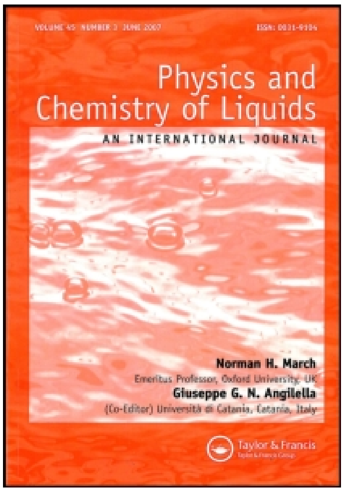

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N. H. March[a]; M. P. Tosi[b]
[a] Theoretical Chemistry Department, University of Oxford, Oxford, England [b] International Centre for Theoretical Physics, Miramare, Trieste, Italy

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Interpretation of X-ray Diffraction from Liquid Alkali Metals

N. H. MARCH

Theoretical Chemistry Department, University of Oxford, 1 South Parks Rd., Oxford OX1 3TG, England.

and

M. P. TOSI

International Centre for Theoretical Physics, Miramare, Trieste, Italy.

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It is known that, near freezing, the peaks in the liquid structure factors of Na and K reflect the ordering of a body-centred cubic lattice. Therefore, we have considered the modifications introduced into the electron distribution of a body-centred cubic, nearly-free electron, metal by destruction of the long-range order. Use of the Wannier representation, as has been pointed out by Matthai *et al.*, leads naturally in a metal to bond charges at the centres of near-neighbour, next-near neighbour, etc., bonds. Because of the absence of long-range order in the nuclei of liquid Na and K, it is argued that only near-neighbour and perhaps next-near neighbour bond charges remain meaningful. Thus, whereas in crystalline Na and K, the totality of the bond charge distributions, including however many longer and longer bonds, adds up to an almost constant electron density of the valence electrons, in the liquid the local angularity of the electron density is significant. We find then that a model which can explain the observed reflections, which are characteristic of a face-centred-cubic lattice, can be built up by:

a) Using local sp^3 type bonding charges, with Pauling resonance invoked between occupied and unoccupied bonds and

b) Assuming, once local electron coordination characteristic of such bonds is formed, Wigner-type lattice ordering can propagate the face-centred lattice over distances of 30 to 40 Å.

The differences to be expected between nearly-free electron metals and tight-binding metals in the liquid state are finally stressed.

1 INTRODUCTION

Egelstaff *et al.*[1] pointed out that there were small systematic differences between the liquid structure factors of simple metals near their freezing points. In particular, they stressed that the first peak of the structure factor determined by X-rays was higher than that for neutrons and this they interpreted as due to longer range ordering of the electrons than the ions. Subsequently Dobson[2] has extended their analysis away from the first peak and has argued for the existence of face-centred cubic type reflections in the "difference" diffraction data for liquid Na. New measurements on liquid K by Johnson[3] have also led to the peaks and valleys in the difference between the X-ray and neutron structure factors near to those of a face-centred cubic lattice.

Independently of this work on liquid metals, Matthai *et al.*[4] have studied the angularity of the electron distribution in body-centred-cubic crystalline metals. From their analysis using Wannier orbitals, they emphasized that in metals a natural way of apportioning electronic charge was to place contributions arising from the overlap of Wannier functions, on sites $\mathbf{R}_i$ and $\mathbf{R}_j$ say, at the midpoints of the bond joining nuclei i and j. They emphasized that their discussion was most readily practicable for rather localized Wannier functions, i.e. to tight-binding metals, and least applicable to nearly free-electron crystalline metals, e.g. body-centred cubic Na, because of the need to include many longer and longer bonds.

Returning to the liquid state, it is known from the work of Ivanov *et al.*,[5] Ferraz and March[6] and Chaturvedi *et al.*,[7] that the freezing of liquid Na and K is quite like classical Wigner crystallization. This means that as the freezing temperature is approached, the peaks in the liquid structure factor $S(k)$ as determined by neutron scattering reflect more and more the reciprocal lattice of a body-centred-cubic crystal. Thus, at least for the local short-range order, the body-centred-cubic lattice of Na^+ ions, say, is a useful description. It seems fair to assume that such a description allows bond charges still to be meaningfully allocated on near-neighbour and (perhaps also) next-near neighbour bonds.

2 PROPOSED MODEL INCORPORATING ELECTRON-ION AND ELECTRON-ELECTRON CORRELATIONS

Whereas in crystalline body-centred-cubic Na, the bond charges described by the overlap of Wannier functions led to a more and more uniform distribution of electrons as longer and longer bonds were added, according to the analysis of Ref. 4, in liquid Na we argue that because of the short-range ionic order the X-ray scattering will be, away from $k = 0$, predominantly from the near-neighbour bond charges, once the almost spherical distributions of core charge centred on the ions are subtracted away following the procedure of Ref. 1.

Such a picture represents then an approximate treatment of electron-ion correlations. But the alkalis, being low electron density metals, are known to exhibit important Coulomb repulsion effects. As Wigner[8] first emphasized, and as was discussed in Ref. 1, this would lead to body-centred cubic ordering if the ions are taken to be smeared out into a uniform background. The fact that experiment shows face-centred cubic ordering[2,3] immediately tells us that this cannot be due solely to electron-electron interactions; the lattice structure being changed by the electron-ion correlation. This is our essential conclusion of the present paper and we must demonstrate how this can come about. Nevertheless, it is also essential, in explaining the observation[1] that the range of electronic ordering is longer than that of ionic ordering to invoke electron correlations also; these tend to drive electrons as far apart as possible and this is satisfied by their striving to order on a lattice. Of course, even in Wigner's low density jellium model, the Madelung energy difference favouring the body-centred cubic ordering over face-centred cubic is very small and therefore it is easy to understand how relatively weak electron-ion interaction, as in the alkalis, can lead to a different type of local coordination of electrons from that in low density jellium.

We now turn to our proposed model to explain the findings of Refs. 1–3. In arriving at this model, we have examined the X-ray diffraction pattern to be expected from a number of different models for the arrangement of bond charges. Models in which bond charges are placed between (a) all near-neighbour ions or (b) all next near-neighbour ions can be excluded. This is because, unless one breaks the correlations between first neighbour ions, one will necessarily obtain a diffraction pattern characteristic of a body-centred-cubic structure. Such a breaking of correlations has in fact been examined but still does not lead to a face-centred cubic diffraction pattern.

However, a model that does lead to face-centred-cubic reflections is to consider bond charges between each ion and four of its near-neighbours, in a tetrahedral configuration. In the language of chemical hybridization, we could think of mixing 3s and 3p atomic orbitals in Na, with sp^3 hybridization. We caution again that atomic orbitals are however very poor as a starting point for Na, Wannier orbitals being the proper tool.[4] This is made quite clear from the fact that, in crystalline Na one must add up many longer and longer bonds to regain the known, almost uniform, distribution in the crystal for the valence electrons.

The tetrahedral configuration we therefore propose is shown in the figure. The electron "bond charges" add up to a face-centred cubic lattice.

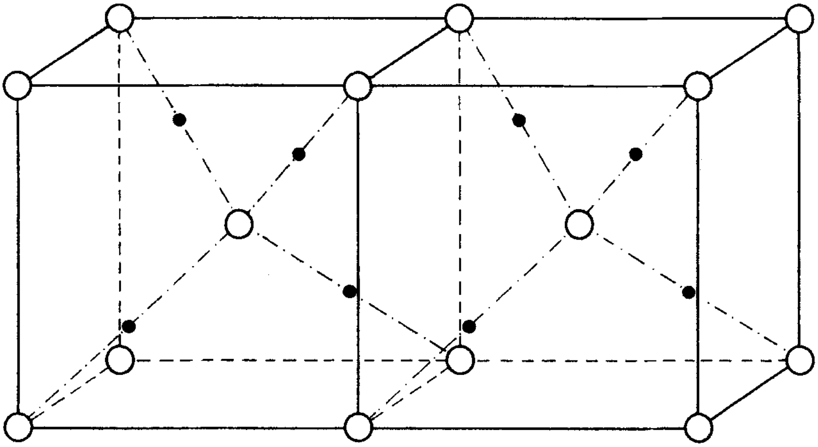

FIGURE 1 Shows lattice model for electron-ion and electron-electron correlations in body-centred cubic metal. Open circles. Alkali metal ions. Dots. Electron bond charge centres on bonds joining ion at body centre to four near neighbours in a tetrahedral configuration. We stress that, of course, the bond charges have a profile determined by the overlap of Wannier orbitals.

The "unoccupied bonds" to the remaining four corners of the cube from the body-centre would have to resonate with those drawn in the figure, in the manner of Pauling. But, we must stress that Pauling's picture is not tenable in the crystal for Na and K because with long-range ionic order the Wannier functions are of such long range that longer and longer "bonds" have to be included. This is not meaningful in the liquid however, because of the known short-range order among the ions.

3 DISCUSSION AND SUMMARY

Of course, as Egelstaff *et al.*[1] have emphasized, the observed systematic diffraction differences we are considering are quite small. That is why it is so important to difference the neutron and X-ray data, because one has thereby subtracted out from the X-ray data the major component of the scattering due to the almost spherical ionic charge clouds centred on the nuclei. In case it might seem that the model we propose has such pronounced directionality that it could lead to totally different X-ray scattering from that of spherically averaged electron clouds placed on the nuclei, we record in the Appendix a lattice model based on extreme angularity of the blobs of electron charge centred on the nuclei, namely such that the charge is bunched entirely along bonds. Corrections of a few percent due to angularity are typical at the lowest order reflections.

To summarize, a model has been proposed here to account approximately for both electron-ion and electron-electron correlations in liquid Na and K near to the freezing point. All important to the argument is that the nuclear structure factor $S(k)$, as determined experimentally by neutron scattering, is reflecting local ionic coordination typical of the body-centred-cubic lattice. This we regard as established experimentally and as understood from basic theory.[5–7]

The burden of our argument then rests on the way in which the electrons distribute themselves in the presence of such local coordination. It is well known that in a body-centred-cubic Na crystal the valence electron distribution is almost uniform. Following Ref. 4, it has been stressed that, in a Wannier representation, such a uniform distribution is to be built up only by including many longer and longer bonds, or in the language of Ref. 4, many superlattices of bond centres.

Assuming that some local, Wannier-like, distribution is still appropriate in the liquid, no doubt with some damping of the long-range oscillations in the crystal Wannier orbitals due to finite electronic mean free path effects, which result in Fermi surface blurring,[9] it is argued that a directional description locally, consistent with sp^3 type hybridization, is required to conform with the local ionic short-range order. The short-range order thereby imposed on the electrons due to electron-ion correlations is then, it is argued, propagated by electron-electron repulsions into a Wigner-lattice type order over a longer range of 30–40 Å.

Naturally the valence electrons in the liquid are still itinerant and so no complete Wigner localization can actually be occurring. What the diffraction data reveals is that, in the low-density alkalis, one is already seeing, in the difference of structure factors, interesting effects due to both electron-ion and electron-electron correlations.

We want to stress that markedly different behaviour, if our model is correct, for electron-ion and electron-electron correlations is to be expected for nearly-free electron metals and in tight-binding metals. In the latter category, we would place the light metals Li and Be, because there are no *p* electrons in the core against which to pseudize the valence electrons. Our model would leave the local electron distribution in Li quite like that in the solid (because of short range Wannier orbitals) and this would account for the fact that the density of electronic states at the Fermi surface in liquid Li is much nearer to that in the solid than it is to a nearly-free electron value.[10] X-ray and electron diffraction experiments on Li are evidently quite practical but neutron absorption remains a problem for this metal. Be, unfortunately, being toxic, presents huge experimental problems but if these could be overcome we believe this metal, known to exhibit large angularity in its electron cloud in the crystal,[11,12] would also reveal very worthwhile information on electron-ion and electron-electron correlations.

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Appendix

Extreme directional model of scattering from a lattice of localised electron density distributions.

We summarize here a model of a lattice in which the electron charge is bunched entirely along bonds, but in which the total periodic density is built from localised distributions, say $\sigma(\mathbf{r})$, in a body-centred cubic lattice through

$$\rho(\mathbf{r}) = \sum_i \sigma(\mathbf{r} - \mathbf{R}_i) \tag{A1}$$

where $\mathbf{R}_i$ denote the direct lattice vectors. Since we wish to establish only a semi-quantitative point, consider for simplicity only the next-nearest neighbour bonds. Then $\sigma(\mathbf{r})$ can be chosen, with extreme angularity, such as in the bond network model of crystals, as

$$\sigma(\mathbf{r}) = n(r)[\delta(x)\delta(y) + \delta(y)\delta(z) + \delta(z)\delta(x)] \tag{A2}$$

which bunches the electrons purely on the cubic axes. Such a model has been employed earlier in connection with *d*-electron directionality in body-centred-cubic transition metals like Fe and Cr by Freeman and Weiss.[13]

The spherical average $\overline{\sigma(\mathbf{r})}$ is proportional to $n(r)/r^2$ and if we model $n(r)$ by a form

$$n(r) = \mathrm{A}r^2 \exp(-\alpha r) \tag{A3}$$

it is easy to compare the X-ray form factors for spherically averaged and for extreme directionality models. Corrections of a few percent due to angularity are typical at the lowest order reflections, as can be seen from the work of Freeman and Weiss.[13]