

Polarons, Bipolarons, and Possible High- T_c Superconductivity in Metal-Ammonia Solutions¹

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We examine the nature of fluid metal-ammonia solutions with a special emphasis on the electronic structure and dynamics of polaronic and bipolaronic charge carriers. Importantly, we find that close to the compositionally-induced Nonmetal-to-Metal Transition in the fluid at low temperatures (*ca.* 240K), the vast majority (*ca.* 85% or above) of current carriers are highly mobile, diamagnetic ($S = 0$) bipolarons. This raises the intriguing possibility, first proposed by R. A. Ogg in 1946, of a Bose–Einstein Condensation (BEC) of trapped electron pairs in vitreous, quenched metal-ammonia solutions. From a “modern” (2000) perspective we believe that there are important similarities to the situation in the crystalline layered cuprates, where we have argued elsewhere that High- T_c superconductivity derives from the BEC of bipolarons in the electronically active CuO_2 planes [A. S. Alexandrov and P. P. Edwards, *Physica C* **331**, 97 (2000)]. We now propose that the search begins for high temperature superconductivity in quenched metal-ammonia and related solutions.

KEY WORDS: Metal-ammonia; high T_c ; polarons; bipolarons; metal–nonmetal transition.

1. PREAMBLE

This talk will highlight the physics and chemistry of both fluid and rapidly frozen solutions of alkali metals in anhydrous liquid ammonia. The scope of MTSC 2000 has been correctly set to encompass recent developments and trends in the subject with a specific focus on experiments and theories which are relevant to the microscopic pairing mechanism in superconducting materials. Also, special emphasis has been placed on phenomena related to nanoscale phase separation. In all of these areas, the nature of metal-ammonia solutions impacts naturally on the phenomenon of superconductivity at high temperatures; for in these venerable systems, we see issues relating to polaron and bipolaron formation, the metal–nonmetal transition, liquid–liquid phase separation, and the first-ever report of high-temperature superconductivity.

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2. THE OGG SAGA: HIGH- T_c YESTERDAY³

In 1946, a night letter [1] from the chemist Richard A. Ogg, Jr., to *The Physical Review* announced a startling discovery to a sceptical scientific community. Superconductivity had been discovered at the temperature of liquid air. A ring sample of a deep blue solution, made by dissolving metallic sodium in anhydrous liquid ammonia, on being quenched in a dewar of liquid air in a magnetic field showed, on removal of that field, a persistent electric current that did not decay with time. Ogg reported in that letter [1] that such frozen solid metal–ammonia solutions became superconducting at temperatures of the order of 180–190 K. Furthermore, he proposed a remarkable explanation for the observed phenomenon, arguing that superconductivity at these exceptionally high temperatures derived from a Bose–Einstein condensation of trapped electron-pairs. Ogg additionally stated

³Richard Ogg’s paper appeared in 1946, and this date thus classifies this contribution as “*High Temperature Superconductivity Yesterday (1942–1986)*” according to Ginzburg’s conditional demarcation of the history of superconductivity (V.L. Ginzburg, this conference; *Journal of Superconductivity*, **13**, 2000).

that by rapid quenching, the resulting frozen sodium–ammonia solution entered a metastable or ‘forbidden’ state which then permitted the Bose–Einstein condensation of trapped electron pairs within the vitreous solid [1].

Ogg’s observations were soon challenged by a large number of investigators who attempted to reproduce his experimental results without any real success [2]. However, there were one or two exceptions; for example, in 1947, Hodgins [3] reported the observation of persistent currents in his quenched sodium–ammonia samples, and much later (1973) Dmitrenko and Shchetkin [4] reported unusual (and time-dependent) conductivity in a quenched metal–ammonia solution, and the possibility “that this system may be superconducting” (p. 331).

The entire episode was highly unfortunate for Ogg. The failure to reproduce—at ease—his experimental observations meant that the work was ridiculed and largely disregarded; this unfortunate state of affairs then also impacted on perceptions of Ogg’s remarkably astute physical insights into the microscopic origins of superconductivity. Thus, according to Blatt [5] and also Bloch [6], Ogg was the first to propose the idea of a Bose–Einstein condensation of electron pairs in a superconductor, but he never received due or proper credit for this seminal advance in physical reasoning. In 1966, Blatt [5] courageously attempted to rectify this situation by pointing out the importance of Ogg’s proposals of 1946—recall, that date was more than a decade before the publication of the work of Bardeen, Cooper, and Schrieffer [7]. Blatt also noted perceptibly that Ogg’s ideas were cast largely in the language of an experimental chemist instead of those of a theoretical physicist, and this factor also, unfortunately, contributed to their instant dismissal by the vast majority of the scientific community. Ogg himself was the subject of highly public and targeted ridicule, culminating in an abrasive and ungracious limerick by Gamow⁴

In Ogg’s theory it was his intent
That the current keep flowing, once sent;
So to save himself trouble,
He put them in double,
And instead of stopping, it went.

Of course, it has now (2000) emerged that the Bose–Einstein condensation of excess hole-pairs is indeed one viable model for high-temperature superconductivity in the layered cuprates [9–13], and Ga-

mow’s limerick—originally penned to humiliate and presumably discredit Ogg—may now even be seen as taking on a supportive tincture! I would argue therefore that it is both timely and entirely appropriate to review the electronic structure of metal–ammonia solutions, and this process is coupled here with my own personal perception of Ogg’s process of reasoning and deduction for possible high-temperature superconductivity in these fascinating systems. My task, of course, now benefits not only from the science of hindsight, but also from over a further half-century of experimental and theoretical study on the nature of these liquids [14–16]. We must also view Ogg’s vision in the aftermath of the discovery of high-temperature superconductivity in the layered cuprates [17,18]. I stress that it is not my intention here to review anything of detail concerning the experiments and observations reported by Ogg [19], but rather to try and recapture just some of his arguments and contributions relating to the electronic structure of fluid metal–ammonia solutions. Such considerations, I believe, were behind Ogg’s reasoning for, and deduction of, possible high-temperature superconductivity in quenched metal–ammonia solutions.

The plan of the review is as follows: In the following section, I will briefly review the electronic structure of metal–ammonia solutions, and attempt to make a casual link to Ogg’s 1946 report of high-temperature superconductivity in quenched metal–ammonia solutions. In Section 4, I attempt to place Ogg’s remarkable ideas and contributions within something of a modern context.

3. THE ELECTRON IN SOLUTION: THE NATURE OF METAL–AMMONIA SOLUTIONS

Alkali metals dissolve readily in pure, anhydrous liquid ammonia (Fig. 1) and various other aprotic solvents to yield intensely colored and highly conducting solutions—generally called *metal solutions* [14–16, 20,21]. These metastable solutions are brilliant blue and electrolytic (saltlike) in the dilute concentration regime, and bronze/copper/gold-colored and genuinely metallic in the concentrated range. At intermediate metal concentrations, there thus exists a composition-induced electrolyte (nonmetal)–to–liquid metal electronic phase transition. In Fig. 2, we show the behavior of the dc electrical conductivity of Na–NH₃ solutions at 240 K across a large composition

⁴G. Gamow; this limerick has been transmitted to me by Dr. G. A. Thomas, Lucent Technologies, USA.



Fig. 1. An artist's representation of the process of the dissolution of a piece of sodium in anhydrous liquid ammonia. The "streams" of black color (in reality, of course, these are dark blue) represent the formation of the blue "metal solution" to yield (at low concentrations) solvated sodium cations and solvated electrons. Taken with permission from Brixon and Jortner [Ref. 20].

range, from *ca.* 10^{-4} mole percent metal (MPM)⁵ to 22 MPM, the saturation limit [14,15,21,22]. For sodium compositions above about 20 MPM, the conductivity exceeds the value of liquid mercury (*ca.* 10^4 $\text{ohm}^{-1} \text{cm}^{-1}$), even though the concentration of conduction (itinerant) electrons in the metal solution is far less than that in elemental mercury.

Concentrated metal–ammonia solutions consist of solvated metal cations, M_s^+ , free-solvent (ammonia) molecules, and genuinely delocalized (itinerant) electrons. Accordingly, values of the Ioffe–Regel product [23], $k_F \ell$, where ℓ is the mean free path and k_F the Fermi wave number, range from 1 to 30 in concentrated solutions of Li in NH_3 at 240 K. Ashcroft and Rusakoff [24] have proposed that the electrical resistivity in concentrated metal solutions is dominated by the scattering of high-velocity itinerant electrons from both solvated cations and from the

⁵This is the accepted concentration scale: mole percent metal, $\text{MPM} = [\text{moles of metal}]/[\text{moles of metal} + \text{moles of } \text{NH}_3]$.

dipole moments of individual ammonia molecules not bound to alkali cations. This physical picture then naturally explains the rapid increase in electrical conductivity for high concentrations of alkali metal, as unbound ammonia molecules progressively become complexed to alkali metal cations; for instance, every Li^+ cation is known to be strongly complexed by four ammonia molecules in a tetrahedral array in Li - NH_3 solutions [25,26].

In contrast to the behavior of the concentrated metal–ammonia solutions, for highly dilute solutions the bulk of the electrical current is carried by a single, charged electron [14,15,22]. These dilute (electrolyte) solutions are characterized by the presence of a variety of localized (nonmetallic) solvated species such as solvated metal cations, solvated electrons, e_s^- , and various neutral and charged agglomerates—polaronic states *par excellence*, and all coexisting in dynamic equilibrium within the fluid metal solution [16,27–31].

The perceived "simplicity" of such solutions, which thus exhibit the localization of the fundamental unit of electrical charge in dilute solutions and its itineracy in concentrated solutions, has attracted interest and attention for almost two centuries follow-

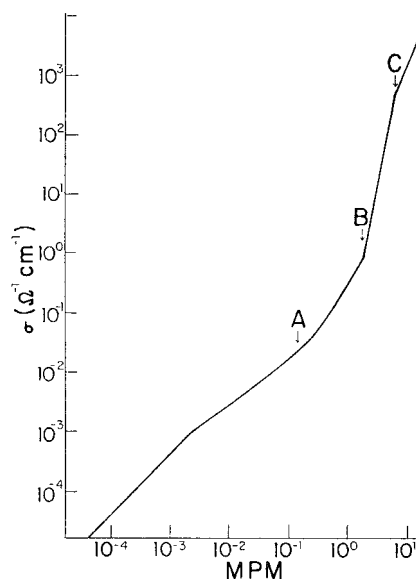


Fig. 2. The electrical conductivity of solutions of sodium in liquid ammonia at 240 K due to Kraus and Lucasse (1921; Ref. 22(c)). A denotes the location of the minimum in the equivalent conductance (formation of the ion-pair $\text{Na}_s^+ e_s^-$), B and C mark the beginning and end of the metal–nonmetal transition. This figure taken from Cohen and Thompson [Ref. 14], with permission.

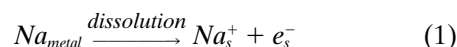
ing their initial discovery by Davy [16] and by Weyl [14–16,21,27–31].

One of the most dramatic visual features of the composition region in the vicinity of the metal–nonmetal (M-NM) transition region relates to the immiscibility gap leading to phase separation of concentrated and dilute solutions below a critical consolute temperature (for Na-NH₃, *ca.* 231 K). Below this consolute temperature, the metal solution physically separates into two distinct layers—the concentrated, but patently less dense, bronze metallic phase, which floats out on top of a more dense, dark-blue electrolytic phase. A representation [30] of the phase diagram of a Na-NH₃ solution is shown in Fig. 3. In 1946, Ogg [1] proposed a fundamental link between this spectacular liquid–liquid phase separation in fluid Na-NH₃ solutions and the occurrence of high-temperature superconductivity in the corresponding

quenched solutions. We will further discuss this potential link in Section 3.3.

3.1. Polarons

The accumulated evidence for the electrolytic nature of very dilute metal solutions is overwhelming, the dissolved alkali metal being present in the form of conventional solvated cations and unique “solvated electrons”. For instance, a lump of sodium dissolving in pure liquid ammonia spontaneously produces a blue solution in which each sodium atom undergoes a facile electron transfer process [20] to form a solvated sodium cation, Na_s^+ , and a solvated electron, e_s^- , viz,



In the early part of the last century, Kraus [22] proposed that the positive solvated ion, Na_s^+ , in the metal solution would be identical to that found in solutions of conventional ionic salts (say, halides) of the corresponding metal in anhydrous liquid ammonia. The negative ions in metal solutions are, however, quite unique; they consist of “excess electrons” that have been spontaneously released into the ammonia by the very process of dissolution of metal [20]. A schematic representation [31] of the solvated cation and the solvated electron in liquid ammonia in very dilute metal solutions is given in Fig. 4. Kraus [22] viewed the electron in ammonia solution in terms of “electrons surrounded with an envelope of NH₃” (p. 1557). He also proposed that the excess, or solvated electron existed within a physical cavity in the solvent in which one or more of the ammonia molecules have been excluded, thereby accounting for the remarkably low densities of these metal solutions. For instance, a saturated solution of Li in NH₃ is the lightest liquid known at room temperature, having a density of only 0.477 g/cm⁻³ [15].

Ogg can be credited with establishing the very first detailed picture for the solvated electron in liquid metal–ammonia solutions [32–34]. Taking a lead from the emerging ideas of polarons in crystalline solids [35], during the period 1940–1946 Ogg argued that excess electrons in ammonia are “self-trapped” by virtue of their interaction with the polar molecules surrounding the physical cavities created in the solvent. On this description, the envelope of ammonia molecules around the electron (Fig. 5) creates an effective (spherical) potential well within an infinitely high (repulsive) barrier for the trapped or solvated

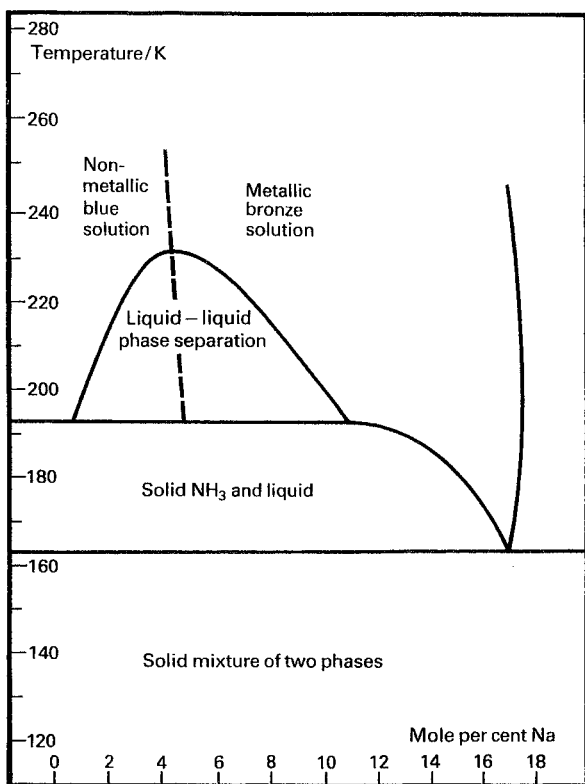


Fig. 3. A representation of the phase diagram of Na-NH₃ solutions (a) is the locus of the metal–nonmetal transition (dotted line) and the region of liquid–liquid phase separation. This phase separation occurs when a 4 MPM Na-NH₃ solution is cooled below the critical temperature of 231 K. The solution separates physically into a bronze metallic region and a blue nonmetallic phase. Taken from Holton and Edwards [Ref. 30], with permission.

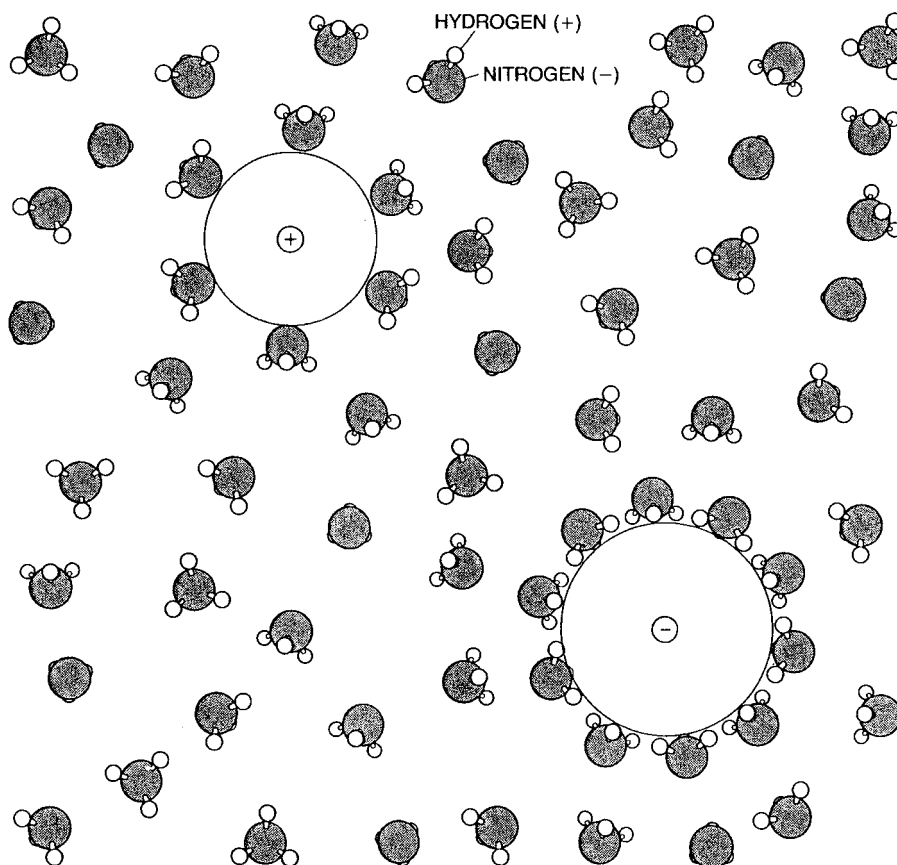


Fig. 4. A schematic representation of the solvated alkali metal cation, M^+ , and the solvated electron, e^- . Taken from Dye [Ref. 31], with permission.

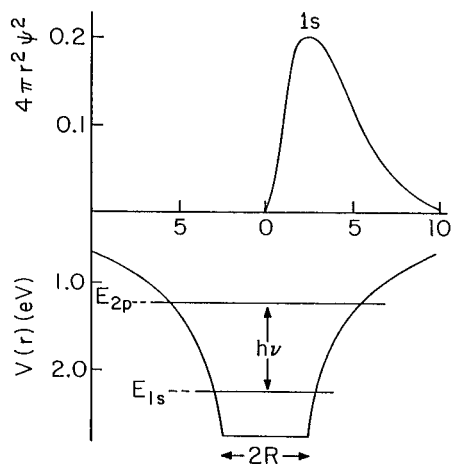


Fig. 5. The potential $V(r)$ and the 1s wavefunction $\psi(r)$ used by Jortner [Ref. 36] to describe the solvated electron, e^- . The characteristic color of a metal-ammonia solution (Fig. 1) derives from the transition between the 1s and 2p states of the solvated electron. The radius of the cavity is $R \sim 3.2 \text{ \AA}$. Taken from Cohen and Thompson [Ref. 14], with permission.

electron. A decade later, in a milestone contribution [36], he developed and refined this simple physical picture into the first detailed description of the solvated electron. Jortner [36] proposed that the electron resided in a cavity of radius, R of *ca.* 3–3.2 \AA . The liquid ammonia in the vicinity of this cavity is polarized by the presence of the electron, producing a constant potential, $V(r)$, within the cavity, *viz.*,

$$V(r) = \frac{-e^2}{R} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right), \quad r < R \quad (2)$$

and acting back on the electron; here, ϵ_∞ and ϵ_0 are the high- and low-frequency dielectric constants of NH_3 , respectively.

Outside of the cavity ($r > R$), the electron will experience a different potential, namely

$$V(r) = \frac{-e^2}{r} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right), \quad r > R \quad (3)$$

giving a total potential for the solvated electron as

shown in Fig. 5. The potential $V(r)$ and corresponding $1s$ wavefunction, $\psi(r)$, used by Jortner to describe the nature of the solvated electron are also given in Fig. 5. Thus, Jortner's model combines the ideas of Kraus and Ogg for a physical cavity in the solvent with the first quantitative attempt at describing the electron-solvent interaction. Following a variational solution of the ground ($1s$) and first excited state ($2p$) of the excess electron in this potential well, various other important polarization terms were added by Jortner, and a variety of key defining characteristics for the solvated electron (optical transition energy, heat of solution, etc.) could then be calculated. The agreement between experiment and theory for this polaronic picture of e_s^- was excellent. The motion of the electron within the cavity plus its polarization cloud (i.e., solvation shells) as a negative ion accounts for the sizeable, electron mobility in metal-ammonia solutions.

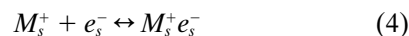
Following Cohen and Thompson [14], we, therefore, define the very dilute solution range in metal solutions as that in which there is no significant association between the solvated electrons and solvated cations. This concentration range can be traced from infinite dilution up to metal concentrations of *ca.* 10^{-3} MPM.

For metal concentrations above 10^{-3} MPM there is ample experimental evidence for a variety of association or aggregation processes involving solvated electrons and solvated cations [14-16]. It is within this concentration range that we witness the formation of "electron pairs" in the solution. The intermediate concentration range, from 10^{-1} to *ca.* 5 MPM, also sets the scene for the impending M-NM transition itself and the phenomenon of liquid-liquid phase separation (Fig. 3) again, all these interrelated phenomena being key facets of Ogg's view of possible high-temperature superconductivity in metal-ammonia solutions [1].

3.2. Bipolarons

The appearance of various aggregate species is to be expected for any electrolyte solution within a polar solvent as the concentration of solute (metal) increases. What sets metal-solutions apart, of course, is the existence of solvated electrons as one of the constituent ions. In the concentration range 10^{-4} to 10^{-3} MPM, the appearance of the neutral, aggregate ion-pair species, $M_s^+e_s^-$, in metal-ammonia solutions is signalled [14,15,27-30] by the behavior of both

the metal (Knight shifted) NMR and the equivalent conductance (exhibiting a minimum in the conductance/concentration curve). As anticipated for a high dielectric solvent such as ammonia, the ion-pairing association



is best viewed as a short-lived ($\sim 10^{-12}$ sec) "encounter complex" in the solution.

The magnetic behavior of Na-NH₃ solutions in this concentration range also signals the presence of extensive electron-electron interactions. The rapid decrease in the molar spin susceptibility of metal-ammonia solutions (Fig. 6) in the concentration range 10^{-3} to 1 MPM below that expected for an assembly of noninteracting electrons represents direct evidence for the formation of diamagnetic complexes containing an even number of excess electrons (Eq. 1), being spin-paired in a singlet ($S = 0$) ground state [37]. For instance, at a concentration of 0.1 MPM, a remarkable 90% of the excess electrons in solution exist as spin-paired states at a temperature of 240 K. The resulting diamagnetic state is known to be several times $k_B T$ lower in energy than the corresponding triplet state, or the dissociated doublet states ($2 \times$

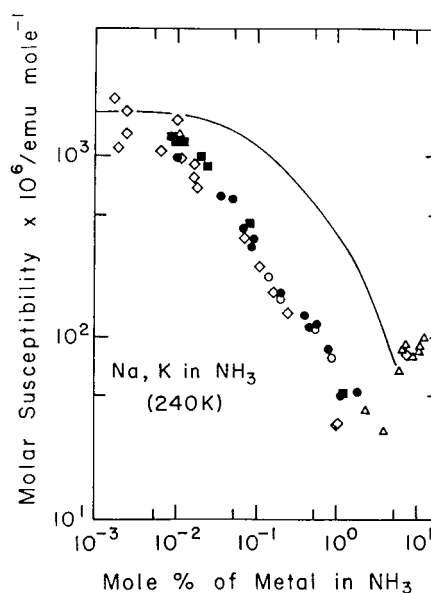


Fig. 6. The concentration dependence of the molar spin susceptibilities (from various sources) of Na-NH₃ (open symbols) and K-NH₃ solutions (solid symbols) at 240 K. The solid line indicates the calculated extrapolation between Curie and Pauli-like behaviour, assuming a noninteracting electron gas. Taken from Page *et al.* [Ref. 37]. Note that the system moves from an extensive electron (spin)-pairing regime to the liquid metal (Pauli susceptibility).

$S = 1/2$). The precise nature of this diamagnetic, electron-pair state has been the subject of healthy controversy and debate for some considerable time [38].

In early important contributions, Ogg extended his treatment of the “cavity trapping” of a single excess electron in ammonia to the case of two electrons existing within a cavity in the solvent [32–34]. He proposed that the resulting electron pair, located within a single cavity, would be stable with respect to dissociation to two electrons trapped separately. A schematic representation [31] of possible electron pair ions in solutions of the alkali metals in liquid ammonia is shown in Fig. 7.

Schindewolf and Werner [39], on the basis of extensive and accurate electrochemical studies of metal–ammonia solutions, characterized the electron-paired species in metal–ammonia solutions as a three particle cluster or ion triple, $e_s^- M_s^+ e_s^-$, consisting of two single electron cavity species and one sodium cation adjacent to both cavities. Electron (spin) pairing is then almost certainly assisted via the intermedi-

ary of M_s^+ . Kestner and coworkers [40] found sizeable electron spin-pairing energies—typically in the region of ~ 0.1 eV—for such an aggregate triple-ion species. Modern applications of Car-Parrinello local spin density functional methods for Cs-NH₃ solutions by Klein and coworkers have shown that at *ca.* 0.5 MPM, solvated electrons are spin paired, forming peanut-shaped bipolarons in the solution [41]. The distance between the average position of spin-up and spin-down density in the bipolaron (Fig. 8) is about 6.5 Å. On this model, however, the Cs⁺ cations are solvated in the bulk ammonia solvent and are not in close contact with the electron density [41].

3.3. The Transition to the Metallic—and Possibly Superconducting—State

Between a concentration of 1 to 10 MPM a rapid variation with concentration is observed in many of the physicochemical properties of, for instance, Na-NH₃ solutions [14]. Most notable is the behavior of

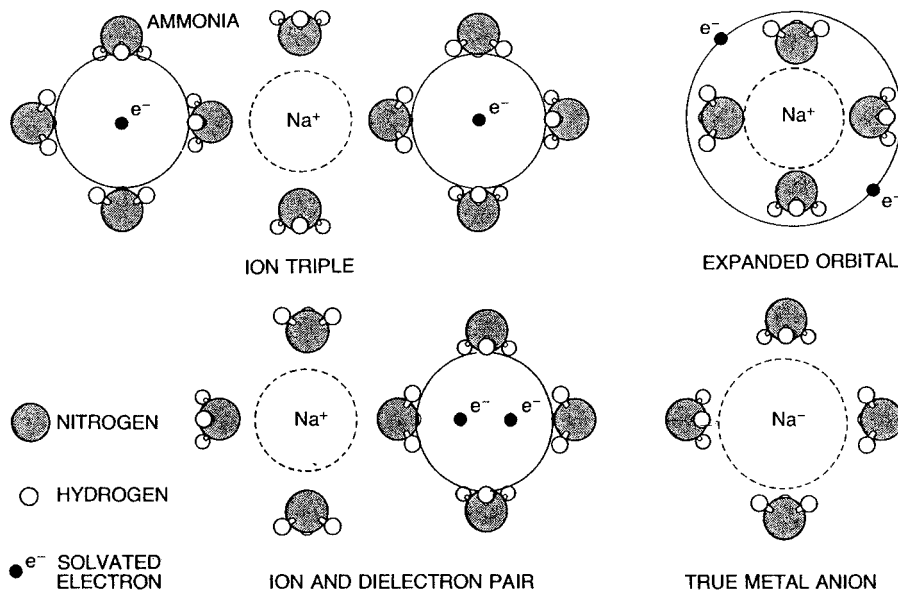


Fig. 7. A representation of the possible diamagnetic, negative ions in metal solutions. These include several candidate structures for the case of sodium dissolved in ammonia. A sodium cation (Na^+) might attract two independent solvated electrons to form the diamagnetic ion triple. An alternative is that the cation might attract a “dielectron”—an entity composed of two electrons, spin-paired inside a single cavity in the solvent. Two electrons might also be associated in an “expanded orbital” that encompass solvent molecules as well as the cation itself. A true alkali metal anion has two electrons occupying a normal $3s$ orbital on sodium. It is generally assumed that the diamagnetic (spin-paired) state in Na-NH_3 is best represented as the ion-triple. A genuine metal anion, Na^- , is found in solution of sodium in other solvent systems (see Refs. 27–31). Taken from Dye [ref. 31], with permission.

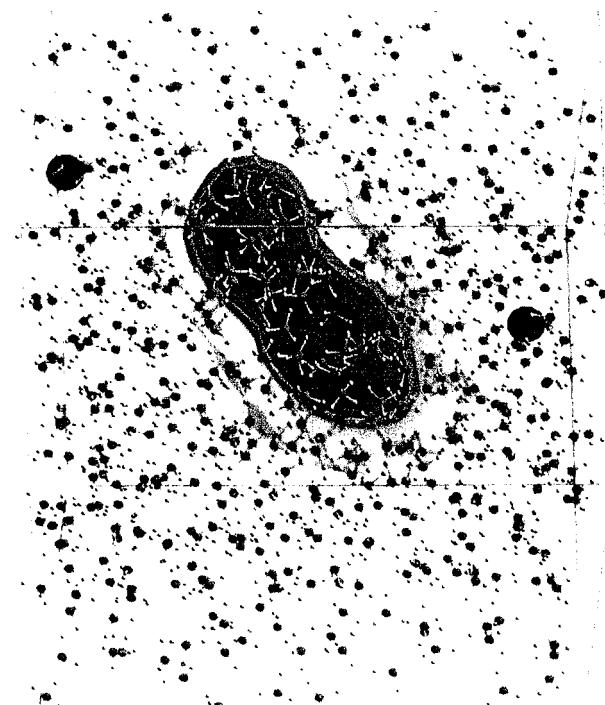


Fig. 8. Electron density profile of a representative configuration of a Cs-NH₃ solution at *ca.* 0.5 MPM taken from Car-Parrinello LSDA calculations. The simulation cell (*ca.* 29 Å edge) consists of 512 NH₃ molecules and two caesium atoms. The Cs⁺ ions are shown with covalent radii (shaded balls) and NH₃ molecules with a ball-and-stick representation. The shaded contour contains 95% of the electron density in the bipolaron. Taken from Deng *et al.* [Ref. 41], with permission.

the dc electrical conductivity which changes by more than eight orders of magnitude (240 K) between 10⁻⁴ MPM and saturation (*ca.* 22 MPM). The most rapid variation in electrical conductivity is reserved for the composition range between *ca.* 2 and 10 MPM (Fig. 2).

This rapid variation has been generally ascribed to a composition-induced M-NM transition; by some authors it has been attributed to a M-NM transition of the type originally envisaged by Mott [23,42,43]. However, it is interesting to recall that the very first consideration of the M-NM transition in Na-NH₃ solutions was by Herzfeld in 1927 [44] in relation to a (presumed) composition-induced “dielectric catastrophe” occurring at compositions close to 2–4 MPM. Such a dielectric catastrophe in Na-NH₃ solutions was indeed observed [45] over 40 years after the publication of Herzfeld’s picture. The Herzfeld criterion predicts that electrons trapped or solvated in polaronic centers become itinerant at the metalliza-

tion onset because of a divergence in the dielectric constant [46,47].

The M-NM transition is in effect a zero-temperature electronic phase transition, with the $T = 0$ K dc electrical conductivity equal to zero on the insulating side of the transition, and of finite value on the metallic side [23,42,46,47]. In the Na-NH₃ system, as well as other systems, useful indications of the M-NM transition which would take place at $T = 0$ K can be obtained for the high-temperature regime ($T > 0$ K) appropriate to experimental study [23,42,46–49].

One of these indicators relates to a remarkable characteristic of the M-NM transition that numerous systems and materials have in common, namely the relationship between the critical carrier concentration, n_c , and the value of the effective Bohr-orbit radius, a_H^* , given by the Mott criterion [42,48–50] for a M-NM phase transition at $T = 0$ K, namely [50]

$$n_c^{1/3} a_H^* = 0.26 \quad (5)$$

Sienko [51] drew attention to the Mott description of the M-NM transition and proposed that the chemical dissolution process (Eq. 1) is best viewed as the dissolving alkali atom behaving as an electron donor in the host liquid ammonia dielectric, with the binding of the resulting excess electron to a localized center being treated in terms of the hydrogen atom problem, suitably corrected for the presence of the background ammonia dielectric. Setting $a_H^* = 2.6$ Å, this leads to $n_c = 8.85 \times 10^{20}$ metal atoms per cc. For an alkali metal in liquid ammonia, this is equivalent to a concentration of 3.87 MPM; interestingly, this composition is very close to the observed consolute concentrations of 4.12 MPM for Na in NH₃, and 4.35 MPM for Li in NH₃.

Thomas [52] has compared the situation of “Na-doped liquid NH₃” with that existing in a crystal of P doped Si (a P atom replaces a Si atom in a Si crystal) and the situation of electron-hole pairs in pure Ge. In terms of such a semiconductor analogy, the dopant in Na-NH₃ solutions would be the Na_s^+ ion and its weakly bound electron, both with their surrounding (polarized) entourage of ammonia molecules. Other systems (as compiled elsewhere [43,46–50]) are also contained in Fig. 9, which shows the estimated M-NM transition density, n_c , as a function of the Bohr radius of the isolated (low concentration range) species. The three systems, Na-NH₃ (represented NH₃ : Na in semiconductor notation) solutions, the electron-hole system in Ge- (Ge : e-h) and P-doped Si (Si : P) are also illustrated schematically in Fig. 9. The solid line in the figure is the Mott

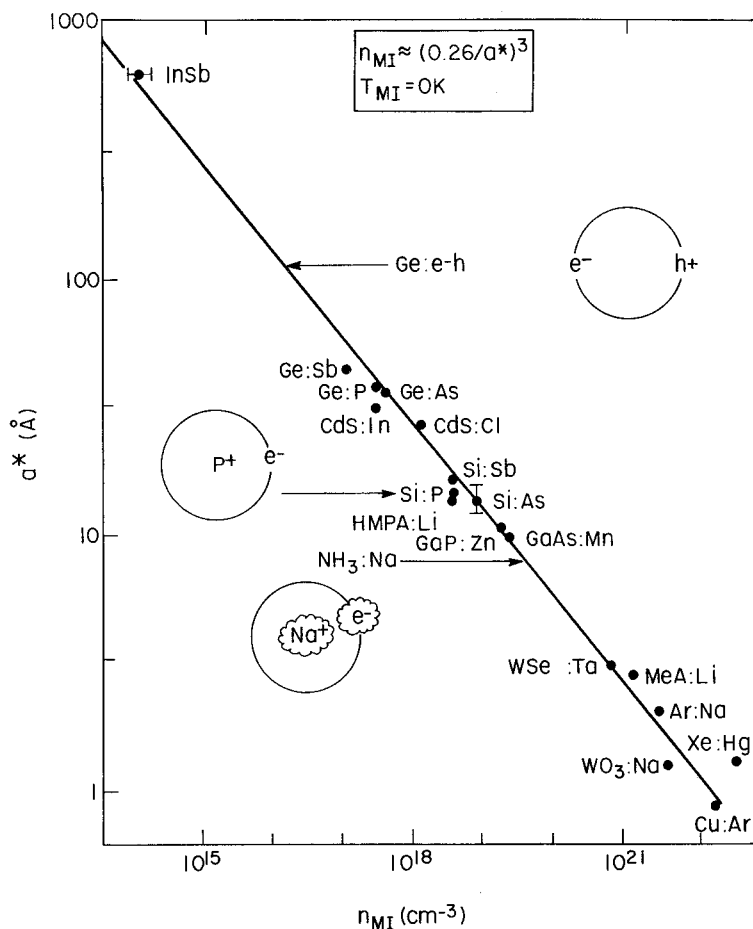


Fig. 9. The Bohr radius, here a^* , (in our text, a_{ii}^*), of isolated species as a function of the estimated metal-insulator or metal-nonmetal transition density; here, n_{MI} , in our text, n_c . The three systems discussed in the text are illustrated schematically here. The Mott criterion (Eq. 5) is recast here as $n_{MI} \sim (0.26/a^*)^3$ and shown as a solid line through the figure. Taken from G. A. Thomas [Ref. 52], with permission.

criterion (Eq. 5). In the case of Na-NH₃ solutions, the Mott criterion predicts a M-NM transition at compositions close to the observed liquid-liquid phase separation (Fig. 3).

Several authors have drawn attention to the possibility of a coincident thermodynamic phase transition accompanying the electronic phase transition at the M-NM transition [42,43,53]. Stated simply, the nature of the electronic interactions between localized electron states changes in a qualitative manner at the M-NM transition; for instance, from a van der Waals-type interaction or a direct covalent (chemical) bond to the metallic cohesion associated with the itinerant electron gas. This qualitative change in electronic structure at a M-NM transition means that conditions therefore appear highly conducive for a

thermodynamic phase transition to accompany any potential electronic M-NM transition at n_c , the critical density for metallization. On this basis, Mott [42] and also Krumhansl [53] have argued that both the liquid-liquid phase separation in metal-ammonia solutions, and the gas-liquid separation in supercritical (expanded) metals at high temperatures represent a direct manifestation of the M-NM transition at $T = 0$ K in both systems. This link, also noted by Sienko [51], was further amplified for metal solutions by Edwards and Sienko [43,50]. (Incidentally, the possibility of a gross electronic instability in the locale of a M-NM transition also figures prominently in Goodenough's seminal work on the electronic structure of narrow-band solids [54,55]).

Pitzer [56] had earlier suggested that the solvent

ammonia in these systems can be regarded as a dielectric medium in which the solute, sodium, can be considered to undergo a “liquid–vapour” phase separation—taking place entirely within the host ammonia matrix—when the temperature drops below a certain critical temperature, the *consolute temperature*. On this view, the dilute side of the two-phase region (Fig. 3) corresponds to “gaseous” sodium (no metallic properties observed) and the concentrated side to “liquid” sodium (possessing all the properties of a metallic form of sodium and embedded within the ammonia matrix).

Ogg [1], on the other hand, proposed a much more drastic departure, arguing that the observation of the liquid–liquid phase separation in Na-NH₃ solutions in which both phases are dilute solutions of metal in ammonia (Fig. 3) strongly suggested that this phenomenon had an origin fundamentally different from that of other critical liquid phase separations [see also 51].

In the early 1940s, Ogg had correctly identified that the rapid increase in electrical conductivity with metal concentration in metal–ammonia solutions (Fig. 2) originates in quantum mechanical tunnelling as solvated electrons become sufficiently close for the exponential tails of their electronic wavefunctions to overlap (Fig. 5). The feeble, temperature-independent paramagnetism of the highly conducting metallic solutions (~20 MPM) was identified by Ogg [1] and others [57] as originating from the Pauli magnetic susceptibility expected from a degenerate gas of itinerant electrons obeying Fermi–Dirac statistics. One might even say here that for this composition range in Na-NH₃ solutions, for example, we have a true Fermi liquid!

Ogg also speculated on the behavior of metal–ammonia solutions in the intermediate concentration range (*ca.* 10⁻² to MPM), characterized by an extensive pairing of electron spins (Fig. 6) and, according to him, the concentration regime in which we have an optimum fraction of trapped electron pairs within the liquid. Here, the measured magnetic susceptibility of the metal–ammonia solution is actually diamagnetic, more so at low temperatures [57]. The relatively large values of the electrical conductivity—and a constantly increasing conductivity (Fig. 2) at that signified to Ogg that the trapped electron pairs, or at least part of them, must be mobile. Of course, one might also visualize such “trapped electron pairs” as the diamagnetic triple-ion species, $e_s^- M_s^+ e_s^-$, or the bipolaronic centers shown in Fig. 8.

Ogg proposed [1] that the statistical behavior of

this concentration of electron pairs in the intermediate concentration range would approach that of a gas—just as the single electrons at higher concentrations (as in ordinary metals) show a quasi-gaseous character. Because the electron pairs would have zero angular momentum, they would, according to Ogg [1], if independent, obey Bose–Einstein rather than Fermi–Dirac statistics. Of course, such electron pairs are self-trapped entirely within the host ammonia liquid; one might therefore also say that the Na-NH₃ solution in this intermediate concentration range is an example of a true Bose liquid!

Perhaps the most striking feature of the Bose–Einstein statistics is the remarkable “condensation” phenomenon [58], predicted to occur below a critical temperature, T_c , defined by the following relation for an ideal Bose-gas of zero spin particles of effective mass m^* [58,59,60]

$$T_c = \frac{3.31h^2 n^{2/3}}{m^* k_B} = 2.9 \times 10^{-11} \left(\frac{m_e}{m^*} \right) n^{2/3} K \quad (6)$$

where $m_e = 9.1 \times 10^{-28}$ g is the free electron mass, n is the concentration of bosons (in number per cm³).

For Na-NH₃ solutions, the liquid–liquid phase separation at the upper-consolute temperature occurs at 4.2 MPM (Fig. 3.). The corresponding concentration of trapped electron pairs would be *ca.* 5 × 10²⁰ pairs cm⁻³. Assuming $m^* \sim 2m_e$, then $T_c \sim 900$ K. This condensation temperature would be lowered by incomplete pairing (reducing n in Eq. (6)) or by having $m^* > 2m_e$. Ogg’s working hypothesis [1], therefore, was that the liquid–liquid phase separation in Na-NH₃ solutions was a critical electrical phenomenon similar in basic cause to the phase transition into the superfluid/superconducting state, usually observed (at that time) at very low temperatures in helium and metals, respectively. In 1946, therefore, he tentatively proposed [1] that the consolute temperature in fluid metal–ammonia solutions corresponds to the critical Bose–Einstein condensation temperature for a system containing *ca.* 10²⁰–10²¹ charged Bose particles cm⁻³. Furthermore, he proposed [1] that the fluid Na-NH₃ system physically separates into two distinct liquid phases (Fig. 3) rather than undergoing a Bose–Einstein condensation.

Ogg’s own observations [1] indicated that very slow freezing of dilute Na-NH₃ solutions led to a normal eutectic (Fig. 3). However, rapid freezing, as by plunging a Na-NH₃ solution into liquid air, produced blue vitreous solids which still displayed electrical conductivity behavior reminiscent of that of the corresponding liquid Na-NH₃ solutions.

These effects suggested a characteristic relaxation time for the system which may have made it possible to “freeze-in” the solution-based species. Ogg [1] believed that it might therefore be possible to freeze-in the configuration of the intermediate concentration solutions containing the requisite concentration of trapped (bosonic) electron pairs. Thus, liquid–liquid phase separation might be avoided and the Bose–Einstein condensation made manifest by some extraordinary physical property of the metastable solid solution. The proposal of F. London (*loc. cit*) that Bose–Einstein condensation is responsible for the superfluidity observed below the λ point of liquid helium [58] suggested to Ogg [1] that the corresponding property to be exhibited by such a “condensed” electron pair gas in quenched Na-NH₃ solution would be electrical superconductivity. Given Eq. (6), this situation would correspond to high-temperature superconductivity in a quenched Na-NH₃ solution. This line of reasoning, therefore, led to Ogg’s experimental search for high- T_c superconductivity in a Na-NH₃ solution rapidly cooled through its consolute temperature (Fig. 3).

4. THE OGG SAGA: HIGH- T_c TODAY (AND TOMORROW?)

In his own insightful review at MTSC 2000, Ginzburg [60] has correctly identified that any landmark contribution to our field should initiate deep insights into the mechanism of high-temperature superconductivity. My own judgment as of April 2000 is that Ogg’s [1] 1946 paper in *Physical Review* can unquestionably be viewed as such a landmark in the development of high-temperature superconductivity; for in that writing we witness deep insights into, and application of, both the physics and the chemistry of Bose–Einstein condensation and high-temperature superconductivity. For that, we owe a great debt to Ogg. His work should have been a catalyst for a consideration of electron-paired superconductivity as a spectacular, high-temperature kind of superfluidity of the electron liquid in metals. In my introductory remarks I have attempted to set out just some of the many reasons why, unfortunately, this proved not to be the case.

However, the idea of electron-pairing with a subsequent Bose–Einstein condensation and appearance of superconductivity was further developed in a comprehensive series of papers by Schafroth and coworkers [61,62]; again, prior to the advent of the

microtheory of superconductivity [7] by Bardeen, Cooper, and Schrieffer (BCS). Ginzburg writes [60] about the development of the BCS work, “But, what is typical, in the BCS paper there is not a single word about the Bose–Einstein condensation and, obviously, they failed to recognize the direct relation between this condensation and pairing and its role for the explanation of superconductivity”. Bardeen did not mention Ogg in his extensive survey [63] of the theory of superconductivity in 1956, and as Ginzburg has observed [60], “although he [Bardeen] knew the papers by Schafroth, he never even mentioned the possibility of pairing!” In 1968, Ginzburg [59] himself made the important comment that, in an ideological sense, superconductivity can just be treated as a consequence of the formation of electron pairs and their condensation—even within the BCS framework.

The very short coherence length of the high-temperature superconducting layered cuprates has led several authors [9–13] to propose that superfluid condensation in these systems is of the Bose–Einstein type, hole-pairs being formed well above T_c , and with a binding energy, Δ_p , per particle ($\Delta_p \gg T_c$) and condensing at T_c . We now know that BCS and Ogg–Schafroth Bose–Einstein condensations are two limiting cases, and in fact it has been shown that it is possible to go continuously from one limit to the other [64,65].

But was Ogg right in terms of the experimental observation of high-temperature superconductivity in quenched Na-NH₃ solutions? My own belief is that this key issue has not yet been finally settled; I restrict myself here to just a few remarks [19].

In the 1940s, Ogg unquestionably made seminal contributions to the study of metal–ammonia solutions. It was Ogg who took Kraus’s essential chemical concept of the solvated electron and placed it upon a rationale physical basis. He also further developed and refined the early experimental synthetic and measurement techniques of Kraus in such a manner that the remarkable liquid–liquid phase separation was investigated in great detail—and indeed, discovered in other metal–ammonia solutions. The experimental details in Ogg’s short *Physical Review* papers of 1946 and thereabouts simply do not do justice to the careful and thorough techniques he had developed for synthesizing and handling such unusually complex—and in fact, dangerous—systems [66]. One feels that this was symptomatic of Ogg’s impulsive desire to rapidly communicate his results, and his ideas, to the broad scientific community. It is well established that the quenching of metal–ammonia solutions presents

very great technical challenges—none the least being the central issues of specimen cracking upon rapid cooling, the control and reproducibility of quench rates, and the supercooling of solutions through the deep eutectic point. During the period 1975–1977 in the Baker Laboratory of Chemistry at Cornell University, as a visitor to Professor M. J. Sienko's laboratory, I made initial attempts to reproduce Ogg's experimental conditions, but to no avail. Sienko also reported to me at that time that during his 2-year research position in Ogg's laboratory at Stanford during the period 1947–1949, he never once saw evidence of persistent electric currents in his own experiments on quenched Na-NH₃ solutions. However, Sienko told me that Ogg's collaborator Alvarez-Tostado [67] "swear they got them"—persistent currents in quenched Na-NH₃ solutions—but only in 7 experimental trials out of 200!

5. CONCLUDING REMARKS

What is now abundantly clear is that Ogg made an important step forward both by highlighting the (then) recent advances by London on superfluidity in fluid helium and linking this phenomenon to the intriguing possibility of a corresponding Bose–

Einstein condensation of charged electron-pairs in a frozen metal–ammonia solution. If our reasoning is correct (Section 3), the concentration of such electron pairs in metal–ammonia solutions is at a maximum in the intermediate concentration range, *ca.* 10⁻³ to 3 MPM. Parenthetically, this is also the concentration range where we witness the onset of a M-NM transition, and the possibility of a Bose–Einstein condensation at a condensation temperature close to the liquid–liquid consolute temperature.

In Fig. 10, we collect together various key pieces of experimental information on Li-, Na-, and K-NH₃ solutions; in this figure, we attempt to represent the evolving, and interrelated, processes of electron (spin)-pairing, the M-NM transition and liquid–liquid phase separation. For example, line (a) shows the maximum rate of increase of electrical conductivity with increase of concentration; we take this as a qualitative indicator of the locus of the M-NM transition for $T > 0$ K in the temperature/composition plane; (b) is the known liquid–liquid (phase coexistence) curve. Curves (c) and (d) represent the situations for 50% and 85% electron pairing, again in the composition/temperature plane. We also highlight the location (on the MPM axis) of the $T = 0$ K M-NM transition at $T = 0$ K, as given by the Mott criterion (Eq. 5).

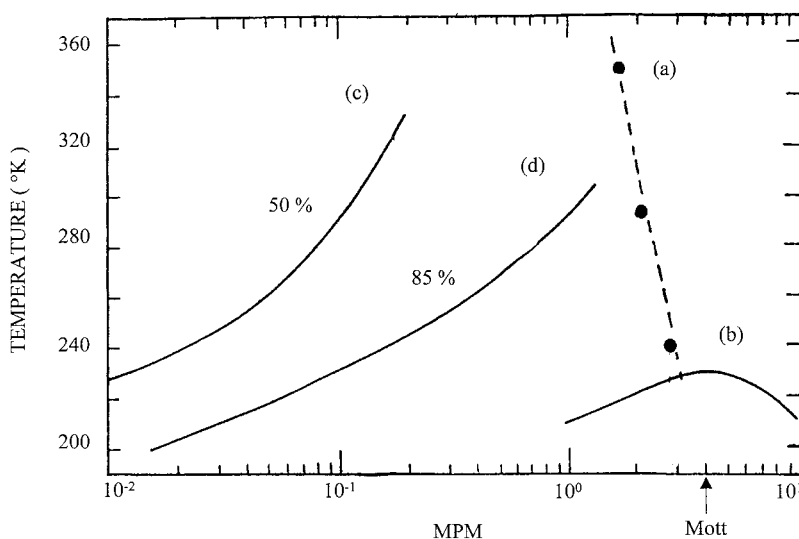


Fig. 10. A representation of some of the key features of the electronic phase diagram of fluid metal–ammonia solutions. The line (a) shows the maximum rate of increase of electrical conductivity with increase of concentration; (b) is the phase coexistence curve for Na-NH₃ solutions. We also show the situation for (c) 50% and (d) 80% pairing of electron spins for (variously) Li, Na, and K-NH₃ solutions. We also highlight the (presumed) location of the $T = 0$ K metal–nonmetal transition (Mott criterion, Eq. 5).

It is very important to stress that the fluid Na-NH_3 system, for example, approaches the onset of a M-NM transition at low temperatures (*ca.* 240 K) from an electronic regime in which a very significant percentage of the excess or solvated electrons exist as singlet ($S = 0$) electron-pair states. This is entirely consistent with Mott's view [23] that in fluid metal-ammonia solutions, the charge carriers at low temperatures in the liquid (Fig. 10) may well be predominantly bosons rather than fermions. Onsager [68] made the telling observation that the electrical conductivity of metal-ammonia solutions continues to remain high, even after the majority of electrons are paired, which necessitates the presence of a very mobile diamagnetic species (see Fig. 2 and 6).

It is important in the broader context to note that Edwards, Mott, and Alexandrov [12] have modeled the layered high- T_c cuprates as doped 2D semiconductors with both polaronic and bipolaronic carriers partly localized by disorder. On this viewpoint, the composition-induced transition to a metallic state in the cuprates may well vie with a competing Bose condensation to the superconducting state.

In metal-ammonia solutions, therefore, one sees the natural interplay/instabilities associated with both the composition-induced M-NM transition developing from an electron-paired regime (Fig. 10), and the possibility, raised by Ogg in 1946, of a *Bose-Einstein Condensation of Trapped Electron Pairs*.

The venerable metal-ammonia systems are undoubtedly worthy of further intensive experimental study, using modern techniques for detecting superconductivity, especially in the light of one's experience derived from over a decade of study and thought on high-temperature superconductivity in the layered cuprates [69]. The search must begin.

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