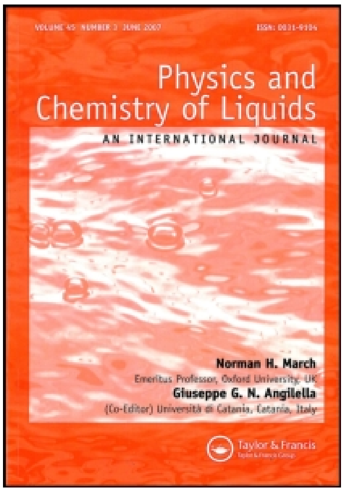

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Spatial Ordering of Conduction Electrons in Metals from Liquid Phase Diffraction

N. H. March[a]
[a] Theoretical Chemistry Department, University of Oxford, Oxford, England, UK

To cite this Article March, N. H.(1987) 'Spatial Ordering of Conduction Electrons in Metals from Liquid Phase Diffraction', Physics and Chemistry of Liquids, 17: 3, 173 — 180

To link to this Article: DOI: 10.1080/00319108708078554

URL: http://dx.doi.org/10.1080/00319108708078554

Phys. Chem. Liq., 1987, Vol. 17, pp. 173-180
Photocopying permitted by license only

Printed in the United Kingdom

Review Article

Spatial Ordering of Conduction Electrons in Metals from Liquid Phase Diffraction

N. H. MARCH

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

(Received 29 May 1987)

Egelstaff, March and McGill proposed the idea that electron-electron correlation functions for conduction electrons in liquid metals could be extracted from experiment by combining X-ray, neutron and electron diffraction studies. Though electron diffraction studies are still only in early stages of development, evidence has nevertheless gathered that conduction electrons have a significant degree of ordering near the melting point of liquid metals. In the latter part of the review, this conclusion is brought into contact with current ideas on strongly correlated electronic ground states in crystalline metals. In both areas, resonating bonds proposed by Pauling seem an essential ingredient in understanding the electronic behaviour.

KEY WORDS: Conduction electrons, spatial ordering, electron diffraction, resonating bonds.

1 INTRODUCTION

Almost fifteen years ago, Egelstaff, March and McGill[1] (referred to below as EMM) proposed the idea that electronic correlation functions for the conduction bands of liquid metals could be extracted by combining X-ray, neutron and electron diffraction experiments.

In the present review, the principles underlying this proposal are briefly summarized in Section 2 below. Since, unfortunately, high quality electron diffraction data to complement X-ray and neutron studies is still lacking, Section 3 is concerned with what might be gleaned presently, near the melting point of liquid metals, by combining the available X-ray and neutron data. While a number of difficult points remain to be clarified, as discussed from a theoretical angle by Chihara[2] very recently, and from an experimental standpoint by Steeb and co-workers,[3] yet evidence remains in support of the major conclusion of the work of EMM that conduction electrons in "simple" sp metals exhibit, just above the melting temperature, spatial ordering which, though certainly short-range, nevertheless extends over larger distances than the short-range ionic order.

Accepting this conclusion as starting point, even though it cannot be quite decisive until confirmed by adding suitable electron diffraction data to the analysis, a model appropriate for liquids Na and K, due to March and Tosi[4], will be described. This appeals to (a) Pauling's resonating valence bond ideas and (b) incipient tendency of electrons in these low density metals to correlate in a manner which is a precursor to Wigner lattice ordering[1] in the insulating phase expected if the density could be further lowered.

In Section 4, an attempt is made to bring this type of picture into contact with both experiment and very recent theoretical ideas relating to ground-state properties of conduction electrons in crystalline metals. Be is the simple metal most extensively studied experimentally. Matthai *et al.*[5] proposed an early interpretation of Bragg reflection data in terms of bonding, described by localized orbital theory. However, Messmer[6] has recently proposed an alternative explanation in terms of a strongly correlated ground state in which appeal is again made to Wigner lattice-type correlations, as well as to a very chemical picture. Section 5 contains some proposals for areas deserving further study.

2 CORRELATION FUNCTIONS AND DIFFRACTION DATA

EMM demonstrate that the cross-sections for X-ray and electron scattering reduce to

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_x = (\mathrm{const})S_x(q) \tag{2.1}$$

and

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_e = \frac{(\mathrm{const})}{q^4}S_e(q) \tag{2.2}$$

while that for neutron scattering can be written

$$\begin{aligned}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_n &= (\mathrm{const})S_n(q)\\ &= (\mathrm{const})S_{ii}(q).\end{aligned} \tag{2.3}$$

In terms of these "experimental" structure factors S_x, S_e and the ion–ion correlation function $S_{ii}(q)$ determined directly by the neutron scattering experiment, the valence–valence electronic correlation function $S_{ee}(q)$ can be expressed (cf. Eq. (12) of Ref. 1).

The data, however, must be accurate and reliable since the terms expressing the difference between S_x and $f^2(q)S_{ii}(q)$, with f the form factor of the ion, are "corrections" involving the desired electron–ion and electron–electron correlation functions. A similar situation obtains for the difference between $S_e(q)$ and $f_e^2(q)S_{ii}(q)$, where

$$f_e(q) = Z - f(q) \tag{2.4}$$

with Z the atomic number. Thus, given "experimental" data for S_{ii}, S_x and S_e as functions of q for the three different types of experiments, the electronic correlation function $S_{ee}(q)$ in particular can be extracted.

3 PRELIMINARY EVIDENCE OF ELECTRONIC ORDERING FROM X-RAY AND NEUTRON DIFFRACTION DATA

EMM emphasized the importance of amassing diffraction data for X-rays, electrons and neutrons on the same liquid metal; preferably a light metal (see also Ref. 2) to maximize valence effects relative to core scattering for X-rays and electrons. To date though, electron diffraction data of a quality to match the X-ray and neutron data on, for example, Na and K, is lacking. Therefore, following EMM, it is worthwhile to difference this data. In EMM this was done at the principle peak of the structure factor. Dobson[7] subsequently pressed essentially the same analysis as a function of momentum transfer q on liquid Na and Al, as also did Johnson[8] on K.

March and Tosi[4] subsequently gave an interpretation of this data from Refs 7 and 8 which is interestingly related to proposals being utilized currently in relation to high temperature superconductivity theory in crystalline metals.[9,6] We therefore discuss the main points of their model here.

3.1 Model of diffraction from liquid Na and K near melting temperature invoking strong electron–electron correlations plus chemical picture of resonating bonds

Dobson[7] on liquid Na, and Johnson[8] on liquid K, both using data near the melting point, have argued for the existence of face-centred-cubic type reflections in the difference diffraction data for these metals.

March and Tosi start out from a near-neighbour coordination in liquid Na say, just above the melting point, which is characteristic of a body-centred cubic lattice. Their proposed model was arrived at by examining 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, of necessity, obtain a diffraction pattern characteristic of a body-centred cubic structure. Such a breaking of correlations was in fact examined[4] but still does not lead to a face-centred cubic diffraction pattern.

However, the model of March and Tosi,[4] 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, one could think of mixing $3s$ and $3p$ atomic orbitals in Na, with sp^3 hybridization.

The tetrahedral configuration proposed therefore by March and Tosi is shown in Figure 1. The electron "bond charges" add up to a face-centred cubic lattice. The "unoccupied bonds" to the remaining four corners of the cube from the body-centre would have to resonate with those drawn in Figure 1 in the manner of Pauling.

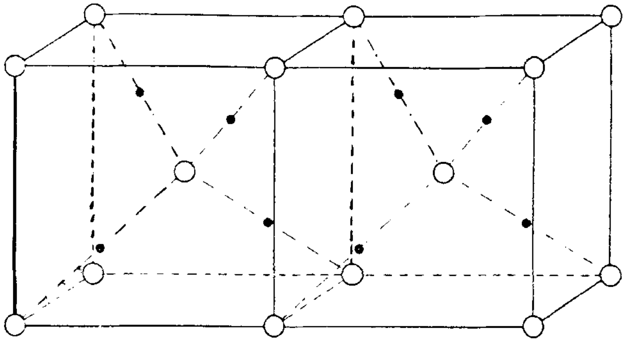

Figure 1 Depicts lattice model for electron-ion and electron-electron correlations in body-centred cubic metals Na and K. Open circles—alkali metal ions. Dots—electron bond charge centres on bonds joining ion at body centre to four near neighbours in a tetrahedral configuration. It is to be stressed, of course, that the bond charges have a profile determined by overlap of appropriate localized orbitals. (After Ref. 4).

4 RELATION TO CURRENT IDEAS ON STRONGLY CORRELATED GROUND STATES IN SIMPLE CRYSTALLINE METALS

Though the emphasis in this article is on the method by which it should be possible, in longer terms, to build up, by combining theory and experiment, a detailed picture of spatial ordering of conduction electrons in liquid metals, it is highly relevant here, in view of extreme current interest in mechanisms for high temperature superconductivity, to relate this topic to recent ideas on strongly correlated ground-state descriptions of simple crystalline metals.

Following earlier work by Anderson,[9] who also appeals in crystalline metals to the ideas of Pauling used above in the liquid Na model, Messmer[6] has given a discussion of ideas which, as in the discussion of liquid Na and K above, combine Wigner-type electron–electron correlations with a chemical viewpoint.

While Messmer also discusses a monovalent crystalline metal Cu in this context, let us turn to consider his proposed picture of the light divalent metal Be, already referred to. Messmer uses the wurtzite structure of BeO as starting point. As he emphasizes, this structure can be viewed as two interpenetrating hexagonal close-packed (*hcp*) lattices; he then proposes to replace each 0 atom with a pair of electrons localized in this vicinity. This leads to an hcp Be lattice with electron pairs in tetrahedral interstices of the lattice such that each Be atom has four electron pairs at tetrahedral positions. Messmer views this array of electron pairs as a kind of Wigner lattice which might be a useful zeroth order model in describing a strongly correlated ground state of Be metal. Messmer uses this as a starting point to give a discussion of (a) the charge density of Be metal and (b) a simple qualitative discussion of superconductivity in Be, by using an analogy with resonance between the two Kekulé structures of the benzene molecule, where ring currents and large diamagnetism are well known.

In this present context, we do not know of any data that has so far been susceptible to analysis of electronic correlations on divalent metals (Mg might be an interesting case, Be being a toxic material), and therefore we return to Dobson's use of the EMM proposal as applied to liquid Al near its melting temperature. While his analysis, as repeatedly stressed, cannot be quite decisive, for as EMM[1] observed, three experimental quantities are evidently needed to extract ion–ion, electron–ion and electron–electron correlation functions unambiguously, it is nevertheless suggestive that he can interpret the diffraction data in terms of a specific close-packed structure. This is the "original" BiF_3

structure,[10] but with electrons, only, in the vicinity of the sites occupied by fluorine. As he points out,[7] if the peaks he displays in his Figure 2 are indexed on this basis, a close-packed BiF_3-type structure of lattice parameter (4.3 ± 0.1) Å results. This is close to the value 4.13 Å expected if the three valence electrons per atom in Al are distributed on such a lattice. It is, of course, tempting to take this as some evidence which supports Messmer's ideas, designed however very recently to describe strongly correlated electronic ground states in crystalline metals.

5 CONCLUSIONS AND DIRECTIONS FOR FUTURE WORK

It is tempting, though obviously not quite decisive, because three experiments are needed to extract three correlation functions as already stressed above, in a liquid metal where a sharp distinction can be made between core and valence electrons, to conclude that there is evidence in favour of spatial electronic ordering in the "difference" diffraction data from X-ray and neutron studies (see, however, Ref. 2). For liquid Na and K near melting, an attractive picture which is consistent with available data combines Pauling's picture of resonating bonds with electron–electron correlations which are usefully thought of as the precursor to formation of a Wigner electron crystal[11] if the electron density in Na or K could be further lowered.

Be is obviously a metal of considerable interest, but because of its toxic nature it presents very basic problems for diffraction studies in the liquid phase. However, two ways of interpreting the Bragg data on crystalline Be appeal to directional bonding: though the discussion of Matthai *et al.*[5] presumably now needs refinement or change to incorporate resonating bonds. Messmer's more recent discussion, while incorporating this feature, invokes also the tendency of electrons to correlate in a Wigner-like fashion. The possible relation of all this to liquid phase data on trivalent Al near melting has been emphasized: lattice-like ordering of electrons is again the tempting conclusion to draw; though the order is surely short-range; not genuinely long-range order.

In concluding this article, some questions that need addressing seem to be:

i) In a strongly correlated electron assembly with spatial order, what can constitute off-diagonal long-range order?

ii) Is it useful, as a picture, to think of both electrons and ions in a crystal like Be or Al as "lattice-like," and if so is it to be inferred from the liquid phase diffraction studies reviewed here that the ions "melt" before the electrons (e.g. in liquid Na, K and Al). A rough, though obviously crude, analogy would be with the superionic transition in say $BaCl_2$.

iii) Do we need to radically rethink theories of conduction even in the liquid state, in spite of the success of the nearly free electron theory of transport in liquid metals? Transport in the Wigner limit may be relevant; but most important, Pauling resonance must be an essential ingredient also of a highly correlated metallic phase.

Notwithstanding the above questions, it will obviously greatly accelerate progress in understanding electronic correlation functions in liquid metals if experimentalists are willing to give a good deal more attention to refining electron diffraction data[12–14]. As stressed already, this is not only of considerable interest for the fundamental theory of liquid metals as two-component systems[15,2] but may also perhaps provide rich returns in helping to build up realistic models of strongly correlated ground states in crystalline metals. If that proves to be the case, it might just turn out that liquid metal studies can help to clarify outstanding fundamental questions pertaining to new mechanisms of superconductivity but that, of course, unlike the diffraction proposals of EMM round which this review is built, is a speculative, not to say highly controversial, matter at the time of writing.

Acknowledgement

The writer wishes to thank Dr Yu Lu for a stimulating discussion at ICTP Trieste, during which attention was drawn to Messmer's work. Thanks are also due to Professor J. Callaway for sending the writer a preprint of his paper on resonating valence bond model studied by a cluster calculation using the Hubbard Hamiltonian.

References

1. P. A. Egelstaff, N. H. March and N. C. McGill, *Can. Jour. Phys.*, **52**, 1651 (1974).
2. J. Chihara, *J. Phys.*, **F17**, 295 (1987).
3. See, for instance, H. Olbrich, H. Ruppersberg and S. Steeb, *Z. Naturforschung A. Phys. Chem.*, **38**, 1328 (1983).
4. N. H. March and M. P. Tosi, *Phys. Chem. Liquids*, **10**, 113 (1980).
5. C. C. Matthai, P. J. Grout and N. H. March, *Phys. Letts*, **68A**, 351 (1978); see also *J. Phys.*, **F10**, 1621 (1980).
6. R. P. Messmer, private communication to Yu Lu, and to be published (1987).
7. P. J. Dobson, *J. Phys.*, **C11**, L295 (1978).
8. M. W. Johnson, private communication (cf. Ref. 4).
9. P. W. Anderson, *Science*, **235**, 1196 (1987).
10. R. W. G. Wyckoff, Crystal structures, Vol. 2 (New York: Wiley: Interscience), p. 67 (1964).

11. See the review by C. M. Care and N. H. March, *Adv. Phys.*, **24**, 101 (1975).
12. A. S. Brah, B. A. Unvala and L. Virdhee, *Phil. Mag.*, **B40**, 335 (1979).
13. A. S. Brah, P. J. Dobson, N. H. March, B. A. Unvala and L. Virdhee, *Inst. Phys. Conf. Ser.*, No. **41**, 430 (1978).
14. A. S. Brah, L. Virdhee and N. H. March, *Phil. Mag.*, **B42**, 511 (1980).
15. N. H. March and M. P. Tosi, *Annals of Physics*, **81**, 414 (1973).