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Metal–Ammonia Solutions

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ABSTRACT

In dilute solutions of alkali metals in ammonia electrons are localized in cavities in the solvent, and thermodynamic and transport properties are very similar to those found for dilute solutions of strong electrolytes. At higher concentrations the properties deviate markedly from those of electrolyte solutions and approach those of a liquid metal. In this paper we propose an explanation for cavity formation, and discuss the metal–non-metal transition in the light of recent information about the transition in vanadium oxides and doped semiconductors.

§ 1. INTRODUCTION

THE properties of metal–ammonia solutions have recently been reviewed by Cohen and Thompson (1968 ; this paper will be referred to as CT) and by various contributors to the Cornell conference (Colloque Weyl II, Cornell University, June 1969). The purpose of this paper is to propose some further tentative models for the observed phenomena. In particular we give what we believe to be a new explanation of the formation of cavities around electrons in dilute solutions, and we discuss the metal–non-metal (MNM) transition for this material, comparing it with very recent information about the transition in vanadium oxides and doped semiconductors.

§ 2. CAVITIES AND BJERRUM DEFECTS

The most striking properties of dilute solutions of alkali metals in ammonia are :

(*a*) The metal atoms dissociate into solvated cations and solvated electrons.

(*b*) The solvated electrons produce a marked expansion of the liquid.

(*c*) The solvated electrons are responsible for a broad optical absorption line in the near infra-red (CT, fig. 3).

The current explanation, due to Jortner (1959), of property (*c*) (which we accept) is that a cavity of radius R is formed in the ammonia and round this cavity the medium is polarized by the charge of the electron; the potential round the charge is:

$$\left.\begin{aligned} V(r) &= -e^2/\kappa_{\mathrm{p}} r, \quad r > R, \\ V(r) &= -e^2/\kappa_{\mathrm{p}} R, \quad r < R, \end{aligned}\right\} \qquad (1)$$

where

$$\frac{1}{\kappa_{\mathrm{p}}} = \frac{1}{\kappa_\infty} - \frac{1}{\kappa}$$

and κ and κ_∞ are the low and high frequency dielectric constants of the medium (CT, fig. 6). The absorption band is due to the 1s–2p transition in this potential well. The analogy with the polaron well (Austin and Mott 1969) is very close.

We know however of no satisfactory explanation in the literature of why a cavity is formed. CT introduce a potential energy V_0 which is that of an electron at rest in the conduction band of the liquid†. In helium V_0 is large (>1 ev) and positive and this is why a cavity is formed when electrons are introduced into the conduction band of liquid helium; energy equal to V_0 is given up when an electron moves from the conduction band into a vacuum, and this is sufficient to overcome the surface energy of the cavity and the kinetic energy $\sim \frac{1}{2}\hbar^2\pi^2/mR^2$ which would result from localization in a sphere. But CT give reasons for thinking V_0 to be small in ammonia.

Mott (1967) suggested that V_0 might be large enough to produce the cavity; this conclusion was due to a numerical mistake. CT (§ 2) argue that for ammonia $V_0 \simeq 0$. Blandamer, Catterall, Shields and Symons (1964) have pointed out that the energies of the absorption bands at room temperature for both solvated electrons and solvated iodide anions are shifted strongly to higher values (by 1·0 and 0·8 ev respectively) when the solvent is changed from ammonia to water. Platzman and Franck (1954) and Stein and Treinin (1959) have described the absorption spectrum of iodide anions in solution in terms of a model for the excited state which is formally very similar to that described by Jortner (1959) for solvated electrons. A solvent shell is polarized around a cavity of radius R' which encloses the iodide anion. The excited state then corresponds to an electron detached from the iodide anion (requiring energy equal to the ionization potential of iodide, $\sim$3·15 ev), leaving a much smaller and uncharged iodine atom, and an electron trapped in a potential well similar to that described by eqn. (1). Relaxation of the solvation shell on to the small iodine atom during the absorption process is prohibited by the Franck–Condon principle.

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† We believe that a conduction band with fairly sharp lower limit is a satisfactory concept for liquids in which the electron wave function is s-like, as it will be in argon, ammonia, water, etc. (cf. Mott 1969 a).

Blandamer *et al.* (1964) ignored the κ_p^{-1} term and treated the two systems by a simple 'particle in a box' approach. They attributed the shifts in absorption maxima to increases in the radii R and R' on changing the medium from ammonia to water. The increases in R and R' required to fit the observed absorption energies were 35 and 20%, as shown below :

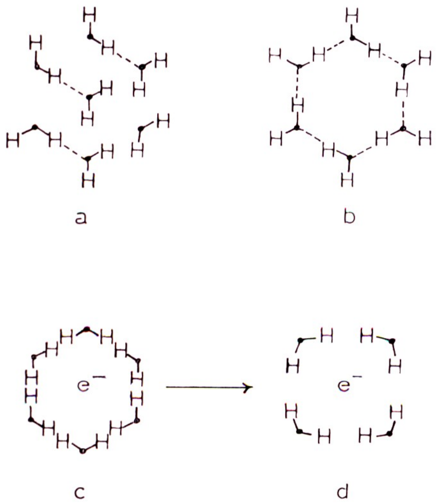
	Iodide		Electron	
	NH_3	H_2O	NH_3	H_2O
E_{max} (ev)	4·69	5·49	0·68	1·72
R and R' (Å)	4·0	4·9	4·7	7·5

Mott (1967) ignored any changes in R and attributed the shift to a difference in V_0 for the two solvents, i.e.

$$V_0(H_2O) - V_0(NH_3) \simeq 0{\cdot}8 \text{ ev}.$$

We presume both factors are operative to some extent. The importance of avoiding the formation of Bjerrum defects in polarized solvent shells (see below) suggests that the greater density of protons in ammonia might lead to larger cavities in this solvent.

Fig. 1



Schematic representation of electron solvation in liquid ammonia (Catterall 1969). (*a*) Normal liquid ammonia structure ; (*b*) normal structure surrounding a vacancy defect ; (*c*) vacancy defect with solvent shell polarized around a central negative charge ; (*d*) shell dilution to minimize Bjerrum defects.

It is not immediately clear, however, why the electron should not form a ‘ large polaron ’ (Austin and Mott 1969) without forming a cavity at all†. We suggest that the reason for the formation of a cavity is that any sharp change of direction of the polarization is equivalent to a ‘ Bjerrum defect ’ (Bjerrum 1951), namely a site at which the positive charges on two adjacent molecules point towards each other. The energy of such defects in ice is ~0·34 ev (Jaccard 1959) and various authors (Blandamer, Shields and Symons 1964, Keven *et al.* 1968, Weiss 1969) have postulated that a water molecule or a hydroxide ion must be absent in ice in order that an electron may be trapped by a potential of type (1). The cavity is formed, then, by the repulsion between the charges on water or ammonia dipoles polarized in opposite directions. It may well be that the true cavity in ammonia occupies the volume of only a single solvent molecule, and the remaining decrease in density is due to a lower coordination number in the surrounding shell of molecules. An estimate of the density of solvent in the region immediately surrounding the electron was obtained from an analysis of magnetic relaxation in metal–ammonia solutions (Catterall 1969). The density ($n{b_{eH}}^{-3}$), where b_{eH} is the average electron–proton separation, decreases from 0·31 Å^{-3} in pure ammonia (Kruh and Petz 1964) to 0·19 Å^{-3} in the electron's solvation shell. Figure 1 shows how this might occur.

§ 3. MONOMERS OR DIMERS ?

As emphasized by Dye (1969) at the Cornell conference, the evidence remains uncertain as to whether a high concentration of dimers is formed (i.e. either two electrons in a single cavity (Catterall and Symons 1966)) which we write e_2 or two closely associated single electron cavities, e_1, bound in a cluster of solvated ions by one or more cations (Gold *et al.* 1962), or the metal anion, M$^-$ (Golden *et al.* 1966). The evidence that dimers are formed is the striking drop in the molar magnetic susceptibility at concentrations above 10^{-4} mole per cent metal (MPM), and the long lifetime of the paramagnetic state with respect to dimerization which is required to account for the low electron spin relaxation rate (Catterall and Symons 1966). The evidence against their existence is that the thermodynamic functions show no evidence of association of electrons to form aggregates higher than simple ion-pairs, M$^+$e$^-$, while the absorption spectrum is shifted only slightly to lower energy as the molar susceptibility drops ; the absorption band position, width, shape and extinction coefficient all remain essentially unaltered by concentration until we approach the MNM transition.

We shall base our discussion of the MNM transition on the hypothesis that on the non-metal side of the transition there is a high concentration

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† By a ‘ large polaron ’ is meant a potential well of type (1) due to polarization, without any cavity ; R being determined in such a way as to minimize the total energy :

$$\tfrac{1}{2}\pi^2\hbar^2/mR^2 - \tfrac{1}{2}e^2/\kappa_p R.$$

of single electrons in cavities, with a strong exchange coupling between them which would, if they were arranged on a crystalline lattice, lead to antiferromagnetism ; the problem of the disordered arrangement, particularly in a liquid where this same exchange interaction must lead to attractive forces, is obviously difficult. We follow CT and Dye (1969) in conjecturing that at intermediate concentrations very loosely bound clusters of e_1 centres must form with even numbers of electrons, and that these are diamagnetic. The long lifetime of the paramagnetic state may arise (Dye 1969, Catterall and Dye 1970) through electron exchange processes of the type :

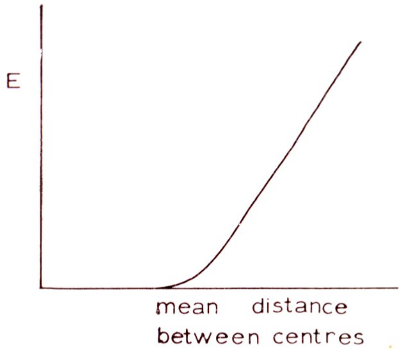
$$e_1^{\alpha} + \text{diamagnetic cluster} \rightarrow \text{diamagnetic cluster} + e_1^{\alpha},$$

which do not interrupt the electron spin state α, or require the lifetime of any particular electron within a cluster to be appreciably longer than the times of normal collisions in solution.

§ 4. THE APPROACH TO THE MNM TRANSITION

It is now abundantly clear that in many materials which show the transition, particularly the vanadium oxides, the ' metal ' near the transition point behaves like a semi-metal in the sense that the carriers are a fairly small number of electrons and an equal number of holes (as in bismuth). The theoretical argument is the following. Suppose one has an assembly of one-electron centres sufficiently far apart that the interaction between them is weak. Then a certain energy E is required to remove an electron from one centre and put it on a distant one. This energy is called the ' Hubbard gap '. Both the electron, and the point from which the electron is missing (the ' hole ') are mobile. As the distance between the centres decreases, E decreases as in fig. 2 (Mott and Davis 1968). In the metallic state, ($E=0$), near the transition, the number of electrons and holes may be quite small. This is particularly apparent in recent work on the metallic phase of V_2O_3 (for refs. see Mott 1969 b),

Fig. 2



Activation energy for conduction in doped germanium (Mott and Davis 1968).

which can be produced by pressure, and in VO_2. In V_2O_3, moreover, there is evidence that the carriers, which correspond to configurations where the vanadium ion is of the form V^{4+} or V^{2+} instead of V^{3+}, have very high effective mass, and one of us (Mott 1969 b) has suggested that this is due to distortion of the surrounding lattice with consequent polaron formation.

If this is a correct description, let us consider what ought to happen in sodium–ammonia as the concentration of metal is increased. If the solvent dipoles were held rigidly in position, the energy, E, required to take an electron out of a cavity and to put it in another cavity (to form e_2) will decrease and eventually vanish as in fig. 2. But in the liquid, when this happens, the first cavity will vanish, and the second (presumably) expand. Thus the MNM transition should show itself by a rapid increase in the number of doubly charged centres, e_2, due to the kinetic energy gained by the ability of the electron to move from cavity to cavity.

We think that the region (1–5 MPM) where the resistivity shows a high temperature dependence (fig. 3 (*a*)) is due to a process of this kind. In the more dilute range ($< 0{\cdot}1$ MPM) the conductivity is well described by the theory of electrolyte solutions (Dye 1969) whilst for concentrations above the MNM transition (> 8 MPM) the transport properties are described adequately by a nearly-free-electron gas (CT) with $m^* \sim m$. In the MNM transition region however, where the conductivity varies exponentially with temperature (CT, fig. 10 (*b*)) we think that this analogy with V_2O_3 is valid. We picture an assembly of singly occupied electron cavities with some disproportionation† to give doubly occupied cavities, e_2, and holes. Unlike the situation in V_2O_3 where both electrons and holes are mobile, the collapse of the polarized shell of ammonia molecules around an unoccupied cavity means that there is nothing corresponding to mobile holes. The observed activation energy W for conduction, when

$$\sigma = \sigma_0 \exp(-W/kT),$$

then arises because the material is not quite metallic and a small value of E (fig. 2) remains *or* alternatively the activation energy may be of a polaron type, because the centres e_1 and e_2 will have different polarization clouds around them and the electrons can only hop when thermal fluctuations make the polarizations equal. We stress that the concentration of carriers may only be a small fraction of the total metal concentration.

The decrease in the ratio $R_{\mathrm{FE}}/R_{\mathrm{meas.}}$, where R is the Hall coefficient (CT, fig. 12) is compatible with either hypothesis, and indicates a small number of carriers in the region 1–5 MPM.

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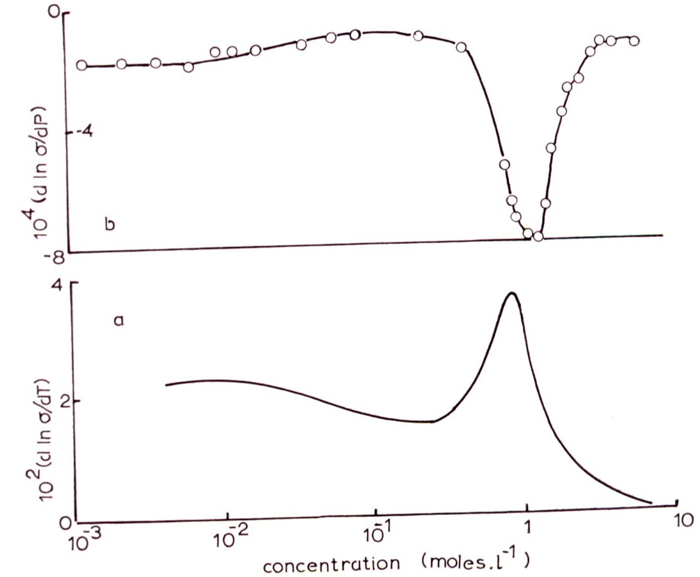
† The disproportionation

$$e_1 + e_1 \rightarrow e_2 + \text{hole}$$

might be described as an equilibrium situation with a mass action constant strongly favouring e_1. This requires that the energy released by the collapse of the polarized solvent shell around the hole is less than the net work required to form a doubly occupied cavity, e_2.

In this region a marked decrease in conductivity with pressure (Schindewolf *et al.* 1966) is observed (fig. 3 (*b*)). At first sight this seems difficult to understand, as pressure should decrease the lattice spacing between molecules and hence the Hubbard gap, making the material more metallic. But in terms of cavities we may perhaps find an explanation. The cavity necessary for e_2 will be bigger than for e_1. Pressure means that additional work must be done to form this large cavity. If the volume of e_2 is *more than twice* as large as for e_1, as is likely in view of the large electrostatic repulsion between two electrons in a cavity and despite the increased binding of solvent dipoles to a di-negative centre, then pressure will increase the quantity which we have called E.

Fig. 3

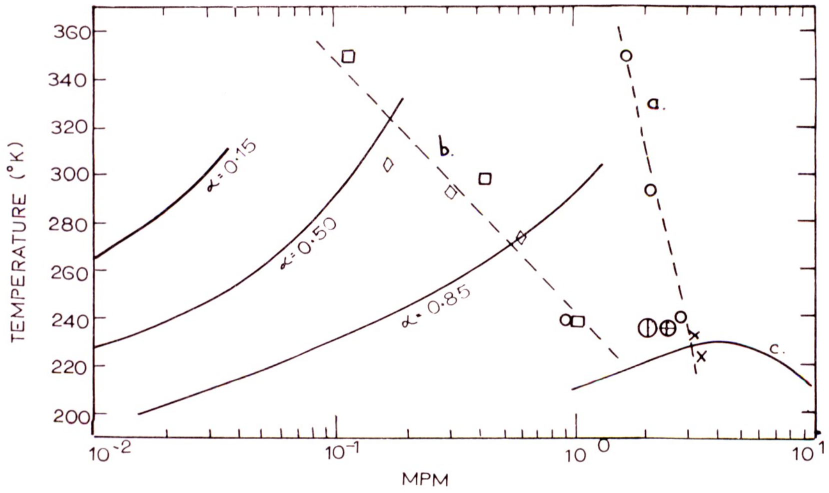


Conductivity in metal–ammonia solutions (Schindewolf *et al.* 1966). (*a*) Temperature dependence ; (*b*) pressure dependence.

Böddeker (1969) has reported the pressure dependence of the area under the electron spin resonance absorption in sodium–ammonia solutions. The change in concentration of unpaired spins, e_1, is $0 \pm 5\%$ over several thousand atmospheres and Böddeker inferred that the spin-pairing process was associated with very little volume change. However, the two electrons in a cavity, e_2, are *not* (we stress) the cause of the drop in molar magnetic susceptibility which arises primarily from the long-range spin exchange interactions between e_1 centres (which are not expected to result in any volume change). A small fraction of e_2 would contribute little to the observed excess volume, although the slight maximum in the excess volume in the MNM region (CT, fig. 4) is consistent with our model. The temperature dependences of the concentrations corresponding to 50% spin-pairing and to the MNM transition (fig. 4) emphasize that the two processes are not related.

The onset of asymmetry of the electron spin resonance signal, which is indicative of the onset of metallic character (Catterall 1965), has a temperature and pressure dependence similar to that of the conductivity: lower pressures (Böddeker 1969) and higher temperatures (Catterall 1965) favour the metallic state.

Fig. 4



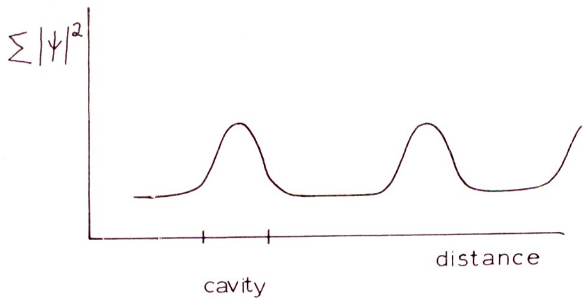
Temperature and concentration dependence of the MNM transition. (*a*) maximum rate of increase of conductivity with increasing metal concentration; (*b*) onset of asymmetry of the electron spin resonance signal; (*c*) phase separation for sodium solutions; and 15% ($\alpha=0{\cdot}15$), 50% ($\alpha=0{\cdot}50$), and 85% ($\alpha=0{\cdot}85$) pairing of electron spins in metal–ammonia solutions. × = Li; ○ = Na; □ = K; ◇ = Cs; ⊕ = maximum in $-(d\rho/dT)$ for Li and K solutions; ⦶ = maximum in $-(d\rho/dT)$ for Na solutions.

§ 5. The Metallic Region (> 8 MPM)

At concentrations above ~5 MPM the abnormally large value of $d\rho/dT$ diminishes (CT, fig. 22) and the Hall coefficient also drops to the free electron value (CT, fig. 12); then we must have a situation where the ammonia dipoles no longer follow the motion of the electrons and in view of the Hall coefficient the semi-metal model can no longer apply. CT have postulated that cavities still exist and that the electron wave functions are of the 'tight binding' type (fig. 5), being piled-up near their cavities. In doped semiconductors this is certainly so (Alexander and Holcomb 1968)†.

CT postulate that the continuing increase of specific volume with electron density is due to this‡, and also the negative value of $d\rho/dT$; rising temperature could smear out the cavities, leading to a decrease in the effective mass of the electrons, and thus (perhaps) a longer mean free path.

Fig. 5



Suggested form of charge density $\sum|\psi|^2$ over all wave functions of the Fermi distribution for metal–ammonia solutions, if cavities still exist in the metallic phase near the MNM transition.

While this may be so near the MNM transition, we follow Lepoutre and Lelieur (1969) and the analogy with doped semiconductors in doubting it for high concentrations, certainly for those in excess of 8 MPM. CT point out that the mean free path is then very long ($k_F L \simeq 30$, where k_F is the wave number at the Fermi energy), and also (p. 873) that many properties such as the magnetic susceptibility, thermopower, Knight shift, and Hall effect agree with the nearly-free-electron approximation. We suppose that for high concentrations the electrons in sodium–ammonia solutions form a free-electron gas with effective mass near to m.

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† Alexander and Holcomb examined in some detail the data on silicon doped with phosphorus, to determine whether for concentrations in the neighbourhood of the MNM transition an impurity band more or less separate from the conduction band of the host lattice remains as calculated by Mott and Twose (1961), or whether the band has merged with the conduction band. They make use of data based on Hall coefficients, conductivity, electron spin resonance, nuclear magnetic resonance, and magnetic susceptibility. They find that the impurity band merges with the conduction band only at concentrations from 5 to 10 times higher than that for the MNM transition.

‡ Lepoutre and Lelieur (1969), on the other hand, favour a composite model: a broad structureless absorption (1–5 μ) from electrons which are nearly free, and a narrower, discrete band (1·3–2 μ) from the few remaining electrons localized in cavities. We prefer not to differentiate between two classes of electron.

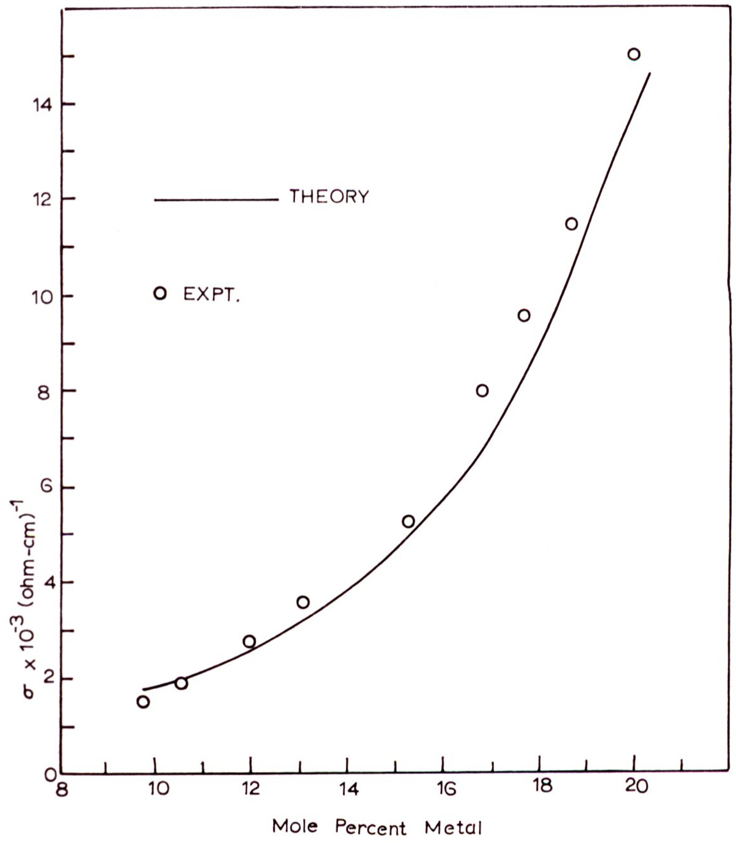
If this is so, we have to explain :

(*a*) The continued expansion of the ammonia lattice with increasing concentration of electrons.

(*b*) The negative value of $d\rho/dT$, fig. 3 (*a*) (except at both very high concentrations and high temperatures).

As regards (*a*), we note that the cations are solvated and that when the concentration is high there must be a rapid change in the sign of the polarization along a line joining two cations. In the sense of Bjerrum's arguments this would lead to cavity formation or at any rate to a drop in density. We suggest, then, that the continuing drop in density is due to the polarization of the solvent around the cations, rather than around the anions (electrons). A similar explanation is given by Lepoutre and Lelieur.

Fig. 6



Comparison of measured and calculated conductivities for lithium–ammonia solutions at 210°K (Ashcroft and Russakoff 1969).

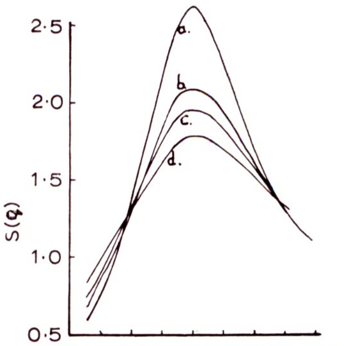
As regards the resistivity, we do not know which scattering mechanism makes the major contribution. The following are the possibilities :

(*a*) Thermal fluctuations in density or polarization of the ammonia ; this would certainly give positive $d\rho/dT$.

(*b*) Scattering of the Conwell–Weisskopf type from the charged cations; since the potential energy of an electron is of the form $-e^2/\kappa r$ and κ decreases with increasing T, this should also give positive values of $d\rho/dT$.

(*c*) Scattering by solvated cations and by solvent dipoles. For lithium–ammonia between 10 and 20 MPM, Ashcroft and Russakoff (1969) have discussed the concentration-dependence of the resistivity, but not its temperature dependence. They get good agreement with experiment (fig. 6) by considering scattering by solvated cations, $M(NH_3)_x{}^+$ and by the dipole moments of ammonia molecules which are not bound to cations ; the rapid decrease in the number of these ' free ' ammonia molecules results in the sharp drop in resistivity as the metal concentration is increased ($\rho \propto n_e{}^{2-3}$). Scattering by ammonia dipoles would give a resistivity proportional to temperature. For the solvated cations, they use the Ziman theory as for liquid metals, and the theoretical analysis of Ashcroft and Langreth (1967) to calculate the structure factor $S(q)$. Naturally for high concentrations the correlation between metal ions is stronger so that $S(q)$ is similar to that found in a metal as shown in fig. 1 of Ashcroft and Russakoff. The high resistivity for lower metal concentrations comes from the comparative lack of correlation between cations.

Fig. 7



$S(q)$ for liquid Pb around the first maximum : (*a*) 340°C ; (*b*) 600°C ; (*c*) 780°C ; (*d*) 1100°C (North *et al.* 1958).

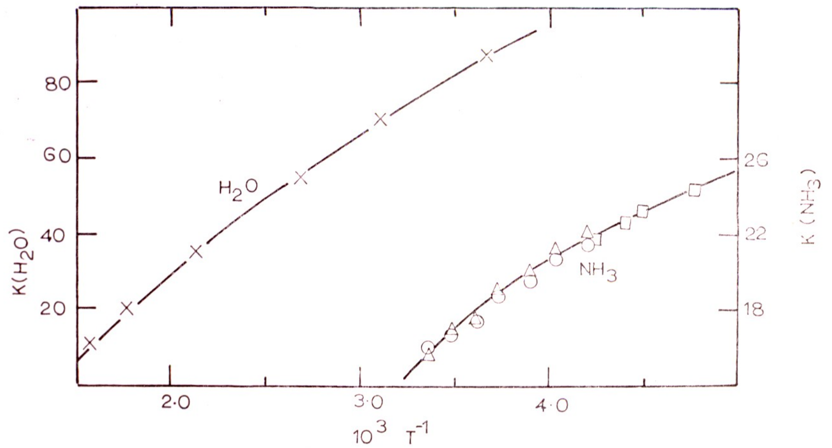
Now for monovalent metals, Ziman's theory (Ziman **1961**) explains the positive value of $d\rho/dT$ by the change in $S(q)$ with temperature.

The work of North *et al.* (1958) shows that for $q=2k_{\mathrm{F}}$, k_{F} being defined for one electron per atom, increasing the temperature leads to an increase in $S(q)$ for all q up to $2k_{\mathrm{F}}$ (fig. 7), so the resistivity must always increase with temperature. But for ammonia the force leading to the correlation between ions is of the form :

$$(e^2/\kappa r^2)\exp(-qr),$$

where q is a screening constant and κ is the *static* dielectric constant. Now the Ashcroft–Langreth theory—as in Debye–Hückel—gives a broadening of $S(q)$ due to the thermal energy kT, but the important factor here is that κ for ammonia, as for water, drops off with increase in temperature more rapidly than T^{-1} (fig. 8 ; Burow 1965, Hasted and Tirmazi 1969, Malmberg and Maryott 1956, Akerlof and Oshry 1950), so one would expect $S(q)$ to drop with increasing temperature for $q<2k_{\mathrm{F}}$, giving the observed decrease in resistivity.

Fig. 8



Temperature dependences of the low-frequency dielectric constants of ammonia and water. × = H_2O (Akerlof and Oshry 1970, Malmberg and Maryott 1956) ; $\Delta=NH_3$ (Hasted and Tirmazi 1969) ; □ = NH_3 (Burow 1965) ; ○ = NH_3 (*Handbook of Chemistry and Physics*).

For very high concentrations, particularly at higher temperatures, where $d\rho/dT$ becomes negative (Naiditch 1963, fig. 12 of Lepoutre and Lelieur 1969), we may assume that the polarization of the medium is so large that this behaviour of κ no longer occurs and the normal variation of S with temperature, as in fig. 7, occurs.

(*d*) Scattering by the Bjerrum defects or fluctuations in density that we have assumed to exist between the cations. This could well give a negative value of $d\rho/dT$, since increasing temperature will make the cavities between solvated cations wider and less well defined.

Until the mechanism of scattering is better understood, it is probably not worth while speculating too deeply about the pressure dependence of conductivity or the thermopower, although the positive thermopower about 13 MPM (CT, fig. 18) is compatible with a sharply peaked $S(q)$. Below 13 MPM the thermopower is negative, presumably because $v(q)$ decreases with increasing energy ; here $|v(q)|^2$ is the scattering probability for a change of momentum q, and the thermopower is given by :

$$\frac{\pi^2}{3}\frac{k^2T}{e}\frac{d\ln\sigma}{dE}.$$

§ 6. THE TWO-PHASE REGION

Figure 21 of CT shows that above the two-phase region the MNM transition occurs at lower concentrations as the temperature is raised. There are various ways of looking at this. If one used the Mott–Twose relationship

$$n^{1/3}\hbar^2\kappa/m^*e^2 \sim 0{\cdot}2 \qquad . \; . \; . \; . \; . \; . \; . \qquad (2)$$

and took for κ the high-frequency dielectric constant, the observed result would imply that m^* must decrease with increasing temperature, which is just what CT assume. This may be part of the answer. But (2) is not really expected to apply to these solutions where the hole, left behind after the transfer of an electron to another e_1, collapses. Another way of looking at the problem is the following. The shift of the e_1 optical band to lower energy with increasing temperature requires a large expansion of the cavity (Jortner 1959)†. We suppose that this expansion of the electron's wave function results in a decrease of the Hubbard gap, E, with increasing temperature and therefore a negative value of $d\rho/dT$. However, the activation energy, W, for the conduction process in the MNM transition region decreases from $\sim 0{\cdot}22$ to $\sim 0{\cdot}1$ ev as the temperature is lowered from $+20$ to -60°C (Lepoutre and Lelieur 1969, fig. 12).

In crystals it is known that the hopping activation energy drops with temperature below $\frac{1}{2}\Theta_{\mathrm{Debye}}$ (for refs. see Austin and Mott 1969) ; however, it is doubtful whether anything of the sort can be expected in a liquid, but if it did, the observed facts would suggest that the activation energy was of polaron type.

As regards the two-phase region, it has been argued that a MNM transition, at any point on a free-energy–volume diagram will probably lie in a region as in fig. 9 (Lifshitz and Kaganov 1963, Zinamon and Mott 1970, Mott 1970) where the curve is concave to the volume axis. As applied to

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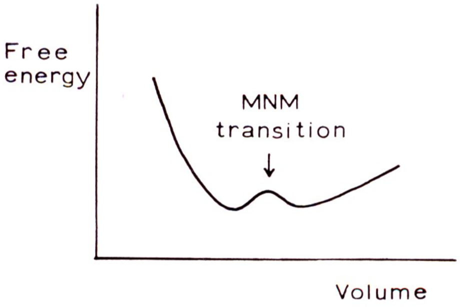
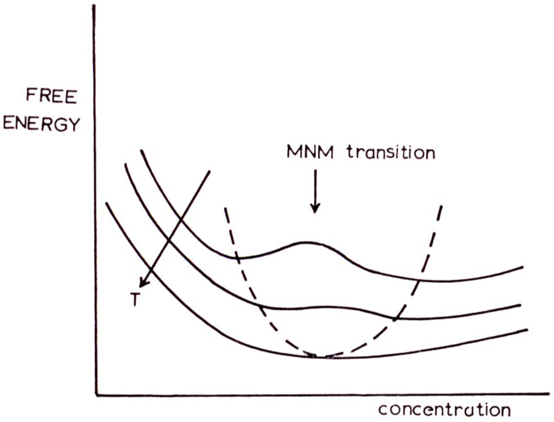
† Jortner (1959) calculated dR/dT on the assumption that the temperature dependence of κ_∞^{-1} is considerably less than that of κ^{-1}. The recent determinations of κ (Burow 1965, Hasted and Tirmazi 1969) and of κ_∞ (Burow 1965) show that $d(\kappa_{\mathrm{p}})^{-1}/dT$ is of opposite sign to $d\kappa^{-1}/dT$, and in fact Jortner's estimate of dR/dT is too low.

Fig. 9



Free energy near the MNM transition.

Fig. 10



Free energy near the MNM transition for metal–ammonia solutions : phase separation.

crystalline solids like V_2O_3, this leads to a discontinuous change in volume under pressure. Similarly, in metal–ammonia solutions fig. 9 would imply that near the transition the free energy would appear as in fig. 10, giving the well-known solubility gap.

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