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## LETTER TO THE EDITOR

# Electron charge distribution in liquid sodium

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**Abstract.** The ion–electron correlation function in liquid sodium, estimated from the difference in measured structure factors determined by x-ray and neutron diffraction methods, has been extended to describe the distribution of conduction electrons around an ion. The present results imply that the conduction electrons in liquid sodium would most likely behave as the atomic wave function at the closed vicinity of the ionic radius, corresponding to the orthogonalised plane wave.

Liquid metals in their pure states are well known to be binary mixtures of ions and a strongly coupled plasma composed of electrons. Based on this idea, it was pointed out that the structure of liquid metals should be explicitly described by three types of correlations, i.e., for electron–electron, electron–ion and ion–ion pairs. X-ray and neutron diffraction studies on the structure of liquid metals are good clues to see these correlations for the following reasons. Neutrons scatter only on nuclei at the centre of ions. On the other hand, x-ray scattering experiments also provide information on the distribution of ions but this is known to be obtained from the scattering of electrons surrounding ions. Such differences in the scattering mechanisms of x-rays and neutrons suggest that a small but certain difference should be observed in the structural data of liquid metals determined by two diffraction methods.

Under these circumstances, we have already engaged in the estimation of the electron–ion correlation functions in several liquid metals from measured structure factors obtained by using x-ray and neutron diffraction methods (Takeda *et al* 1985, 1986a, b, 1989).

Using the Ashcroft–Langreth-type partial structure factors  $S(q)_{ab}$  ( $a, b = \text{ion, electron}$ ), the coherent x-ray scattering intensity is expressed as follows

$$I_x^{\text{coh}}(q) = N[(f_i(q))^2 S_{ii}(q) + 2z^{1/2} f_i(q) S_{ie}(q) + z S_{ee}(q)] \quad (1)$$

where  $f_i(q)$  is the form factor of an ion and  $z$  the number of valence electrons per atom.

On the other hand, it can be often assumed that in liquid metals the small ion cores of charge  $ze$  are embedded in an electron gas which is, more or less, uniformly distributed. Based on this idea, the correlation functions of electron–ion and electron–electron pairs in liquid metals have been investigated by several workers (Cusack *et al* 1976, Baston and Silcox 1983, Mazzone *et al* 1983, Schülke *et al* 1986, Petrillo and Sacchetti 1986, and

Chihara 1987), since Egelstaff *et al* (1974) first pointed out the possibility of their experimental determination.

Chihara (1987) found the coherent x-ray scattering intensity,  $I_x^{\text{coh}}(q)$  by using the structure factors exactly expressed in terms of the static and dynamic direct correlation functions and it is as follows

$$I_x^{\text{coh}}(q) = N[(f_i(q))^2 + 2f_i(q)\rho(q) + (\rho(q))^2]S_{ii}(q) \quad (2)$$

that is

$$I_x^{\text{coh}}(q) = N[f_i(q) + \rho(q)]^2 S_{ii}(q) \quad (2a)$$

where  $\rho(q)$  is the Fourier transform of the charge distribution around an ion denoted by  $\rho(r)$ . Equation (2) is equivalent to equation (1) and each term corresponds. However, it is worth mentioning that the last term in equations (1) and (2) is negligibly small compared to the first and second ones when the atomic number of the liquid metal of interest is not so small (exceptions may be liquid Li and Be). This is quantitatively confirmed in the previous papers (Takeda *et al* 1986a, b Petrillo and Sacchetti 1986).

The partial structure factors  $S_{ii}(q)$  are well-known to be equal to the structure factor measured by neutron diffraction,  $S_N(q) = I_N^{\text{coh}}(q)/Nb^2$ , where  $b$  is the scattering length of neutrons and  $I_N^{\text{coh}}(q)$  is the coherent neutron scattering intensity. Thus, equation (2) can be approximately re-written as

$$I_x^{\text{coh}}(q) = N[(f_i(q))^2 + 2f_i(q)\rho(q)]S_N(q) \quad (3)$$

that is

$$I_x^{\text{coh}}(q) = \{[(f_i(q))^2 + 2f_i(q)\rho(q)]/b^2\}I_N^{\text{coh}}(q). \quad (3a)$$

From equation (3a), the distribution of the conduction electron in the momentum space,  $\rho(q)$  is then given by

$$\rho(q) = [b^2 I_x^{\text{coh}}(q)/I_N^{\text{coh}}(q) - (f_i(q))^2]/[2f_i(q)]. \quad (4)$$

When the values of  $f_i(q)$  are available, the estimation of  $\rho(q)$  is straightforward.

The theoretical ionic form factor  $f_i(q)$  is usually given by the Hartree-Fock method, and it is also obtainable from the x-ray scattering intensity measurements for the ionic crystals. Good agreement in these theoretical and experimental values of  $f_i(q)$  is well known in many cases including  $\text{Na}^+$  ion (James 1954, Weiss and DeMarco 1958, Batterman *et al* 1961).

In previous works (Takeda *et al* 1985, 1986a, b, 1989 and Tamaki 1987), the electron-ion correlation function  $S_{ie}(q)$  in liquid metals has been obtained from measured structural data of x-rays and neutrons in terms of equation (1).

Comparing equation (2) with (1), we obtain

$$S_{ie}(q) = (\rho(q)/z^{1/2})S_{ii}(q) \quad (5)$$

$$\rho(q) = z^{1/2}(S_{ie}(q)/S_{ii}(q)). \quad (5a)$$

Therefore,  $S_{ie}(q)$  can readily be converted into  $\rho(q)$  using (5a), or vice versa. An equivalent formula has also been presented by Petrillo and Sacchetti (1986) using the following expression for the coherent x-ray scattering intensity  $I_x^{\text{coh}}(q)$ ,

$$I_x^{\text{coh}}(q) = N\{(f_i(q))^2 + 2f_i(q)F(q)[V_{ie}(q)/(4\pi e^2/q^2)] + (\rho(q))^2\}S_{ii}(q) \quad (6)$$

where  $V_{ie}(q)$  is the electron-ion interaction potential and  $F(q)$  is the static response function defined by

$$F(q) = (1/\varepsilon(q, 0) - 1)/(4\pi e^2/q^2) \quad (7)$$

$\varepsilon(q, 0)$  being the dielectric function of the electron gas.

Comparing equations (1), (2) and (6), we have an equation for connecting the Fourier transform of charge distribution ( $q$ ) with the static response function  $F(q)$  as follows

$$F(q) = [(4\pi e^2/q^2)/V_{ie}(q)]\rho(q). \quad (8)$$

In the case of pure liquid metals,  $V_{ie}(q)$  is commonly given by the following form (Sham and Ziman 1963, Cusack *et al* 1976, Petrillo and Sacchetti 1986),

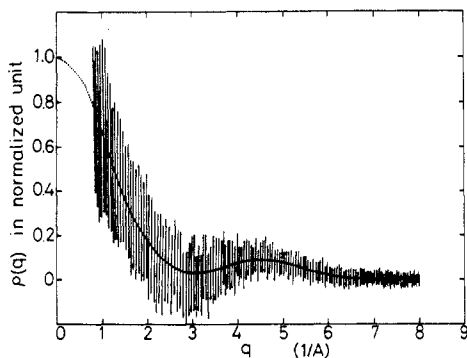
$$V_{ie}(q) = (4\pi e^2/q^2)f_i(q) \quad (9)$$

then, the response function given by Petrillo and Sacchetti (1986) is simply equal to

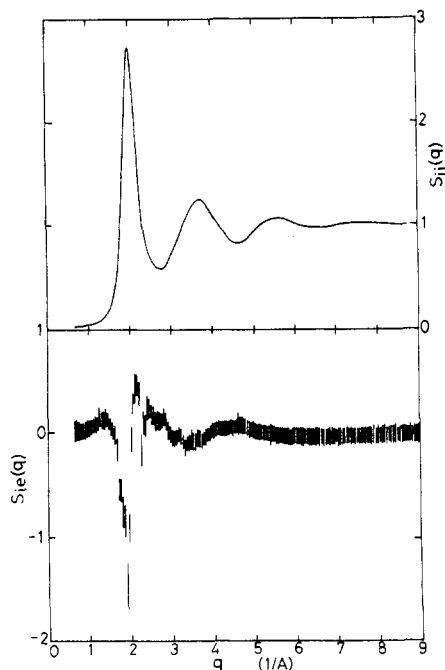
$$F(q) = \rho(q)/f_i(q). \quad (10)$$

In this letter, we present the results of  $\rho(q)$  and  $\rho(r)$  of liquid sodium newly estimated from the structural data of  $I_x^{\text{coh}}$  and  $I_N^{\text{coh}}(q)$  experimentally determined by x-ray and neutron diffraction methods (Takeda *et al* 1989) using equation (4). Here, we use the form factor  $f_i(q)$  given in the International Table for x-ray Crystallography (1974).

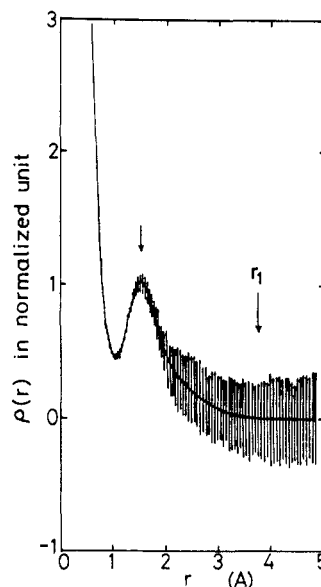
The results of  $\rho(q)$  in liquid sodium are shown in figure 1. The vertical lines in this figure denote the experimental uncertainties. For convenience of discussion, the experimentally determined  $S_{ii}(q)$  and  $S_{ie}(q)$  values of liquid sodium are also illustrated in figure 2. It is found that the estimated values of  $\rho(q)$  have a certain amount of scatter and this is mainly due to the relatively small difference between  $I_x^{\text{coh}}(q)$  and  $I_N^{\text{coh}}(q)$ . This frequently increases the experimental uncertainties because it encounters a numerical singularity in the data processing. The estimation of the electron distribution in the real space  $\rho(r)$  was carried out by the usual Fourier transformation. For this purpose, the profile of  $\rho(q)$  was assumed to be a smooth function: thus, the average values at each  $q$  were employed. The resultant  $\rho(r)$  is shown in figure 3. The vertical line in this figure corresponds to the variation arising from the experimental uncertainties of  $\rho(q)$ . It is found that  $\rho(r)$  is a monotonically decaying function beyond the first peak which is located at 1.6 Å. If the wave function of conduction electrons is expressed, for example,



**Figure 1.** Electron charge distribution function  $\rho(q)$  of liquid sodium estimated from measured structural data using equation (4).



**Figure 2.** Structure factors of ion-ion pairs,  $S_{ii}(q)$  and ion-electron pairs,  $S_{ie}(q)$  in liquid sodium (Takeda *et al* 1989).



**Figure 3.** Electron charge distribution function in the real space  $\rho(r)$  of liquid sodium.  $r_1$  denotes the nearest-neighbour distance of ion-ion pairs.

as in the OPW form, then the conduction electrons would most likely behave as the atomic wave function in close vicinity to the ionic radius. In other words, a sharp increase toward the centre of an ion in  $\rho(r)$  observed at about 0.9 Å may be ascribed to the mixing effect of a part of the conduction electrons with the outer core electrons of ions concerned. However, it is also noteworthy to mention that there is only a small fraction of such conduction electrons in the range less than 1.0 Å, because the electron distribution follows the form  $4\pi r^2 \rho(r)$ .

As easily seen in figures 1 and 3, the present results of  $\rho(q)$  or  $\rho(r)$  should be considered not to be quantitatively accurate and the direct determination of the electron charge distribution in liquid metals from measured structural data of x-rays and neutrons is far from complete. Nevertheless, the present authors take the view that the results shown in this work represent, at least one possible way for experimentally obtaining information on the fundamentals of the electron charge distribution in liquid metals. As a final remark, it is emphasised that very accurate diffraction data with the accumulated counts over  $10^5$  at each  $q$  value is essential for the experimental determination of  $\rho(q)$  or  $\rho(r)$ . Such further efforts may test the usefulness of the present method on a wider basis.

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