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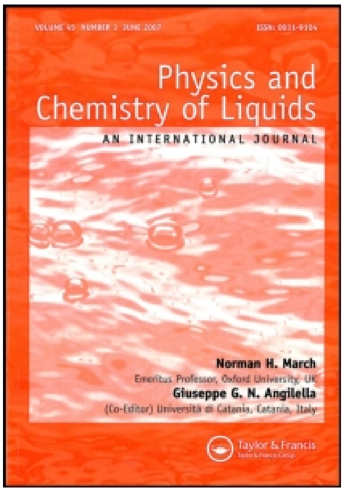

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
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To cite this Article March, N. H.(1989) 'Electron Correlation, Chemical Bonding and the Metal-Insulator Transition in Expanded Fluid Alkalis', Physics and Chemistry of Liquids, 20: 4, 241 — 245
To link to this Article: DOI: 10.1080/00319108908028455
URL: http://dx.doi.org/10.1080/00319108908028455

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Phys. Chem. Liq., 1989, Vol. 20, pp. 241–245
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ELECTRON CORRELATION, CHEMICAL BONDING AND THE METAL-INSULATOR TRANSITION IN EXPANDED FLUID ALKALIS

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(Received 7 February 1989)

Experimental data which demands that one transcends the 'method of neutral pseudoatoms' for expanded alkali metals is first summarized. A chemical 'bond' provides a more basic building block than a pseudoatom. This 'bond' can be characterised by potential curves ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ of the appropriate free-space diatom (e.g. Na_2) plus local coordination properties. The relation to the metal-insulator transition is thereby discussed as the coordination number reduces to 2.

KEY WORDS: Coordination number, Peierls transition.

A simple picture, on which the 'nearly free electron' (NFE) theory of electrical conductivity of s-p liquid metals is based[1,2], views the conduction electrons in plane wave states as scattered by an array of weak spherical ionic pseudopotentials arranged in accord with the known short-range ionic order. While in no way denying the successes of this viewpoint, work on expanded fluid alkali metals has shown that its range of validity is severely limited. Thus departures from this picture can be demonstrated as follows:

i) No spherical pseudoatom model[3] can explain the diffraction data[4] on liquid Na[5] and K[6].

ii) No explanation is afforded by such a model of the results obtained by combining magnetic susceptibility[7] and Knight shift[8] data. This shows that the probability density at the (Cs) nucleus of Fermi level electrons relative to the free atom decreases as the density is lowered[9].

iii) The NFE electrical conductivity theory[1,2] breaks down severely as one moves along the liquid–vapour coexistence curves of the heavy alkalis Rb and Cs[10], towards the critical density d_c.

Chapman and March[11] have utilized the discontinuity, q say, at the Fermi surface of the momentum distribution $n(p)$ to interpret the maximum in the susceptibility of Cs, showing that at the corresponding density, q was 0.5 in the electron gas (jellium) model and about 0.2 in Cs at the maximum of the magnetic susceptibility, this being estimated from

$$k_B T_{\max} \sim q E_f \tag{1}$$

with E_f the Fermi energy. This small value of q is consistent with strong electron-electron correlations as the critical density d_c is approached, while the major difference from the jellium value testifies to the simultaneous importance of electron-ion interaction. In their work, Chapman and March[10,12] write the conductivity in terms of the first-order density matrix, and thereby develop an expansion of the data in a power series in q, around the metal-insulator transition. This approach seems to give the gist of the experimental data.

Because of the factors (i)-(iii) above, it is obviously necessary to adopt another approach than pseudoatoms to describe the expanded alkalis. The treatment below will be motivated by the model of March and Tosi[13], who showed that the use of sp^3 hybridization for normal liquid Na and K, combined with Pauling's resonating valence bond[14] approach, could allow an interpretation of the diffraction data discussed in Refs 3-5.

This chemical bonding point of view, as will be argued below, is now strongly supported by the extensive ionic structural data on the heavy alkalis along the coexistence curve, and especially on fluid Cs which will be a focal point below. The neutron scattering experiments at high temperatures and pressures thereby required have been reviewed very recently by Winter and Bodensteiner[15] as well as by Winter and Hensel[16]. The former workers write 'in comparison to the strong density dependence of the number of nearest neighbours, the distance of nearest neighbours remains almost constant during the expansion'.

An explanation of such behaviour is afforded, as partly anticipated by Warren and Mattheiss[9], by employing a quasicrystalline model of the liquid structure. Then they point out that the coordination number z varies almost linearly with density d and that useful models are given by $z = 8$ body-centred cubic (BCC), $z = 6$, simple cubic (SC) whereas for $z = 4$ both simple tetragonal and diamond structures were considered. Their data relating z and d has been extrapolated linearly to the critical density $d_c = 0.38 \mathrm{g/cm}^3$, with a resulting coordination number near to $z = 2$. This will be argued to motivate a model of the metal-insulator transition below, but for the moment let us note that d_c at $z = 2$, plus the Warren-Mattheiss data[9] for z vs. d is well fitted (to $< 2\%$) by

$$d_{\text{liquid}} = az + b \tag{2}$$

where $a = 0.23$ and $b = -0.08$, both in g cm^{-3}.

The constancy of the near-neighbour distance along the Cs liquid-vapour coexistence curve suggests, when coupled with the work of March and Tosi[13] on liquid Na and K, a chemical 'bond' as a basic building block and this is the point now to be pressed below.

Of course, in classical chemical arguments, one starts from an arrangement of nuclei, and then hybridizes appropriately: in Ref 13 one adopted a BCC arrangement of the ions and tetrahedral directionality plus resonance. This has prompted us to adopt the study of Malrieu *et al.*[17] of crystalline Na to the alkali fluids. This is not as drastic as it might sound, since the arguments of Ref. 17 rest, in fact, purely on consideration of first and second neighbours to a chosen Na ion. These workers, following ideas of Poshusta and Klein[18] on hydrogen, set up a Heisenberg Hamiltonian for Na which was characterized by the ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ potential curves of the free space diatom Na_2. These were taken, in fact from the semi-empirical study of Konawalow *et al.*[19] and were then used to calculate the energy as a function of near-neighbour distance r for both BCC and SC structures. Their results[17] can be summarized as follows:

$$E_{\mathrm{BCC}}(r) = 4R(r) + 3R\left(\frac{2}{\sqrt{3}}r\right) - 4g(r)[1 + f(r) - 15f(r)^3] \tag{3}$$

where[18]

$$R(r) = E({}^3\Sigma_u^+),\ g(r) = [E({}^3\Sigma_u^+) - E({}^1\Sigma_g^+)]/2,$$

with

$$f_{\mathrm{BCC}}(r) = \frac{g(r)}{14g(r) - 12g\left(\frac{2}{\sqrt{3}}r\right)} \tag{4}$$

while

$$E_{\mathrm{SC}}(r) = 3R(r) + 4R(\sqrt{2}r) - 3g(r)[1 + f(r) - 11f(r)^3] \tag{5}$$

with

$$f_{\mathrm{SC}}(r) = \frac{g(r)}{[10g(r) - 16g(\sqrt{2}r)]} \tag{6}$$

It is noteworthy that when $E_{\mathrm{BCC}}(r)$ and $E_{\mathrm{SC}}(r)$ above are used to calculate the equilibrium near-neighbour distance one obtains for Na the values[17] $r_{\mathrm{BCC}} = 7.07$a.u and $r_{\mathrm{SC}} = 6.82$a.u which are remarkably close in spite of the very different densities. The experimental value for normal BCC Na is 6.99a.u.

Equations (3) and (5) respectively can be viewed as characterizing the 'bonds' in BCC and SC structures by the properties of the diatom Na_2 determining $R(r)$ and $g(r)$, plus the near-neighbour and second neighbour coordination, the equilibrium r_{BCC} being a factor of 1.2 larger than the free-space molecular bond length.

This characterization in terms of the free-space diatom Na_2 now prompts one to return to the result (2) for fluid Cs, and to discuss its relation to the metal-insulator transition. First, it is helpful, in contemplating the way that the two-component liquid metal built from Cs^+ ions and electrons e^- could eventually have structure with coordination number $z = 2$, to refer to the classical counterpart of a mixture of charged hard spheres and neutralizing point ions studied by Gillan *et al.*[20] by Monte Carlo simulation. For strong coupling, it is demonstrated there that polymerization can occur.

Returning to the quantum-mechanical case of a linear chain of, say, Cs ions, one has from Peierls theorem that there will be a bond length distortion, since a one-dimensional metal cannot exist. Here then is a mechanism for the metal-insulator transition, which can be expected to coincide with the critical point. This seems to be consistent with presently available data.

In summary, a metallic 'bond', defined by Eqs. (3) and (5) for BCC and SC coordination, emerges as a valuable building block for treating the expanded alkali metals. It relates these directly to properties of the free-space diatoms through the potential curves of the $^3\Sigma_u^+$ and $^1\Sigma_g^+$ states, as well as to local coordination. It emerges that, through Eq. (2), the metal-insulator transition can be understood as occurring at coordination number 2, representing a linear chain. It is then argued that a Peierls distortion will occur, leading to alkali diatoms at a free-space equilibrium bond length which is reduced from that of the metallic 'bond'. This is consistent with what is known about dense Cs vapor which consists of atoms and diatoms[7] whose ground states are spin singlets.

Evidently future structural studies using X-rays and electrons[4] to complement existing neutron data along the coexistence curves of the fluid alkalis will be of considerable interest. If the present viewpoint is supported, one can expect in the difference diffraction data a changing pattern as the ionic coordination is altered by moving towards the critical point. But with presently available neutron data, kindly supplied by Professor F. Hensel in advance of publication, J. Ascough and the writer are presently extracting ionic interaction potentials by inverting the neutron structure data along the coexistence curve for Cs, employing the method proposed by Johnson and March[21], which has recently been brought to full fruition for normal liquid Na by Reatto[22] and coworkers.

Acknowledgements

This work was started during the latter part of a visit to IBM, San Jose, in the Winter of 1988. Thanks are due to Drs F. Herman and J. B. Torrance for their kind hospitality during this visit. The work was completed at UCSD, La Jolla and grateful thanks are due to Professors H. T. Hammel and A. A. Yayanos of the Scripps Institution of Oceanography for making this stay possible. Finally, the writer is most grateful to Richard Chapman and John Ascough for many valuable discussions on the area embraced by this work.

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