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## Electron–ion correlation in liquid metals

S. Takeda <sup>a,\*</sup>, Y. Kawakita <sup>a</sup>, M. Inui <sup>b</sup>, K. Maruyama <sup>c</sup>, S. Tamaki <sup>c</sup>, Y. Waseda <sup>d</sup><sup>a</sup> Faculty of Science, Kyushu University, Ropponmatsu, Fukuoka 810, Japan<sup>b</sup> Faculty of Integrated Arts and Science, Hiroshima University, Higashi-Hiroshima 724, Japan<sup>c</sup> Faculty of Science, Niigata University, Niigata 950-21, Japan<sup>d</sup> Institute for Advanced Materials Processing, Tohoku University, Sendai 980, Japan

### Abstract

The structure factors of liquid Na, Mg and Al have been obtained by neutron diffraction above each melting temperature with sufficient accuracy and compared with the structural data obtained by X-ray diffraction. Neutrons, being scattered by nuclei, determine the ionic structure factor, while X-ray scattering is related to the correlation among electrons. There has been detected a small but clear difference larger than the experimental uncertainties between these two structure factors. The systematic difference of the screening charge around an ion will be discussed for these liquids.

### 1. Introduction

Liquid metals are characterized by a mixture of ions and conduction electrons moving nearly freely through an assembly of ions, and also by the strong correlation between them. As is well known, neutrons are scattered by nuclei at the centers of ions, and the structure factor measured in neutron diffraction gives the pair correlation function between ions. On the other hand, X-rays are scattered by electrons, which include the bound electrons of all ions and valence electrons distributed among the ions. They are sensitive to both the ionic and electronic parts of the liquid, and the X-ray scattering intensity includes the three types of correlations. The three types of correlations in liquid metals can be separated by X-ray, neutron, and electron diffraction measure-

ments [1]. These different scattering mechanisms give a small, but certain difference in the observed structure factor [2–4].

Several efforts [2,5,6,8] have been devoted to the separation of the three types of partial correlations and to the estimation of the electron–ion and electron–electron pairs in liquid metals. Recent experiments with sufficient accuracy of X-ray and neutron diffraction for liquid metals enable us to determine the electron–ion correlations [9–11].

It is interesting to see the systematic difference of the electron charge distribution and screening effect among liquid Na, Mg and Al, because these elements have the same ionic core of 10 electrons and the number of valence electrons is different for each element.

The main purpose of this paper is to present the newly measured structural data of Na, Mg and Al by neutron diffraction with sufficient accuracy, and we also provide information about the charge distribution of valence electrons around each ion in the liquid state.

\* Corresponding author. Tel.: +81-92 726 4728; fax: +81-92 726 4728/4841; e-mail: takeda@rc.kyushu-u.ac.jp.

## 2. Experimental procedure

Neutron scattering measurements for liquid Na, Mg and Al were carried out at 110°C, 680°C and 670°C, respectively, using the two-axis diffractometer of the Institute for Solid State Physics, University of Tokyo, at JRR-2 and JRR-3M. An aluminum tube with an inner diameter of 12 mm and 0.5 mm wall thickness was used for liquid Na, a magnesia (MgO) tube was used for liquid Mg, and a stainless tube with an inner diameter 12 mm and 0.3 mm wall thickness cell was used for liquid Al. The wavelength of the neutron beam was  $\lambda = 1.00$  Å, and fine solar slits ( $20' \times 20'$ ) were used to filter out Bragg reflection peaks from the sample cell in the observed spectrum as long as possible.

The experimental uncertainties in the neutron

structure factor,  $S_N(Q)$ , of all liquid metals were estimated to be less than 1.0%.

The structure factor  $S_X(Q)$  for all liquid metals determined by X-ray diffraction were obtained by one of the present authors [12]. The uncertainty is on the order of 0.02 for the  $S_X(Q)$  near the first peak region. In both cases  $S(Q \rightarrow 0)$  was determined by the thermodynamic measurements of density, sound velocity and specific heat.

## 3. Results

Fig. 1(a), (b) and (c) show the structure factors of liquid Na, Mg, and Al determined by neutron and X-ray diffraction. The systematic differences around the first peak region are easily observed, although

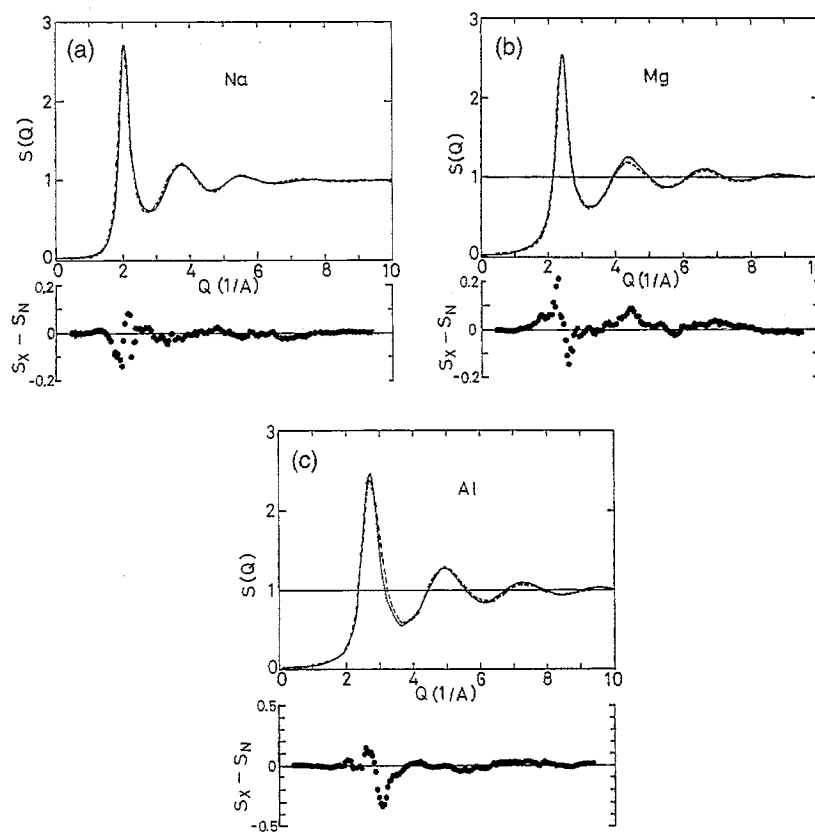


Fig. 1. Structure factors of (a) liquid Na, (b) liquid Mg and (c) liquid Al by X-ray (solid curve) and neutron diffraction (broken curve). Also given is the difference between the two curves,  $S_X(Q) - S_N(Q)$ .

the qualitative coincidences in the structural profile are almost retained. It can be seen that the oscillations in the X-ray curves are slightly sharper than those for the neutron curve. The values of  $S_X(Q) - S_N(Q)$  determined from two structure factors are also plotted at the bottom of each figure. These may be a help in observing the difference and oscillating profile in  $S_X(Q) - S_N(Q)$ .

#### 4. Theoretical background and analysis

X-rays are scattered by the electrons and by both the ionic part and electronic part of the liquids. If we use the Ashcroft–Langreth type partial structure factors of a binary mixture composed of ions (= i) and electrons (= e), the total X-ray scattering intensity except for  $Q = 0$  is expressed as follows:

$$I_X(Q)/N = [f_i^2(Q)S_{ii}(Q) + 2\sqrt{z}f_i(Q)S_{ie}(Q) + zS_{ee}(Q)] + (Z - z)S_i^{\text{inc}}(Q), \quad (1)$$

where  $f_i(Q)$  is the form factor of the ion,  $Z$  is the atomic number and  $z$  the number of valence electrons per atom,  $S_{ii}(Q)$ ,  $S_{ie}(Q)$  and  $S_{ee}(Q)$  are the partial structure factors of ion–ion, ion–electron and electron–electron pairs, respectively, and  $S_i^{\text{inc}}(Q)$  is the incoherent (Compton) scattering factor of ions due to bound electrons.

The static structure factor of valence electrons,  $S_{ee}(Q)$ , is composed of two parts, the local charge density accompanying the ionic core and the uniformly distributed part.  $S_{ee}(Q)$  and  $S_{ie}(Q)$  in liquid metal are also given by the following forms:

$$S_{ee}(Q) = |\rho(Q)|^2 S_{ii}(Q)/z + S_{ee}^{(0)}(Q), \quad (2)$$

$$S_{ie}(Q) = \frac{\rho(Q)}{\sqrt{z}} S_{ii}(Q), \quad (3)$$

where  $\rho(Q)$  is the Fourier transform of the local charge density function of valence electrons, and  $S_{ee}^{(0)}(Q)$  is the structure factor of the uniformly distributed electrons. Both  $(Z - z)S_i^{\text{inc}}(Q)$  and  $zS_{ee}^{(0)}(Q)$  in Eq. (1) are incoherent parts, and they are eliminated from the measured intensity data. Therefore, we can obtain the coherent X-ray scattering intensity,  $I_X^{\text{coh}}(Q)$ , which can be determined from the measured

intensity data, and this term can be rewritten in the following form:

$$I_X^{\text{coh}}(Q)/N = [f_i(Q) + \rho(Q)]^2 S_{ii}(Q). \quad (4)$$

The structure factor of  $S_N(Q)$  for  $N$  atoms is obtained from the coherently scattered intensity of neutrons,  $I_N^{\text{coh}}(Q)$ , and scattering length  $b$  as follows:

$$S_N(Q) = \frac{I_N^{\text{coh}}(Q)}{Nb^2}. \quad (5)$$

Since  $S_{ii}(Q)$  is equal to  $S_N(Q)$ , the local charge density distribution in the momentum space,  $\rho(Q)$ , can be obtained by Eqs. (4) and (5),

$$\rho(Q) = \sqrt{\frac{b^2 I_X^{\text{coh}}(Q)}{I_N^{\text{coh}}(Q)}} - f_i(Q). \quad (6)$$

$\rho(Q)$  in Eq. (6) is useful for discussing the local charge density around an ion, while  $S_{ie}(Q)$  in Eq. (3) is convenient for discussing the electron charge distribution for an intermediate region, say, a few times larger than the atomic distance.

#### 5. Discussion

Eq. (6) enables us to evaluate the local charge density,  $\rho(Q)$  from the measured structural information of  $I_X^{\text{coh}}(Q)$  and  $I_N^{\text{coh}}(Q)$ . Since  $\rho(Q)$  has large uncertainty due to the relatively small contribution of the electron–ion correlation to the total correlation in liquid metals, especially for liquid Na, the profile of  $\rho(Q)$  was assumed to be a smooth function and the average values at each  $Q$ . Then we obtained the  $\rho(Q)$  by the back transform technique.

Fig. 2 shows the resulting local charge density functions,  $\rho(Q)$ , together with those of isolated Na, Mg and Al atoms (dotted curve) obtained from  $f_a(Q) - f_i(Q)$ . The corresponding  $S_{ie}(Q)$  is shown in Fig. 3, and the result for liquid Na is consistent with the theoretical one obtained by the pseudopotential method [7].

Fig. 4 shows the local charge density distribution functions,  $\rho(r)$ , together with the charge density for isolated atoms. As shown in the figure, a systematic difference can be seen among  $\rho(r)$  curves. The theoretical results for Na and Al by the pseudopotential method are also shown in the figure.

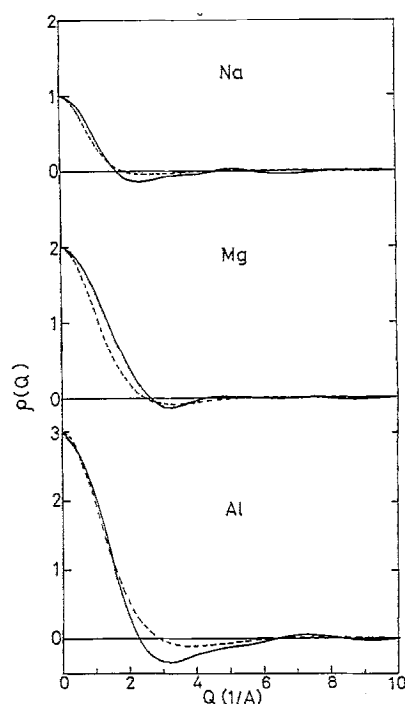


Fig. 2. Charge density function,  $\rho(Q)$  (solid curve), obtained from back-transformed spectrum and charge density of an isolated atom for Na, Mg and Al (chain curve).

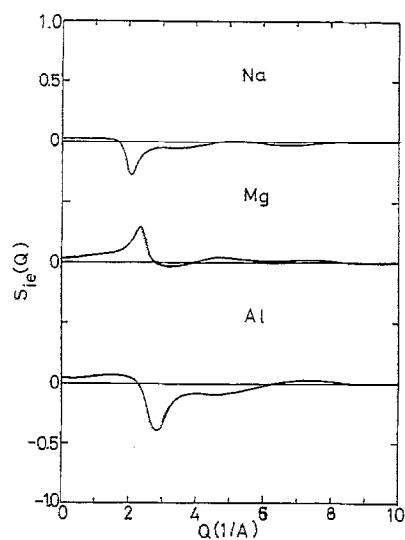


Fig. 3. Ion-electron structure factor,  $S_{ie}(Q)$ , obtained from structural data.

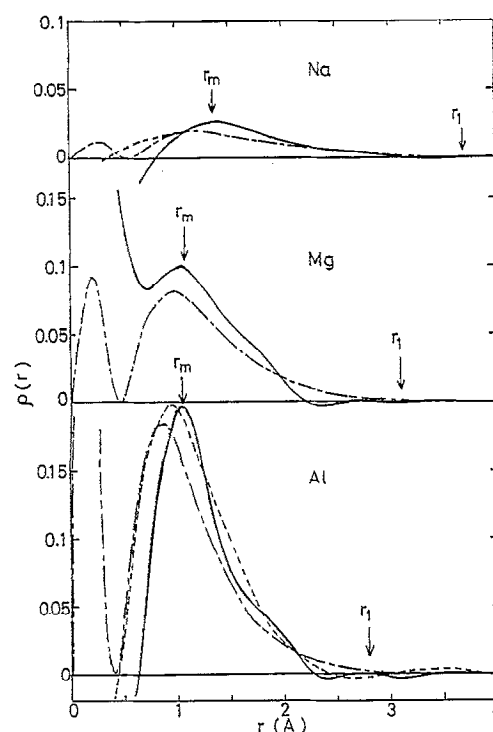


Fig. 4. Charge density function,  $\rho(r)$  (solid curve), and charge density of an isolated atom (chain curve).  $r_m$ : the first maximum position of  $\rho(r)$ ,  $r_l$ : distance of the nearest neighbour ions. Broken curves are the theoretical results obtained by the pseudopotential method [7,13].

The curve of  $\rho(r)$  crosses zero around 0.80 Å and 0.60 Å in liquid Na and Al, respectively, while the curve in liquid Mg has a minimum value at 0.75 Å and a sharp increase toward the center of an ion can be seen. Although these values are close to the ionic radii, accurate spectra of  $\rho(Q)$  in the high  $Q$  region will be required for the further understanding of the charge distribution in the very small  $r$  region less than 0.75 Å. However, the structural information outside the region larger than 0.75 Å should be valid and useful for understanding the charge distribution outside the ionic core region. The charge density function shows that the electron charge screens the ionic charge, and those maximum values are 1.35 Å, 1.10 Å and 1.05 Å for liquid Na, Mg and Al, respectively. The maximum charge density for isolated atoms is 1.25 Å for liquid Na, 0.95 Å for liquid Mg, and 0.85 Å for liquid Al.

The ratios for the resulting distance of the maxi-

mum charge density distribution in the metallic liquid state and the isolated one are 1.08 for Na, 1.16 for Mg and 1.24 for Al. This may be due to the difference of the electron charge density among them. A detailed discussion for electron charge distribution among them will appear elsewhere [11].

## 6. Conclusion

In conclusion, we have obtained new structure factors for liquid Na, Mg and Al from newly measured neutron diffraction spectra. We have deduced the various electron charge distributions around the same ionic core of 10 electrons for liquid Na, Mg and Al by the difference in the structure factors obtained from neutron and X-ray diffraction spectra.

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