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Velocity of Ultrasound in Lithium-Ammonia Solutions*

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The velocity of 10-MHz sound waves in lithium-ammonia solutions has been determined for 23 different metal concentrations over the temperature range 89 to 240°K. By combining these data with the available density data, the adiabatic compressibility of these solutions has been determined. The compressibility is a monotonic increasing function of the concentration. An analysis of the sound velocity revealed a change in the dependence on concentration at a concentration of 5 mole %. This is the concentration at which the metal-nonmetal (Mott) transition occurs and is interpreted as evidence for a "structure" change accompanying the Mott transition.

I. INTRODUCTION

Recently attention has been focused on two striking properties of metal-ammonia solutions: the miscibility gap or mixed-phase region[1] and the metal-nonmetal (Mott) transition.[2] These two features of the phase diagram will first be discussed in order to provide a background for the experimental results which are to be presented. We refer the reader to one of the recent review articles for general descriptions of the properties of the solutions.[1,3–5]

Mixed-Phase Region

If a solution of lithium in ammonia is prepared at a metal concentration of 5 mole %[6] and the temperature lowered below 206°K, the solution separates into two phases, one floating above the other. Both phases contain lithium; i.e., there are two immiscible solutions of the same metal in equilibrium. Figure 1 shows the phase diagram of the lithium-ammonia solutions,[7,8] with region I being the mixed-phase region.

Pitzer[9] has compared the two phases in the solutions to those present in an ordinary vapor-liquid condensation, in an attempt to explain the nature of the mixed-phase region. He suggests that the ammonia be considered as a dielectric medium in which the lithium can undergo liquid-vapor separation. In effect, the dilute side of the two-phase region corresponds to gaseous atomic lithium (no metallic properties observed) and the concentrated side to liquid lithium (possessing the properties of a liquid metal). This appears to be a very attractive treatment of the miscibility gap. The phase diagram shown in Fig. 1 can be converted to a temperature-volume diagram by using the experimentally determined relation between the molar volume of the solutions and the concentration.[10] Since the volume is a smooth function of the concentration and temperature, the phase diagram would have the same general shape as Fig. 1, which is similar to that for a pure substance. However, the diagram is not in a plane perpendicular to the pressure

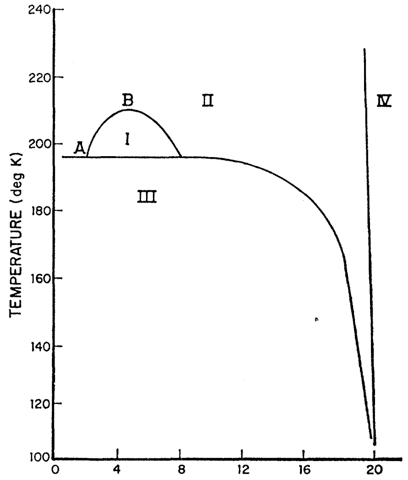

Fig. 1. Phase diagram of lithium-ammonia solutions. Region I is the mixed-phase region; region II is a single-liquid region; in region III, solid NH_3 precipitates out of the solutions; and in region IV, solid lithium precipitates out. The significance of A-B is given in Fig. 4.

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[1] *Metal-Ammonia Solutions*, edited by G. Lepoutre and M. J. Sienko (W. A. Benjamin, Inc., New York, 1964); J. L. Dye, G. Lepoutre, P. R. Marshall, and P. Pajot, *ibid.*, p. 92.

[2] D. S. Kyser and J. C. Thompson, J. Chem. Phys. **42**, 3910 (1965).

[3] T. P. Das, Advan. Chem. Phys. **4**, 303 (1962).

[4] M. C. R. Symons, Quart. Rev. **13**, 99 (1959).

[5] J. C. Thompson, in *The Chemistry of Non-Aqueous Solvents II*, edited by J. J. Lagowski (Academic Press Inc., New York, 1967), p. 265.

[6] For this paper, the concentration will be expressed either in mole fractions x, where $x=$ (moles metal)/(moles metal+moles NH_3), or as a mole ratio R, where $R=$ (moles NH_3)/(moles metal); hence $R=x^{-1}-1$.

[7] J. A. Morgan, R. L. Schroeder, and J. C. Thompson, J. Chem. Phys. **43**, 4494 (1965).

[8] P. D. Schettler and A. Patterson, J. Phys. Chem. **68**, 2870 (1964).

[9] K. S. Pitzer, J. Am. Chem. Soc. **80**, 5046 (1958).

[10] W. E. Johnson, A. W. Meyer, and R. D. Martens, J. Am. Chem. Soc. **72**, 1842 (1950).

axis in *PVT* space, as the data from which the phase diagram is constructed were taken at the vapor pressure of the solutions. The dissociation of ion and electron[3,5,11] in dilute solutions is not considered. On the other hand, the view that the phase separation is qualitatively similar to a liquid-vapor phase transition is supported by the activity calculations of Dye *et al.*[1]

Mott Transition

Most of the ideas concerning the metal-nonmetal transition were first developed by Mott.[12] We now give a brief statement of his analysis.

Mott believes that a monatomic material undergoes a sharp transition between a metallic state and a nonmetallic state as the interatomic spacing is changed. This is in contrast with the standard band-theory picture which says that as the atoms are brought together, the electron wave functions on adjacent atoms overlap, bands are formed, and the solid conducts, however far apart the atoms might be. Mott points out that this is a paradoxical result and probably not true. For conduction to occur, energy must be supplied to remove electrons from their atoms. Even an electron removed from an atom may be bound to the resulting ion by Coulomb attraction, so that there is no conduction at the absolute zero. As the density of the ion-electron pairs increases, the presence of other electrons will screen the Coulomb attraction, thus weakening it. Conduction (at the absolute zero) can only occur when the density of electrons is high enough that overlap between the screened Coulomb potentials eliminates any bound states. Mott believes that this transition is a very sharp one, at least at the absolute zero, and that once the transition takes place, all the valence electrons are free. There is, thus, a critical electron density necessary for metallic conduction. Mott has given rough values for the critical density as a function of the interatomic spacing for a lattice of hydrogenlike atoms. For the case of hydrogenlike atoms, the energy should vary with the interatomic spacing as shown in Fig. 2. The minima at A and B correspond to stable configurations in the metallic and insulating phases, respectively, and indicate the possibility of phase separation. In the absence of minima, the Mott transition occurs at the density where the two curves intersect. More detailed discussions[13–16] of the nature and origin of the metal-nonmetal transition, and of possible associated phase changes, have appeared since Mott's major paper,[12] but will not be discussed here.

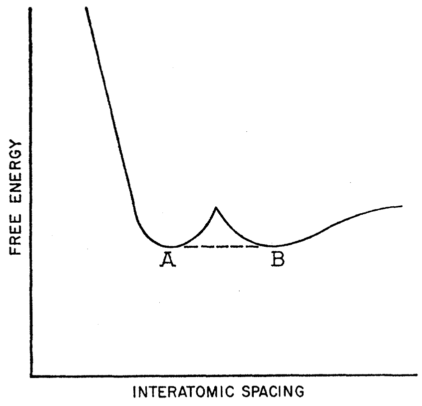

FIG. 2. Free energy versus interatomic spacing for hydrogenlike atoms, after Mott (Ref. 12). A and B denote equilibrium spacings of two phases.

We now turn to the evidence for a Mott transition in the metal-ammonia solutions.

Concentrated metal-ammonia solutions are metallic in nature. This can be seen from the following[5]: (a) high electrical conductivity; (b) low temperature coefficient of conductivity; (c) metallic reflectivity; (d) free-electron magnetic susceptibility; (e) low thermoelectric power; (f) free-electron Lorenz number; and (g) free-electron Hall coefficient. Each of the above effects can be explained by assuming that the valence electron of every metal atom is free and, together with the other valence electrons, forms an electron gas in the solution. Dilute solutions, on the other hand, show properties appropriate to an electrolyte,[5] e.g., low conductivity and little or no Knight shift. The usual evidence of association (ion pairs, etc.) as expected for weak electrolytes is also present.[3]

The metal-nonmetal transition may be seen in several electronic properties. In the concentration range 2 to 4.5 mole %, the electrical conductivity increases with increasing concentration by a factor of 100.[7,11] The electron-spin-resonance (ESR) line is symmetric in the dilute region, but becomes asymmetric as the concentration is increased. The asymmetry is a consequence of a high conductivity and thus is an indication of a metallic state.[17] The static susceptibility approaches that of a degenerate electron gas.[18]

The Mott transition described above occurs when the overlap between the screened Coulomb potentials of adjacent ions becomes sufficient to cause formation of a band. This description may be valid for a lattice of hydrogenlike atoms (with a varying lattice parameter) but is much too simple for metal-ammonia solutions. As required by the Mott model, the ionic spacing decreases in the solutions as the concentration increases; however, the number of ions and of NH$_3$ molecules

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[11] C. A. Kraus, J. Am. Chem. Soc. **43**, 749 (1921); **45**, 2551(E) (1923).

[12] N. F. Mott, Proc. Phys. Soc. (London) **A62**, 416 (1949); Can. J. Phys. **34**, 1356 (1956); Phil. Mag. **6**, 287 (1961).

[13] J. Hubbard, Proc. Roy. Soc. (London) **281**, 401 (1964).

[14] D. Adler and H. Brooks, Phys. Rev. **155**, 826 (1967).

[15] D. Jerome, T. M. Rice, and W. Kohn, Phys. Rev. **158**, 462 (1967).

[16] W. Kohn, Phys. Rev. Letters **19**, 439 (1967).

[17] R. Catterall, J. Chem. Phys. **43**, 2262 (1965).

[18] R. Suchannek, S. Naiditch, and O. J. Klejnot, J. Appl. Phys. **38**, 690 (1967).

near a given ion may also vary with concentration. Such structural changes can affect the Mott transition as much as the overlap between a pair of electron trapping centers. Since the electron in dilute solutions is localized on the NH_3 molecules,[1-5] the possibility of two types of electron traps must be considered. A change in the structure might cause the Mott transition; conversely, the Mott transition might cause a structural change. Whichever view is held, it is of interest to determine if there is any structural change in the metal-ammonia solutions in the region of the Mott transition (at such temperatures that the solutions are not in the mixed-phase region).

Krumhansl[19] has pointed out that the conditions appropriate for a metal-nonmetal transition are also highly conducive for a phase transition of first or higher order. The possibility of the phase transition arises because the concentration (or volume) dependence of the ionic part of the free energy is related to the metallic cohesive energy when the solution is metallic, while in the nonmetallic state, the atomic free energy is more closely approximated by a van der Waals–like term. If the difference in dependence on density of these two terms is pronounced, then a phase separation may occur. The first-order phase transition may eventually disappear with increasing T; that is, a critical point will occur. Though the first-order phase transition disappears at high T, the Mott transition persists in the vapor. These ideas are consistent with some recent resistivity data in Hg vapor by Hensel.[20] Krumhansl, as did Mott, indicates that this argument may as well be applied to metal-ammonia solutions, inasmuch as the phase separation corresponds to a liquid-vapor separation, as suggested by Pitzer.

If, as Krumhansl suggests, the structural (ionic) part of the free energy has different dependences on metal concentration above and below the Mott transition, so also should the compressibility. Because of the nature of the solutions, it would be difficult to measure the isothermal compressibility directly. However, by measuring the sound velocity, it is possible to obtain the *adiabatic* compressibility β_s of the solutions from the formula

$$\beta_s = C_s^{-2}\rho^{-1}, \tag{1}$$

where C_s is the sound velocity and ρ is the density. The density of the solutions has been measured.[10] We report here the results of ultrasound-velocity measurements in lithium-ammonia solutions for 23 different metal concentrations between pure NH_3 and saturation, and for temperatures between 80 and 240°K.

II. EXPERIMENTAL DETAILS AND RESULTS

As shown in Fig. 3, the solution was contained in a cylindrical quartz cell 2.0 cm long and 1.6 cm in diam. The velocity of sound was determined by a standard time-of-flight technique, using pulsed 10-MHz compressional waves generated by crystal transducers cemented to the outside of the cell. This system was calibrated by measuring the velocity in liquids with a well-known velocity.[21,22] The quartz sound cell was placed in a system in which the temperature was regulated to within ±0.1°K between 200 and 240°K. The temperature was measured by calibrated copper-constantan thermocouples placed next to the sample cell. Pure Li metal (99.8%) was cut and weighed in a helium-filled dry box. 99.95%-pure NH_3 was further purified by preparing a sodium-ammonia solution and allowing the solution to stand for at least 12 h. The ammonia was then distilled from this solution into the previously evacuated (less

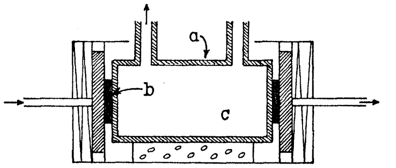

FIG. 3. Details of sample cell and cell holder. The cell is at a, a transducer at b, and the sample at c.

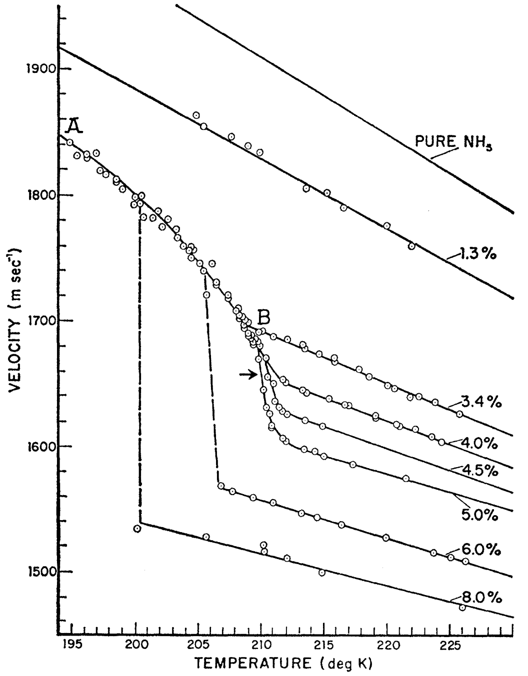

FIG. 4. Sound velocity versus temperature for solutions with concentrations between 0.0 and 8.0%. The numbers on each curve refer to the concentration. The curve A-B gives the sound speed along the low-concentration portion of the phase-separation boundary, curve A-B of Fig. 1. The arrow refers to the point of maximum slope of the 5% curve.

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[19] J. A. Krumhansl, in *Physics of High Pressures*, edited by C. T. Tomizuka and R. M. Emrick (Academic Press Inc., New York, 1965), p. 425.

[20] E. U. Franck and F. Hensel, Phys. Rev. **142**, 109 (1966).

[21] A. J. Barlow and E. Yazgan, Brit. J. Appl. Phys. **17**, 807 (1966).

[22] R. M. Rao, Indian J. Phys. **14**, 109 (1940).

than 10^{-3} Torr) cell. Further details may be found in Refs. 2 and 7.

With the time-of-flight technique, it is possible to determine the sound velocity to within one part in 10^3; however, with the present system, this was not possible because of temperature fluctuations; thus for these experiments the velocity as a function of the temperature was determined to about one part in 10^2.

The sound velocity was determined as a function of temperature for 23 different concentrations between 0.0 mole % and saturation. A portion of the data is shown in Figs. 4, 5, and 6. It is seen that the sound velocity above 150°K is a linear function of the temperature with a negative slope. The velocity also decreases as the metal concentration is increased. Figure 7 shows the temperature coefficient of the sound speed. The densities of lithium-ammonia solutions at 240.1°K were measured by Martens.[10] Densities at other temperatures for various concentrations have been reported by Coulter,[23] Jaffe,[24] and Lo.[25] These results are shown in Fig. 8. Some of the solutions densities have been extrapolated from Coulter's data for convenience. The adiabatic compressibility as calculated from the sound speed and density is shown in Fig. 9.

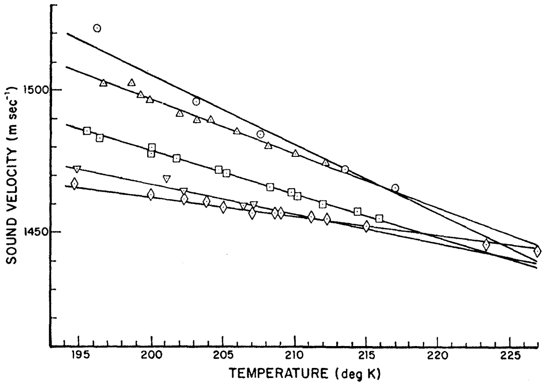

FIG. 5. Sound velocity versus temperature for solutions with concentrations between 10.0 and 18.0%. The concentrations of the various curves are: ○, 10%; Δ, 12%; □, 14%; ∇, 16%; and ◇, 18%.

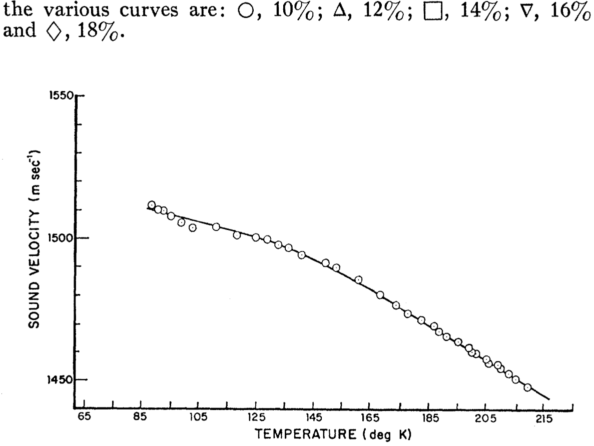

FIG. 6. Sound velocity versus temperature for a saturated lithium-ammonia solution (20%).

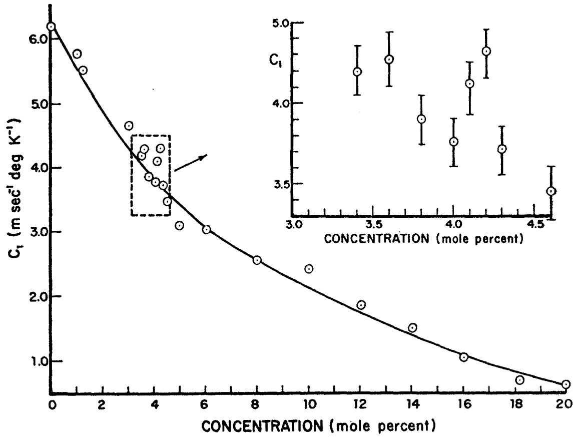

FIG. 7. Temperature coefficient of sound velocity C_1 versus concentration (in mole %) for lithium-ammonia solutions.

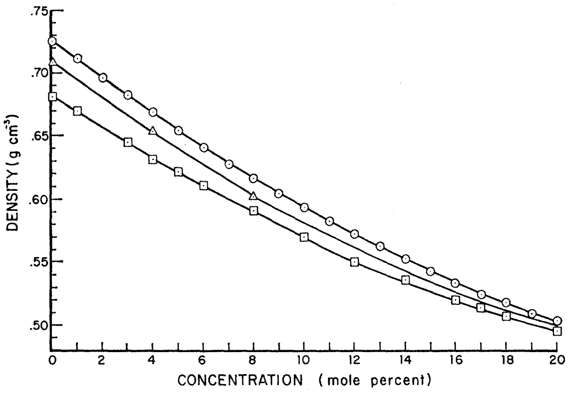

FIG. 8. Density versus concentration (in mole %) for lithium-ammonia solutions (see Refs. 23 and 25). The ○ denote data at 203°K; the Δ, 218.3°K; the □, 240°K.

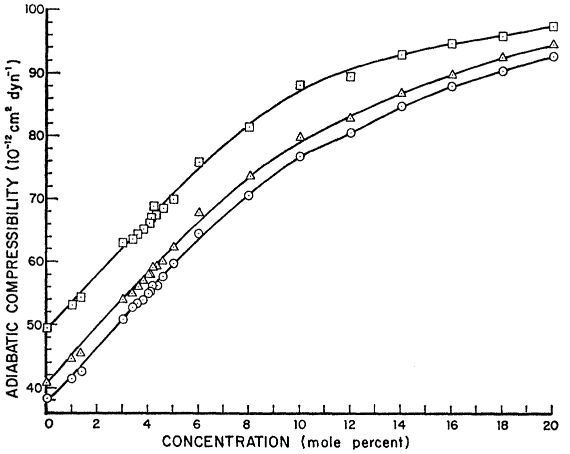

FIG. 9. Adiabatic compressibility versus concentration for lithium-ammonia solutions. The ○ denote data at 210°K; the Δ and □, as in Fig. 8.

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[23] L. V. Coulter, Northwest Sci. **16**, 80 (1942).

[24] H. Jaffe, Z. Physik **93**, 751 (1935).

[25] R. E. Lo, Z. Anorg. Allgem. Chem. **344**, 230 (1966).

III. DISCUSSION

For purposes of discussion, we separate the concentration range into three regions: (1) the concentrated, or metallic; (2) the dilute, or nonmetallic; and (3) the mixed-phase and Mott-transition region.

Concentrated Region

Figure 6 shows the sound speed for a saturated Li-NH_3 solution. The sound velocity increased linearly with decreasing temperature until a temperature of 143°K was reached, at which point some curvature appears in the C_s-versus-T plot. It is possible that this curvature is due to the solution crossing the freezing curve before it reaches the eutectic point. The freezing curve is quite steep in this region, and a slight amount of decomposition would cause the concentration to be such that the solution would cross the freezing curve at temperatures well above the eutectic temperature. It was also noted that the attenuation increased as the temperature (143°K) was passed which made velocity measurements difficult. We thus do not attach significance to the curvature; a linear variation of C_s with T is assumed.

In order to determine the functional dependence of C_s on the concentration, we express C_s in the form

$$C_s=C_0-C_1T\,,\tag{2}$$

where

$$C_0=C_0{}^0-AR^{-\alpha}\,,\tag{3}$$

and

$$C_1=C_1{}^0-A_1R^{-\beta}.\tag{4}$$

Here $C_0{}^0$ and $C_1{}^0$ are the constants appropriate for pure NH_3, and R is the mole ratio (NH_3/metal). Our analysis yields

$$A=2.7\times10^3 \text{ m/sec}\,,\quad \alpha=0.353\pm0.010\,,$$
$$A_1=9.98 \text{ m/sec°K}\,,\quad \beta=0.406\pm0.023\,,$$
$$C_0{}^0=3209\pm3.6 \text{ m/sec}\,,\quad C_1{}^0=6.19\pm0.05 \text{ m/sec°K}.$$

The above constants are valid for $R<17$.

Since much of the available data for the metallic region can be understood in terms of a free-electron gas, we first view the sound data in that context. In a jellium model, the sound speed C_s depends on the Fermi velocity V_f:

$$C_s=(mZ/3M)^{1/2}V_f,\tag{5}$$

where m is the electron mass, M the ion mass, and Z is the valence.[26] This is generally a satisfactory representation of the sound speed in liquid metals.[27] We find experimentally that C_s decreases as the Fermi velocity increases. In view of the obvious oversimplification of (5), we should not expect agreement. In particular, the effect on C_s of the ammonia molecules must not be omitted. Ashcroft and Langreth[28,29] have recently calculated the compressibility of simple solid metals from the pseudopotential viewpoint and obtain excellent agreement. Such a computation cannot at present be made for metal-ammonia solutions, as no accurate estimate of the effect of the NH_3 molecule on either the structure factor or the pseudopotential is available. Nevertheless, order-of-magnitude agreement is found between the observed compressibilities and those computed by the Ashcroft-Langreth procedure, without the pseudopotential contribution.

Dilute Region

The lowest concentration studied here (~1%) is well above the concentration range wherein these solutions exhibit electrolytelike behavior.[5] It is thus unrewarding to attempt interpretations in terms of electrolyte theory.[30] We can only remark that the addition of a salt to a pure solvent tends to increase the sound velocity,[31] in contrast to the effect observed here. We may attribute the difference to the unique properties of the solvated electron.[5]

Nevertheless, we find a simple representation of the data, since the sound velocity is again a linear function of the temperature and may be represented by (2). However, the functional dependence of C_0 and C_1 is different. Here we have

$$C_0=C_0{}^0-BR^{-\gamma}\,,\tag{6}$$

$$C_1=C_1{}^0-B_1R^{-\delta}\,,\tag{7}$$

where

$$B=2.2\times10^4 \text{ m/sec}\,,\quad \gamma=1.06\pm0.010\,,$$
$$B_1=7.8\times10^1 \text{ m/sec°K}\,,\quad \delta=1.11\pm0.013\,.$$

The above constants are valid for $R>19$.

Mixed-Phase Region

In order to interpret the results for the mixed-phase region, it is necessary to discuss the events which occur when a solution enters this region. Since the dilute phase is more dense, it settles to the bottom of the cell; thus the signals are always propagated through the dilute phase. In several instances, the boundary between the two phases lay in the cell, and velocities appropriate to each phase were simultaneously observed. In some cases, signs of the phase separation were found at temperatures above the accepted phase boundary. The data were taken on both increasing and

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[26] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, London, 1964), p. 173.

[27] R. T. Smith, G. M. B. Webber, F. R. Young, and R. W. B. Stephens, Advan. Phys. **16**, 515 (1967).

[28] N. W. Ashcroft and D. C. Langreth, Phys. Rev. **155**, 682 (1967).

[29] N. W. Ashcroft and D. C. Langreth, Phys. Rev. **156**, 685 (1967).

[30] J. Stuehr and E. Yeager, in *Physical Acoustics II*, edited by W. P. Mason (Academic Press Inc., New York, 1965), Part A, p. 351.

[31] R. H. Maybury and L. V. Coulter, J. Chem. Phys. **19**, 1326 (1951).

decreasing temperature cycles, with the solution being well stirred by a magnetically operated plunger. The data were taken after a period of about 2 h, following a temperature change of 1.0°K. The data thus are expected to be characteristic of an equilibrium system. As may be seen in Fig. 4, the 5% solution shows a departure from linearity at temperatures well above the phase boundary (denoted by the arrow) as determined by Schettler and Patterson.[8] The slope of this curve has a maximum at a temperature of 210°K. By taking this as the transition temperature, good agreement with the published value, which was derived from visual observations, is obtained. We therefore emphasize the data obtained above 210°K in what follows.

The sound velocity may be expressed by Eq. (2) in this region as long as the temperature is above that of the phase boundary. Figure 10 shows $(C_0^0-C_0)$ and $(C_1^0-C_1)$ as a function of R for the entire concentration range. We see that the concentration dependence of both $(C_0^0-C_0)$ and $(C_1^0-C_1)$ changes abruptly in the region between $R=17$ and $R=19$. Our analysis shows that for this region the sound velocity is given by

$$C_s=(C_0^0-BR^{-\gamma})-(C_1^0-A_1R^{-\beta})T, \qquad (8)$$

where the values for the constants are given above.

Thus the sound velocity has a different concentration dependence in the insulating and conducting phases of the solutions. This change in concentration dependence occurs in a region between $R=17$ (5.5 mole %) and $R=19$ (5.0 mole %), the same concentration as that for the Mott transition observed by Kyser and Thompson.[2] Thus there is evidence for a mechanical change in the lithium-ammonia solutions at the Mott transition. It is not possible to describe the exact nature of this mechanical change without a detailed model for the solution. However, by considering a minor modification of the model proposed by Maybury and Coulter,[31] it is possible to account qualitatively for this change.

Maybury and Coulter interpreted the large value of the compressibility of the solutions by describing a solution as an expanded metal in which the lattice unit is the cation solvated by six ammonia molecules. This complex is reasonable for saturated calcium-ammonia solutions, in view of the existence of solids such as $Ca(NH_3)_6$, and is consistent with the known coordination number of Na. Only the number of ammonia molecules involved in the solvation need be changed, and the model becomes applicable to the present data. The lithium-ammonia solutions saturate at a mole ratio of 4 (four ammonia molecules to one lithium atom), and there is evidence for the existence of the compound $Li(NH_3)_4$.[7] Thus it seems reasonable to postulate the complex for the saturated lithium-ammonia solutions to be the lithium ion solvated by four ammonia molecules.

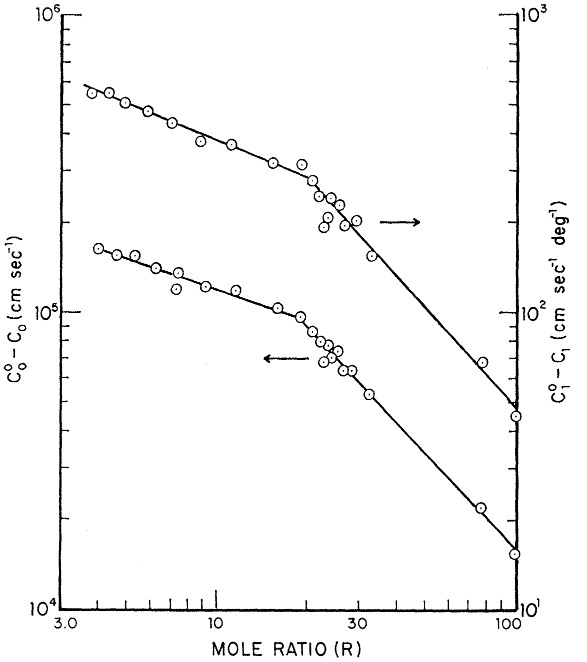

FIG. 10. Coefficients for the change of sound speed with T; $C_s=C_0-C_1T$ in a solution, as compared with those in pure NH_3, $C=C_0^0-C_1^0T$.

The additional ammonia molecules which dilute a saturated solution may either be free in the space between these complexes, or they may be bound to the complexes. Either of these cases accounts for the smooth increase in the sound velocity as the solutions are diluted. However, if additional ammonia molecules either simply cluster around the complex or fill in the space between the complexes, the concentration dependence of the sound velocity should not change abruptly as the concentration is changed. The fact that the concentration dependence does change near 5% leads to the conclusion that the complex or complexes existing in the solutions must change as the solutions are diluted. Thus the concentrated and dilute solutions have different units of structure.

If the concentrated and dilute solutions have different units of structure, other thermodynamic properties should show different concentration dependences in the two regions. Figure 11 shows the vapor-pressure data of Marshall[32] for lithium-ammonia solutions at 238.2°K. This curve shows a knee quite similar to that seen in the sound-velocity curves. It occurs at $R=14$ ($x=6.6$ mole %). Figure 12 shows the surface-tension data of Sienko[33] for sodium-ammonia solutions (no surface-tension data for lithium-ammonia solutions are available) plotted in the same manner as the vapor-pressure data. Here the precise value (3–4%) at which the knee occurs is not to be considered significant because of possible decomposition effects; the presence

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[32] P. R. Marshall, J. Chem. Eng. Data **7**, 399 (1962).

[33] M. J. Sienko, in *Metal-Ammonia Solutions*, edited by G. Lepoutre and M. J. Sienko (W. A. Benjamin, Inc., New York, 1964), p. 33.

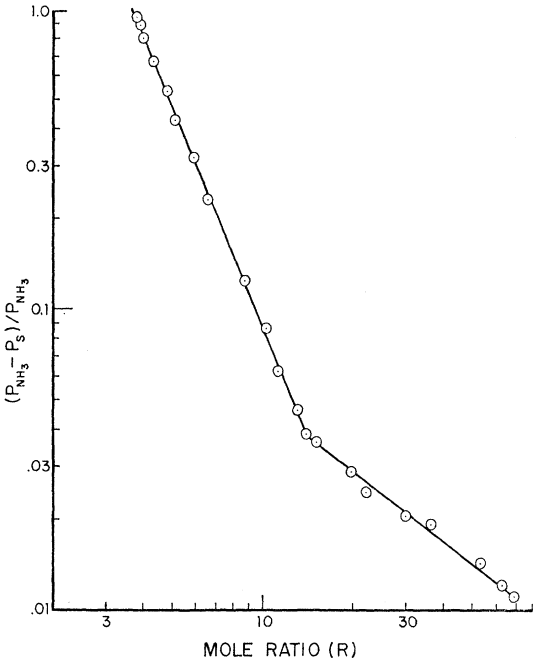

FIG. 11. Vapor-pressure change versus R for lithium-ammonia solutions (see Ref. 32); the temperature is 238°K.

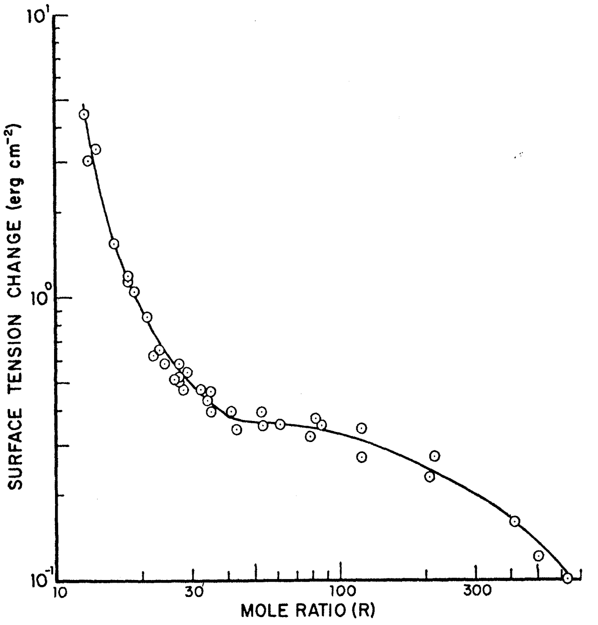

FIG. 12. Surface-tension change versus R for sodium-ammonia solutions (see Ref. 33); the temperature is 243°K.

of the knee is, however, significant. Such properties as density and viscosity do not show pronounced changes at the metal-nonmetal transition.[1] These data support the view that the structural change is more related to a change in the particle-particle interaction resulting from the screening produced by the delocalized electron than to a change in the interacting particles.

There is no doubt that the structure of the solutions changes in the region of the metal-nonmetal transition. In the absence of a theory of the solutions[5] or of the metal-nonmetal transition[19] (see also the remarks of Kohn[16] for several possibilities), it is difficult to describe the nature of the transition. Three structures may be considered in the metallic range: ion-ion, ion-ammonia, and ammonia-ammonia. In the nonmetallic phase, there is also the solvated electron,[1] and therefore structures in addition to those cited. The rearrangements occasioned by the delocalization of the electron are doubtlessly the sources of the effects reported here, but a description of those rearrangements has not yet been made. An x-ray or neutron determination of the structure should be of considerable interest.