mg, as predicted by Jank and Hafner [18].

The maximum energy is larger than those of the alkaline earth elements. It is noteworthy that the maximum position of liquid Cd shifts to $Q/Q_p = 0.4$ smaller than those of liquid Ca and Mg. This behavior may be correlated with the profile of the first maximum of $S(Q)$ in liquid Cd that is broadened toward lower Q than those in liquid Ca and Mg, as shown in Fig. 5.

5 Summary

IXS measurements of liquid Ca and liquid Cd provide the dynamic structure factors of these liquids that exhibit distinct acoustic excitations at low Q . The dispersion curves are compared with each other including that of liquid Mg. We found that although $S(Q)$ of liquid Ca and Mg is similar after the atomic size is normalized, the dispersion curves of these elements are not perfectly consistent after atomic size and mass are normalized. Meanwhile, the structure and dynamics of liquid Cd must be much different from these liquid alkaline earth elements. The results are qualitatively consistent with the difference in the effective pair potential between these liquids reported by Jank and Hafner [18].

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