

Structure of a metallic solution of lithium in ammonia

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Neutron diffraction has been used in conjunction with isotopic substitution to measure the structure of a saturated metallic solution of lithium in ammonia (21 mole % metal). This concentration of solution is of particular interest due to its high electrical conductivity, low density, and position above a deep pseudoeutectic. We find that the solution is highly structured over both short and intermediate length scales. The local coordination around each Li^+ cation consists of a well defined solvation shell containing an average of 3.5 ammonia molecules. These molecules direct their dipole moments away from the cation, and are undistorted relative to the pure solvent. The delocalized electrons are therefore fully dissociated from the cations. A strong first diffraction peak at 0.97 \AA^{-1} is seen in both Li^+ - and N-centered correlations, and provides evidence of intermediate-range order in the solution.

I. INTRODUCTION

Alkali metals dissolve readily in ammonia without chemical reaction. The resulting solutions have been the subject of numerous experimental and theoretical investigations, primarily because they exhibit a fascinating variety of electronic behavior,¹⁻³ and have densities lower than any other liquids except for the cryogenic fluids.⁴

Concentrated alkali metal ammonia solutions, above 7 mole % metal (MPM), are metallic and are characterized by a bronze coloration. At saturation [21 MPM (Ref. 5)] the solutions have an electrical conductivity of $15\,000 \text{ \Omega}^{-1} \text{ cm}^{-1} \text{ mol}^{-1}$, and are classified as class A metals.⁴ However, both the concentration and temperature dependence of the conductivity are completely different from normal liquid metals. For example, electrical conductivity increases as the cube of metal (and electron) concentration.¹ In addition, the saturated solution lies above the deep pseudoeutectic, at approximately 20 MPM and 88 K. This heralds the formation of an ‘‘expanded metal’’ compound with composition $\text{Li}(\text{NH}_3)_4$.⁶ Further general interest in our system stems from the predominance of electron polarons and bipolarons in dilute solutions, and of the subsequent metal-nonmetal transition between 1 and 7 MPM.^{1,2}

Metal-ammonia solutions have been studied using a variety of thermodynamic, spectroscopic, and computational techniques.⁷⁻¹³ However, interpretation of these data is impeded by the dearth of high-resolution structural data. In fact, the literature records only one relevant set of diffraction experiments, on Li solutions in ND_3 .¹⁴ Moreover, in that work, isotopic substitution and difference analysis techniques were not used to decompose the total structure factor into partial structure factors. The data are therefore insufficient to test the detailed predictions of recent theoretical models and computer simulations.⁸⁻¹²

In this paper neutron diffraction has been used to determine in detail the structure of a saturated (21 MPM) metallic solution of Li in ND_3 . Isotope substitution of $^6\text{Li}/^7\text{Li}$ and $^{14}\text{N}/^{15}\text{N}$ allows us to separate many of the correlations con-

tained in the total structure factors $F(k)$ and thereby to determine the structural environments around both Li and N.

II. THEORETICAL BACKGROUND

The $F(k)$ comprising ν chemical species, labeled α or β , for solution samples are derived from the measured intensities by using the relation¹⁵

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega} \right) &\equiv F(k) + \sum_{\alpha=1}^{\nu} c_{\alpha} [b_{\alpha}^2 + b_{\text{inc},\alpha}^2] [1 + P_{\alpha}(k)] \\ &= \frac{1}{N_S A_{S,SC}(\theta)} \left\{ \left[\frac{I_{CS}(\theta)}{a(\theta)} - M_{CS}(\theta) \right] \right. \\ &\quad \left. - \frac{A_{C,CS}(\theta)}{A_{C,C}(\theta)} \left[\frac{I_C(\theta)}{a(\theta)} - M_C(\theta) \right] \right\}. \end{aligned} \quad (1)$$

The measured differential scattering cross section is given by $(d\sigma/d\Omega)$, and the atomic fraction, bound coherent, and bound incoherent neutron-scattering lengths of chemical species α are given by c_{α} , b_{α} , and $b_{\text{inc},\alpha}$, respectively. The scattering vector k is related to the incident neutron wavelength λ and scattering angle 2θ through the relation $k = 4\pi\lambda^{-1} \sin \theta$. The $P_{\alpha}(k)$ denote the inelasticity corrections calculated using a Placzek expansion¹⁶ and the number of sample atoms illuminated by the incident neutron beam is given by N_S . The attenuation of the neutron beam by the sample is calculated using Paalman-Pings¹⁷ attenuation factors $A_{ij}(\theta)$, and multiple scattering cross sections $M_j(\theta)$ are calculated using the method of Soper and Egelstaff.¹⁸ $I_{CS}(\theta)$ and $I_C(\theta)$ represent the intensities for the sample (S) in its container (C) and the empty container corrected for background scattering. The normalization factor $a(\theta)$ is measured by reference to a vanadium standard.

It follows that $F(k)$ can be expressed by

$$F(k) = \sum_{\alpha=1}^{\nu} \sum_{\beta=1}^{\nu} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} [S_{\alpha\beta}(k) - 1], \quad (2)$$

where $S_{\alpha\beta}(k)$ are Faber-Ziman partial structure factors.¹⁹

We have measured $F(k)$ of three saturated solutions of isotopic composition: ${}^7\text{Li}^{\text{Nat}}\text{ND}_3$, ${}^6\text{Li}^{\text{Nat}}\text{ND}_3$, and ${}^6\text{Li}^{15}\text{ND}_3$, in addition to the bulk solvent, ${}^{15}\text{ND}_3$. The first-order lithium and nitrogen centered difference functions $\Delta_{\text{Li}}(k)$ and $\Delta_{\text{N}}(k)$ are extracted from combinations of the total structure factors;

$$\begin{aligned}\Delta_{\text{Li}}(k) &= {}'F_{\text{Li}}(k) - F_{\text{Li}}(k) \\ &= c_{\text{Li}}^2 ({}'b_{\text{Li}}^2 - b_{\text{Li}}^2) [S_{\text{LiLi}}(k) - 1] \\ &\quad + 2c_{\text{Li}}c_{\text{N}} ({}'b_{\text{Li}} - b_{\text{Li}}) b_{\text{N}} [S_{\text{LiN}}(k) - 1] \\ &\quad + 2c_{\text{Li}}c_{\text{D}} ({}'b_{\text{Li}} - b_{\text{Li}}) b_{\text{D}} [S_{\text{LiD}}(k) - 1]\end{aligned}\quad (3)$$

and

$$\begin{aligned}\Delta_{\text{N}}(k) &= {}'F_{\text{Li}}(k) - F_{\text{N}}(k) \\ &= c_{\text{N}}^2 (b_{\text{N}}^2 - {}'b_{\text{N}}^2) [S_{\text{NN}}(k) - 1] \\ &\quad + 2c_{\text{N}}c_{\text{Li}} (b_{\text{N}} - {}'b_{\text{N}}) {}'b_{\text{Li}} [S_{\text{LiN}}(k) - 1] \\ &\quad + 2c_{\text{N}}c_{\text{D}} (b_{\text{N}} - {}'b_{\text{N}}) b_{\text{D}} [S_{\text{ND}}(k) - 1].\end{aligned}\quad (4)$$

The bound coherent neutron-scattering lengths were taken from Sears²⁰ where $'b_{\text{Li}} > b_{\text{Li}}$ for $\Delta_{\text{Li}}(k)$ and $b_{\text{N}} > {}'b_{\text{N}}$ for $\Delta_{\text{N}}(k)$. Here, $F_{\text{Li}}(k)$ is the total structure factor for the solution of isotopic composition ${}^7\text{Li}^{\text{Nat}}\text{ND}_3$ with scattering lengths: b_{Li} , b_{N} , and b_{D} , $'F_{\text{Li}}(k)$ for ${}^6\text{Li}^{\text{Nat}}\text{ND}_3$ with $'b_{\text{Li}}$, b_{N} , and b_{D} , and $F_{\text{N}}(k)$ for ${}^6\text{Li}^{15}\text{ND}_3$ with $'b_{\text{Li}}$, $'b_{\text{N}}$, and b_{D} .

Fourier transformation of Eqs. (3) and (4) yield the corresponding real-space distribution functions $\Delta G_{\text{Li}}(r)$ and $\Delta G_{\text{N}}(r)$. The average coordination number of species β around α , $n_{\alpha\beta}$, is obtained by integration of the peak area in the r -space functions to the first minimum.

III. EXPERIMENT

Solution samples for the neutron-diffraction experiments were made *in situ* at the D4B instrument of the Institut Laue-Langevin reactor source, Grenoble, using high-purity chemicals: anhydrous ${}^{\text{Nat}}\text{ND}_3$ (99% D); anhydrous ${}^{15}\text{ND}_3$ (98% ${}^{15}\text{N}$, 98% D); ${}^7\text{Li}$; ${}^6\text{Li}$ (95% ${}^6\text{Li}$). Preweighed lithium metal was placed in a cylindrical, null coherent scattering, Ti/Zr container. A measured volume of ammonia was then condensed onto the metal, from a stainless-steel gas rig. Neutron-diffraction data were collected at 235(5) K using an incident neutron wavelength of 0.7041(7) Å.

A significant advantage of performing the neutron-diffraction experiments using a fixed incident neutron wavelength at a reactor source is seen in the context of the data analysis. The neutron absorption cross section for most elements is wavelength dependent and typically increases with the wavelength,²⁰ e.g., $\sigma_{\text{abs}}(0.7041 \text{ Å}) \sim 0.39\sigma_{\text{abs}}(1.798 \text{ Å})$ for our ${}^6\text{Li}^{15}\text{ND}_3$ sample. The sample attenuation factor $A_{S,SC}(\theta)$ will therefore vary with scattering angle alone and will have no wavelength dependence, as for example on a time-of flight (TOF) neutron source using a range of incident neutron wavelengths. Hence, if the experiments were to be conducted using a TOF source, correction

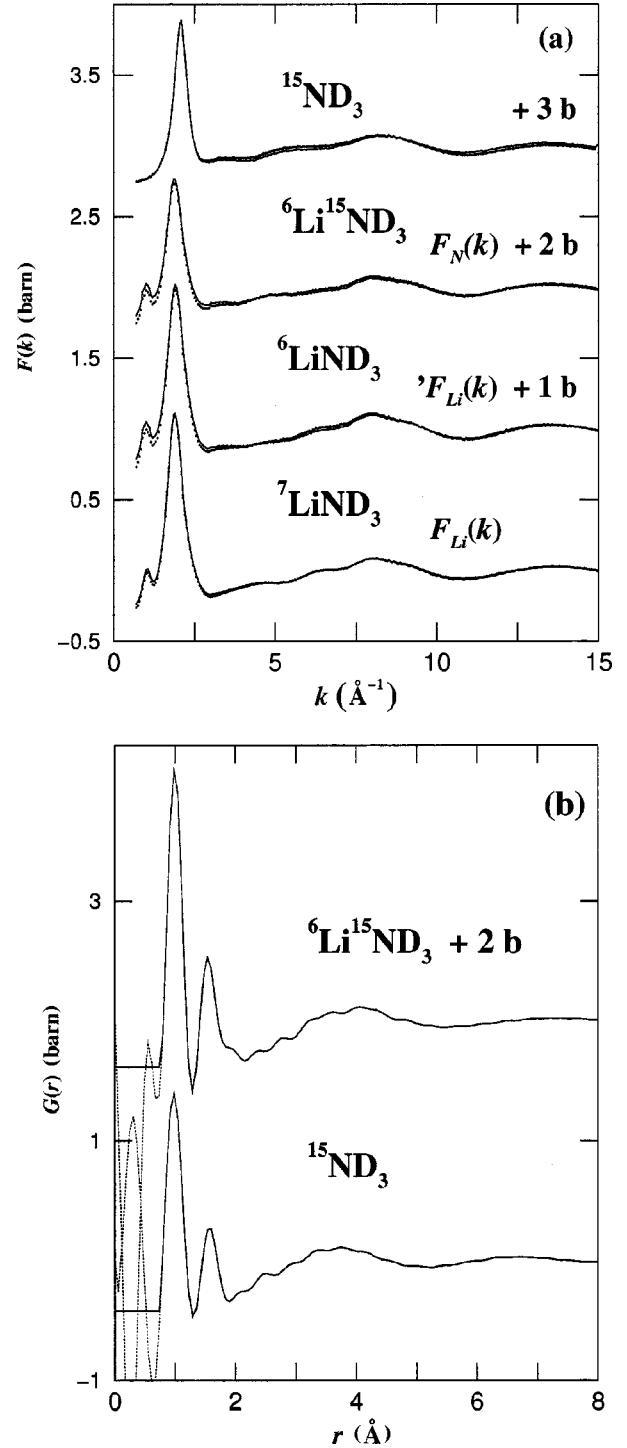


FIG. 1. (a) The total structure factors $F(k)$ for liquid ammonia and saturated lithium ammonia solutions obtained at 235(5) K. The measured data points are given by the error bars and the solid line is the back-Fourier transform, obtained after setting the unphysical low- r oscillations in the corresponding $G(r)$ to their calculated low- r limit. (b) The real-space distribution functions $G(r)$ for ${}^6\text{Li}^{15}\text{ND}_3$ and ${}^{15}\text{ND}_3$ obtained by Fourier transformation of the corresponding $F(k)$ denoted by the error bars in (a).

for sample attenuation could be all the more problematic. The use of a fixed incident neutron wavelength is particularly valuable here, due to the presence of highly absorbing ${}^6\text{Li}$ in one of our samples.

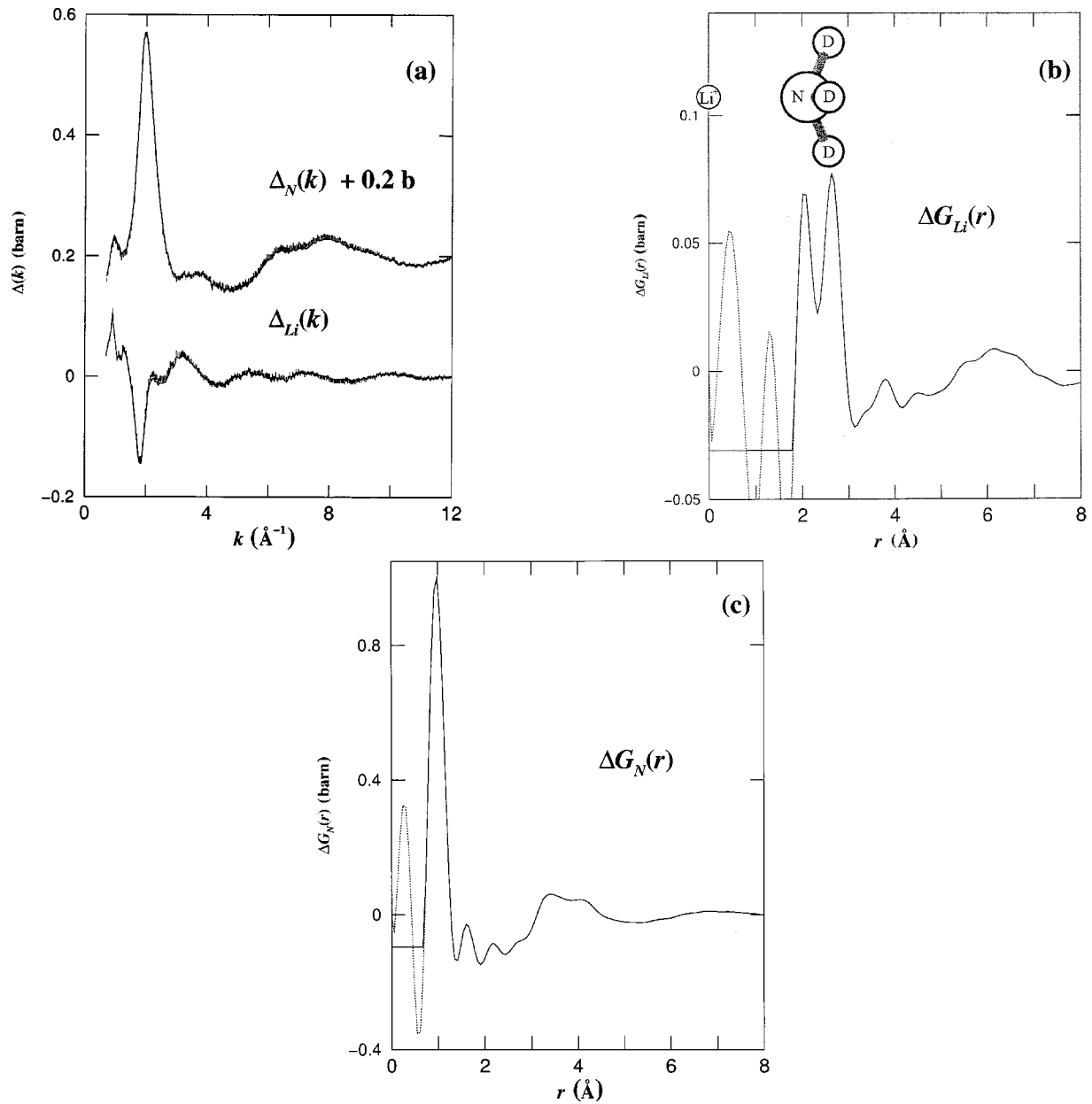


FIG. 2. (a) The first-order difference functions $\Delta_{\text{Li}}(k)$ and $\Delta_{\text{N}}(k)$ for the metallic lithium-ammonia solutions. The measured data points are given by the error bars and the solid line is the back-Fourier transform, obtained after setting the unphysical oscillations at low- r values in $\Delta G_{\text{Li}}(r)$ and $\Delta G_{\text{N}}(r)$ to their respective calculated low- r limits, shown by the solid lines in (b) and (c). (b) $\Delta G_{\text{Li}}(r)$ for the metallic lithium-ammonia solutions. The position and arrangement of the nearest-neighbor ammonia molecule to the lithium ion are shown pictorially. (c) $\Delta G_{\text{N}}(r)$ for the metallic lithium-ammonia solutions. From the mismatch in the isotopic enrichment of deuterium found in our $^{15}\text{ND}_3$ and $^{\text{nat}}\text{ND}_3$ chemicals, a small contribution from D-D and D-Li correlations will be present in $\Delta_{\text{N}}(k)$ and $\Delta G_{\text{N}}(r)$, i.e., in mb, $\Delta G_{\text{N}}(r) = 64.2(4)[g_{\text{ND}}(r) - 1] + 25.1(9)[g_{\text{NN}}(r) - 1] + 1.5(2)[g_{\text{NLi}}(r) - 1] + 6.7(8)[g_{\text{DD}}(r) - 1] + 0.2(7)[g_{\text{DLi}}(r) - 1]$. Hence the small peak at $1.61(3)$ Å in $\Delta G_{\text{N}}(r)$ is identified with intramolecular D-D correlations.

IV. RESULTS AND DISCUSSION

The measured $F(k)$'s for the lithium-ammonia solutions are shown together with the k -space data for the pure solvent, $^{15}\text{ND}_3$, in Fig. 1(a). The efficacy of these data after corrections for background, absorption, and inelastic scattering is tested by their approach to the correct high- k limit, which satisfies the usual sum-rule relation.²¹ They therefore give good overall agreement with their back-Fourier transforms. The latter is obtained once the unphysical low- r oscillations are set to the calculated low- r limit in the real-space functions.

In the lithium-ammonia solutions the principal peak is shifted to a lower k value, $1.90(2)$ Å⁻¹ compared with $2.05(2)$ Å⁻¹ for the pure solvent. This reflects the reduction in overall solvent density, due to the presence of solvated electrons. In addition, a first sharp diffraction peak evolves at $0.97(2)$ Å⁻¹, signifying intermediate-range order within our concentrated metallic solutions.²² Both the solvent and solutions exhibit similar damped oscillations at high- k values, extending out to 15 Å⁻¹, suggesting that the intramolecular correlations of ammonia are unchanged by the presence of Li.¹⁴

The total real-space distribution functions $G(r)$ for both

liquid ammonia and the lithium-ammonia solutions show an intense and well defined peak at 0.99(2) Å, followed by a peak at 1.55(2) Å, see Fig. 1(b). These peaks are assigned to intramolecular N-D and D-D correlations.²³ In the $G(r)$ for ${}^6\text{Li}-{}^{15}\text{ND}_3$, at 1.99(3) Å a shoulder is observed on the high- r side of the second peak, but is absent in the $G(r)$ for ${}^{15}\text{ND}_3$. We will shortly identify this feature with nearest-neighbor Li-N correlations. Beyond 2 Å, the $G(r)$ for both ${}^6\text{Li}-{}^{15}\text{ND}_3$ and ${}^{15}\text{ND}_3$ show a broad feature covering the range $3.0 \leq r$ (Å) ≤ 4.5 . This contains the contribution from N-N correlations between neighboring ammonia molecules.²³

Turning now to our difference analysis, we see that at approximately 1 \AA^{-1} the prepeak is still present in both $\Delta_{\text{Li}}(k)$ and $\Delta_{\text{N}}(k)$, as shown in Fig. 2(a). This tells us immediately that the intermediate-range order in the metallic solutions arises from both Li^+ - and N-centered correlations, consistent with contact of solvated lithium ions.

Figure 2(b) shows that $\Delta G_{\text{Li}}(r)$ is characterized by two intense overlapping peaks, with maxima at 2.06(2) and 2.64(2) Å. We assign these to nearest-neighbor Li-N and Li-D correlations, respectively.^{8-11,23} Integration of the peaks yields coordination numbers $n_{\text{LiN}} = 3.5(2)$ and $n_{\text{LiD}} = 10.3(2)$. This compares with the results of quantum-mechanical simulations of albeit, dilute solutions, which predict a tetrahedral coordination of lithium but with a nearest-neighbor Li-N distance of 2.15 Å.¹¹ Computer simulations using empirical models tend to predict octahedral coordination of lithium by ammonia, in both dilute and concentrated solutions.⁸ An exception, which gave $n_{\text{LiN}} = 4$ and $r_{\text{LiN}} = 2.05 \text{ \AA}$, used *ad hoc* parameters based upon $\text{Li}^+ - \text{H}_2\text{O}$ interaction potentials.⁹

Interestingly, there is evidence of a well defined second solvation shell, at 3.80(2) Å in $\Delta G_{\text{Li}}(r)$. This has been predicted by quantum simulations,¹¹ and is here attributed to ammonia molecules shared between two cations. These solvent separated $\text{Li}^+ - \text{Li}^+$ pairs contribute to the maximum in $\Delta G_{\text{Li}}(r)$ occurring at 6.14(3) Å.

Figure 2(c) shows that $\Delta G_{\text{N}}(r)$ is dominated by the characteristic nearest-neighbor N-D peak of the ammonia molecule, at 0.97(2) Å with $n_{\text{ND}} = 3.3(2)$. A broad peak at 3.40(3) Å is due to adjacent nitrogen atoms. This N-N distance is slightly greater than the 3.28 Å that would be observed for undistorted tetrahedra, and therefore confirms that the cation solvation is based on distorted tetrahedral geometry.

V. CONCLUSIONS

In summary, first-order difference functions have been successfully measured for a saturated solution of lithium in

ammonia, using the method of isotopic substitution in neutron diffraction. The local coordination around each Li^+ cation consists of a well defined solvation shell containing an average of 3.5 ammonia molecules. These molecules direct their dipole moments away from the cation, and are undistorted relative to the pure solvent. The delocalized electrons are therefore fully dissociated from the cations. At this high metal concentration, contacts between solvent separated cations give rise to intermediate-range order.

The picture that emerges from our experiments is that the solution is highly structured, over both short and intermediate length scales. Given the very low density of the solution ($\sim 0.6 \text{ g/cm}^3$),⁵ this conclusion is, at first sight, rather surprising. However, our measured structure is in agreement with the model suggested by Maybury and Coulter²⁴ for concentrated solutions comprising solvated cations, ammonia molecules, and free electrons. This model was later supported by self-diffusion coefficient measurements of Garroway and Cotts.²⁵ The results from the study by Garroway and Cotts²⁵ show lithium ions to be solvated by four ammonia molecules in saturated solutions. At saturation no free ammonia molecules will be present. In this limit our findings strongly support the model used by Schroeder and Thompson.²⁶ They successfully predicted many electrical properties of our system, by assuming the saturated lithium-ammonia solutions to be a “single-component” system of solvated cations, i.e., with no free ammonia. Interestingly, their model could also be applied below saturation to predict the decrease in electrical conductivity with decreasing metal concentration. This dependence is assumed to arise from the increase in the fraction of free ammonia molecules present to scatter the delocalized electrons.

In order to further understand the microscopic mechanisms for the metal-nonmetal transition, which occurs between 1 and 7 MPM, detailed structure of solutions about the transition needs to be measured. These experiments on less concentrated solutions would be more demanding and are to be the subject of our future studies. However, the well defined short- and intermediate-range order of our current solution supports Mott’s suggestion that strong structure, based on solvated ions, would lead to a metal-nonmetal transition dominated by electron-electron interactions (“Mott” type), rather than disorder (“Anderson” type).^{1,2}

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