8-2003

Electrical Conductivity Measurements of Lithium-Ammonia Solutions

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ELECTRICAL CONDUCTIVITY MEASUREMENTS OF LITHIUM-AMMONIA SOLUTIONS

by

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A Thesis
Submitted to the
Faculty of The Graduate College
In partial fulfillment of the
requirements for the
Degree of Master of Arts
Department of Physics

Western Michigan University
Kalamazoo, Michigan
August 2003

For my Dad

ACKNOWLEDGMENTS

I would like to give thanks to my advisor, Dr. Clement Burns, for his help and support while working on the project, and for writing the thesis.

I would also like to thank Dr. Lisa Paulius for reviewing my thesis, and providing valuable input. Her help and support were important in my work.

I want to express my thanks to Dr. Dean Halderson in my own way. If I could go back in time, I would do things differently.

I consider myself lucky having a friend like Valentina Tobos. Thank you, Valentina for everything.

A special thanks goes to Allan Kern, who was always helpful and nice.

I would like to thank David Hoogerheide and Lucian Undreiu. Thanks, you guys. Dave, it was a pleasure to work with you.

And most of all, I would like to thank my husband Paul, for putting up with me, and my tantrums, while working on this thesis.

ELECTRICAL CONDUCTIVITY MEASUREMENTS OF LITHIUM-AMMONIA SOLUTIONS

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Western Michigan University, 2003

The topic covered in this thesis is the study of electronic interactions for liquid metal-ammonia solutions, lithium-ammonia solutions in particular. To obtain a theoretical understanding of so-called correlated electron systems.

The work focuses on sample creation and measurement of electrical conductivity of lithium-ammonia solutions varying with temperature for different concentrations. We have taken measurements in liquid lithium-ammonia mixtures using four-wire method to minimize the contact resistance. We have shown how it is possible to carry out accurate measurements of the electrical conductivity in these systems with the four wire measurements.

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I. INTRODUCTION

Background and History of Metal-Ammonia Solutions

Because of their low electronic density, metal-ammonia solutions represent good systems to test theories of electron interaction in metals. The concentration of solution can be changed at will by changing the amount of metal added which makes possible the study of electrical conductivity and properties of electron transport under different conditions. In the past electron transport were done to provide insight into phase transition and possible superconducting behavior.

Metal-ammonia solutions were discovered by Sir Humphrey Davy around 1808, when he made his first observation on bronze potassium ammonia [1]. In the same year, Seebeck prepared solutions of NH_4 in mercury, which he called "ammonium amalgams" and it was established that the dissolved species was NH_4 [2].

In 1864, Weyl reported experiments in which it was observed that certain metals (sodium and potassium) dissolved in ammonia and he concluded that "metal-ammoniums" (NH_4) were formed [3]. He suggested the existence of these components in which one or more hydrogen atoms was replaced with metal atoms. Weyl claimed in his paper [4] that it would be possible to prepare metal-ammonium MNH_4 solutions by direct combination of ammonia and a highly electropositive metal.

Around 1870, Seely repeated the work of Weyl and extended it to lithium and rubidium. He was the first to consider the metal-ammonia solutions to be true solutions of metals in a solvent rather than compounds of metal and ammonia. Seely stated that alkali metals dissolve in ammonia as salts dissolve in water: "the solid disappears in the liquid and on evaporating the liquid, the solid reappears in its original

form" [5]. Seely concluded that the liquid anhydrous ammonia is a solvent of alkali metals and the metals did not react with the solvent and therefore NH_4^+ (ammonium) did not form.

A major contribution in the investigation and study of the metal ammonia solutions was made by Kraus. Kraus systematically studied the equilibrium vapor pressure of ammonia to determine the compositions of phases for different metal-ammonia systems [6]. He studied solutions of lithium, sodium and potassium in ammonia. Kraus studied the change from electrolytic to metallic properties for metal ammonia systems and concluded in 1908 that the valence electron of the metal associates with the solvent in dilute solutions. The electron is surrounded by "an envelope of solvent molecules" and that the valence electron is free in concentrated solutions [7].

Kraus' work on sodium dissolved in ammonia stated that in dilute solutions the metal dissolves as a salt, having solvated cations and solvated electrons, forming ion-pairs. His work on the conductance of alkali metals in liquid ammonia had a large impact in the study of metal ammonia solutions and was unchallenged for a long period of time. The data of conductance versus concentration were very valuable for testing various models of metal ammonia solutions [8]. Kraus tried to determine the nature of the solutions of the metals in liquid ammonia and to determine the nature of the conduction process in these solutions.

In 1963, a series of conferences with the name Colloque Weyl was begun with the goal of bringing together research on metal-ammonia solutions. One of the remarkable contributions was provided by M. Sienko in his extraordinary work in the

field. Sienko studied phase transitions, conductivity, surface tension, and the metal-nonmetal transition. In the same year, while at Cornell, "Sienko was led to the startling discovery that that the two layer coexistence curves for Li-NH_3, Na-NH_3, and K-NH_3 were almost unique in exhibiting parabolic dependencies, whereas all other critical phenomena (and the best theoretical models) corresponded to cubic coexistence curves." He showed that liquid-liquid phase separation in metal ammonia solutions was related to the metal-nonmetal transition. He demonstrated by electric and magnetic studies under cryogenic conditions, that $Li(NH_3)_4$ and $Ca(NH_3)_6$ represent "expanded metals" on the metallic side of the metal-nonmetal transition [9].

Study of Metal-Ammonia Solutions

Metal-ammonia solutions are solutions of alkali metals (Li, Na, K, Rb, and Cs), alkali-earth metals (Mg, Ca, Sr, and Ba) and lanthanides (Eu and Yb) in anhydrous liquid ammonia. They dissolve readily in pure liquid ammonia without chemical reaction, the result being a positive ion and one or more free electrons.

The metal-ammonia solutions are binary mixtures having solvated ions and free ammonia molecules as components. As the metal dissolves into solution, the valence electron dissociates from the alkali metal and acts as a free electron.

$$M + NH_3 \rightarrow M^{n+} + ne^- + NH_3$$

$$Li + NH_3 \rightarrow Li^+ + 1e^- + NH_3$$

The electric field of an ion polarizes the ammonia molecules and ammonia binds weakly to the ion. When the solid metal is dissolved in liquid ammonia, a

significant increase of volume occurs, which is attributed to the dissociation of the metal atoms into metal ions and solvated electrons.

Metal-ammonia solutions are liquid metals with low electronic densities which offer a simple model to investigate properties of expanded systems. These systems are called expanded metals because the distance between the conduction electrons is far greater than in a regular metal.

Electrons at lower densities have low energy of motion compared to the energy involved in the interaction with the other electrons, which makes the metal-ammonia solutions suitable systems to study and test theories that predict how electrons interact with each other in metals. The low-electron-density system represents a highly correlated electron system. The metal-ammonia solutions are important in obtaining a theoretical understanding of these correlated electron systems, systems in which the electron-electron interaction determines the electrical properties of the material. The electronic density can be varied by changing the amount of Li to be dissolved in liquid ammonia without altering other properties of the material, which makes possible the study of properties of electrons under different conditions. Electrical conductivity measurements provide insight into the metal insulator phase transition and permits the study of electronic interactions in liquid and solid phases. Metal-ammonia solutions illustrate the change from nonmetallic to metallic behavior, and separate into coexisting metal and nonmetal layers under specific conditions of temperature and concentration. Lithium metal is miscible in ammonia in concentrations greater than 20 MPM, or mole percent metal*. At saturation the

* MPM = 100 x moles metal/(moles metal + moles NH_3).

lithium-ammonia solutions are better conductors than mercury (σ_{Hg}= 10000Ω^{-1}cm^{-1}) and have the lowest density (0.48g/cm^3) of any liquid at room temperature [9], [10].

Li dissolves readily in anhydrous liquid ammonia without chemical reaction and produces intense blue inky-colored dilute solutions and metallic bronze-gold-colored concentrated solutions. The solvated electron is responsible for the blue color of the dilute solution. The solvated electron represents an ammoniated electron, an electron trapped in the potential well formed by the surrounding ammonia molecules. These solvated electrons exhibit electronic 1s→2p transitions in the potential well [11]. They are responsible for a broad asymmetric absorption band in the near infra-red. The absorption band peaks near 0.9 eV [12] and has a high-energy tail running to 1.8 eV.

This long tail is responsible for the blue color. The end of the tail corresponds to a wavelength λ=689 nm (red) and since blue is the complementary color of the absorbed red in visible spectra, the lithium-ammonia dilute solutions appear to be blue. The tail is essentially unaffected in shape and location when the metal is changed so all dilute alkali-metal–ammonia solutions have the blue color. In concentrated solutions, as the solvation weakens, the location of the absorbed solvated electron line shifts further into the red [16].

Near 4 MPM, the metal-nonmetal (M-NM) transition takes place. There is also a liquid-liquid phase separation into two liquids (with a bronze colored conducting liquid floating on top of a blue insulating liquid) below T_c=210K [16] for certain concentrations as shown in the picture and in the lithium-ammonia phase diagram.

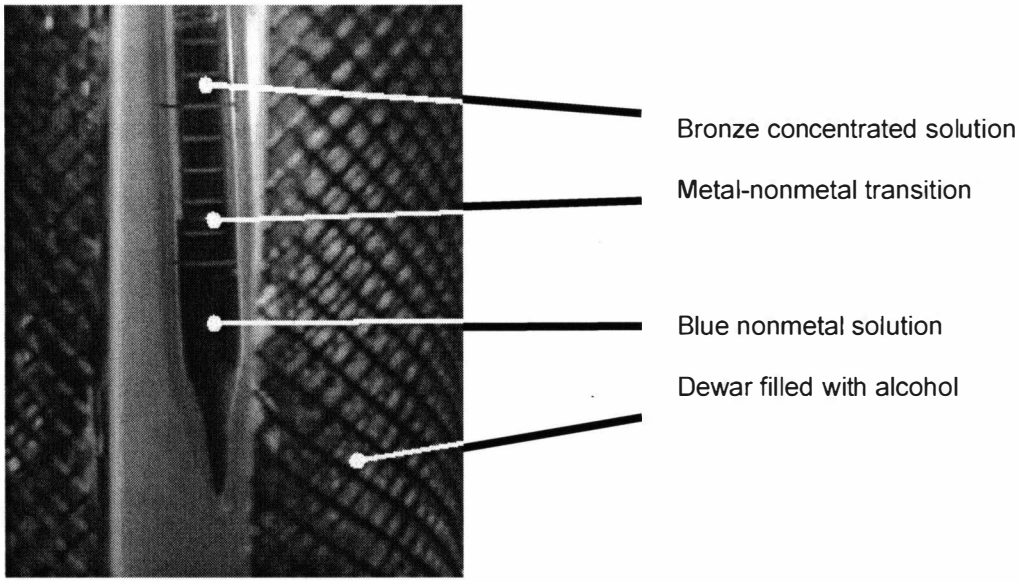

Fig.1.1. Picture of phase separation in sample with concentration of 5 MPM

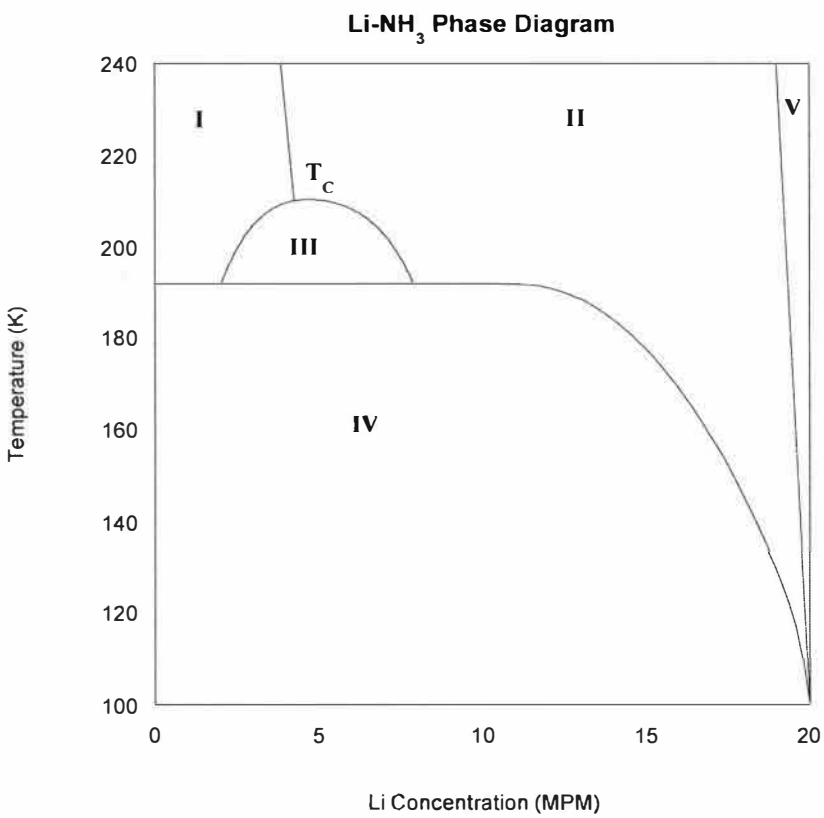

Fig.1.2. Phase diagram for lithium-ammonia solutions

The following distinctive regions can be observed in the phase diagram: Region I represents the homogenous nonmetallic liquid while region II represents the homogenous metallic liquid. Region III represents the immiscibility gap. Solutions are not stable at temperatures and concentrations within this region. There are two immiscible liquid phases, the more concentrated, metallic phase on top of the low concentration, electrolytic phase. Region IV represents the region with excess solid ammonia and region V excess solid metal or metal amine.

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II. PROPERTIES OF Li-NH_3

Metal-Ammonia Solutions as Electrolytes

Dilute solutions of alkali metals in liquid ammonia have transport properties very similar to properties for dilute solutions of strong electrolytes. As the concentration of solute increases the properties change from those of electrolyte solutions to properties of liquid metals.

In an electrolyte solution the predominant interaction is the interaction between the solute ions and solvent molecules, the interaction solute ion-ion being negligible due to the low concentration of solute in solvent. The solute ions orient and bond the solvent dipoles by the Coulomb interaction, the adjacent dipoles repel each other, weakening the ion-dipole force. One solute ion is surrounded by a layer of oriented dipoles with binding energies exceeding thermal energies [1, 2]. As the electrolyte concentration is increased, Coulomb interaction among the solute ions becomes important.

To characterize and understand the behavior of metal ammonia solutions of different concentrations of metal content, different models were proposed and studied. For the dilute solutions the most complete work in the theory of electrons in polar fluid was Jortner's model calculation of an electron in polar fluid, the solvated electron model or electron-in-a-cavity model [3].

Solvated Electron Model

As previously discussed, by adding alkali metals to liquid ammonia

$$M + NH_3 \rightarrow M^{n+} + ne^- + NH_3$$

the metal atoms dissociate into solvated cations and solvated electrons. In dilute solutions of alkali metals in liquid ammonia, the solvated electrons are localized in cavities in the solvent. The solvent molecules are oriented by charge-dipole forces, the oriented molecules forming potential wells which trap the electrons. The mechanism of the solvation electron in liquid ammonia was illustrated by Catterall and Mott [4] and is illustrated in the following figure.

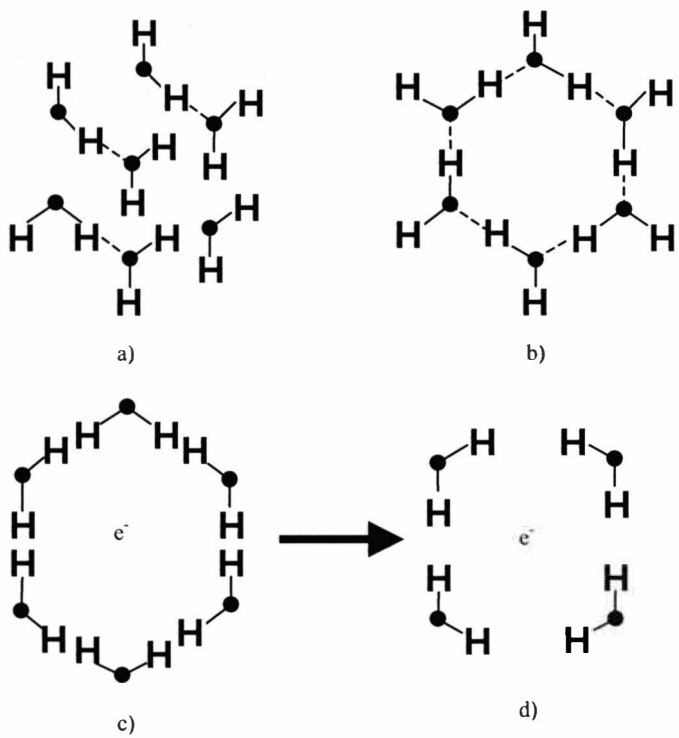

Fig.2.1. Steps in the solvation of an electron in liquid ammonia

(from Catterall and Mott [4])

In Fig.2.1 Step a) illustrates the unperturbed liquid ammonia structure, normal uniform distribution within a given volume. The hydrogen bonds between molecules are indicated by dashed lines and nitrogen atom at the dot. The orientation is random based on the attraction of the hydrogen to the non-bonding electron pair of a different nitrogen atom.

Step b) shows the normal structure surrounding a vacancy defect. A cavity is formed in the fluid comparable with the size of a single ammonia molecule of radius 1.5 Å [5]. The ammonia molecules recombine in this configuration, lowering the density within the same volume. This structure would not exist with an ammonia molecule in the cavity, as its dipole would destabilize the molecular attractions forming the structure.

Step c) shows a vacancy defect with solvent shell polarized around the central negative charge. If there is an electron in the cavity, the dipoles are oriented in a first layer.

Step d) shows shell dilution. The orientation of the molecules in the first layer is opposed by thermal agitation, dipole-dipole repulsion and Bjerrum defects. The Bjerrum defects are defined as the site at which the positive charges on two adjacent molecules point towards each other [4]. In this case, these defects are the hydrogen-hydrogen repulsion. To minimize the Bjerrum defects, the ammonia molecules within the layer rotate, and the structure expands to reach equilibrium, lowering the density of ammonia further.

In his model, Jortner considered the solvent as a continuous, homogenous medium. From this medium a spherical finite cavity of radius R was removed and an electron placed in it. The cavity size was chosen to agree with experimental data.

Jortner assumed that only the inertial (or low frequency solvent modes) polarization is responsible for localizing the electron [6, 7]. The electron is trapped in a potential well by polarization of the dielectric medium caused by the electron itself. The electron interacts with the permanent polarization of the medium and the electronic polarization.

The ammonia molecules surrounding the cavity polarized by the electron introduce the constant potential V(r) within the cavity acting on the electron:

$$V(r) = \frac{-e^2}{R}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right) \qquad r < R$$

where ε_∞ and ε_0 represent the high and low frequency dielectric constant of NH_3.

Outside the cavity, the potential acting on the electron is:

$$V(r) = \frac{-e^2}{r}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right) \qquad r > R$$

The variational solution of the ground and first excited states Ψ_{1s} and Ψ_{2p},

$\Psi_{1s} = (\xi^3/\pi)^{1/2} \exp(-\xi r)$

$\Psi_{2p} = (\zeta^5/\pi)^{1/2} r\cos\theta\exp(-\zeta r)$

were calculated and agreement with the experimental transition energies were found for reasonable choices of the cavity size. The closest agreement for NH_3 is obtained for R=3Å.[8]. The parameters ξ and ζ were evaluated by minimizing the energies of ground and excited state.

The solvated electron proved to be an excellent model due to the agreement between the theory and the experiment for the dilute solutions. The motion of the electron within the cavity and its polarization cloud explains the electron mobility in metal-ammonia solutions well [9].

The schematic of the solvated lithium cation and solvated electron follows.

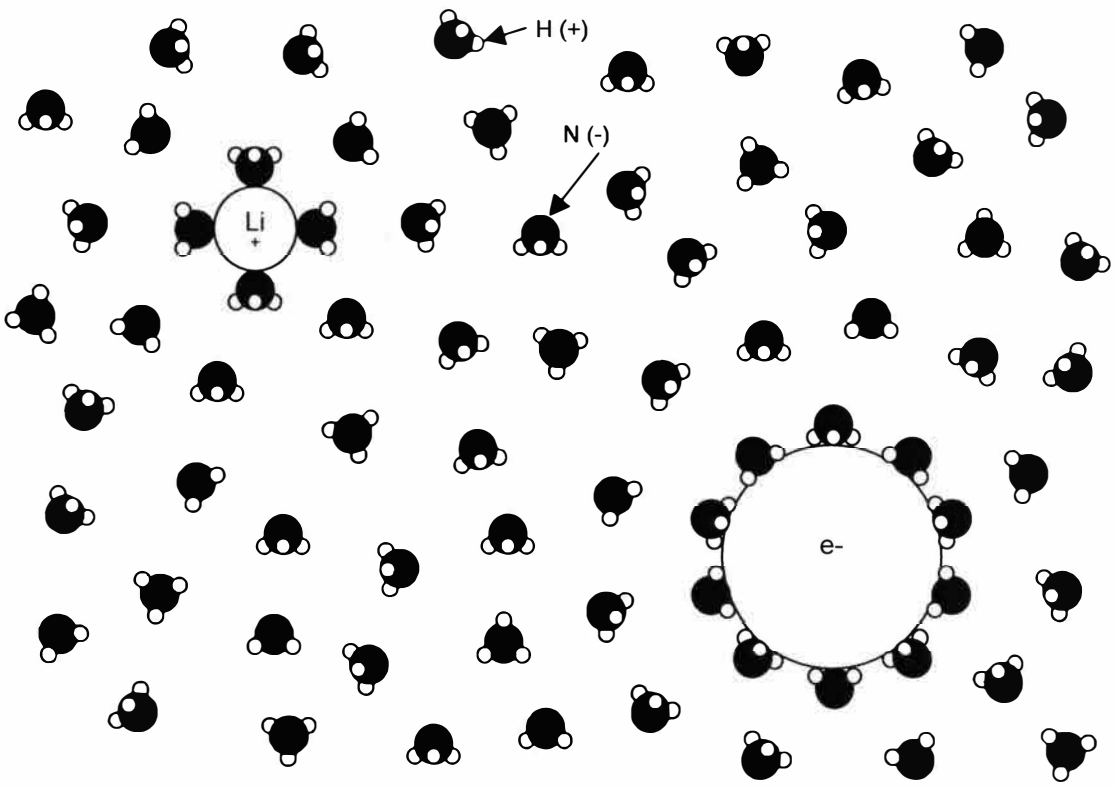

Fig.2.2. Schematic of the solvated lithium cation and solvated electron (from D. L. Dye [9])

Scattering Model

The metal-ammonia solutions in the metallic range represent a mixture of solvated ions, free ammonia molecules and free electrons. When introduced in liquid ammonia, the metal dissolves in the solution and the valence electrons dissociate, each resulting ion combining with ammonia molecules. The field of the solvated ion orients the ammonia molecules binding them weakly to the ion. The scattering centers in the metallic solutions are the ions and ammonia dipoles, weakly bound in solvated ion complexes, and free ammonia dipoles. The solvated ions represent weak scatterers. The weak interaction between electrons and scatterers leads to the NFE (nearly free electron) model, the free electron modified by the presence of a weak periodic potential, or Ziman theory [10, 11, 12].

Ziman's model is based upon the following assumptions:

1. The Fermi surface separating the top filled from unfilled states in ***k***-space is spherical.
2. The density of states per unit energy *N(E)* is

$$N(E) = \frac{V}{2\pi}\left(\frac{2m}{\hbar^2}\right)^{3/4} E^{1/2}$$

compared to

$$N(E) = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{3/2}$$

for the free electron gas.

3. The electron-ion interaction is treated by means of pseudopotentials [13].

The conduction electron-electron interactions and electron-positive ion interactions can be treated as weak potential interactions. The conduction electrons

are not allowed in the close vicinity of the ion because of Pauli's exclusion principle. The core is already occupied by the core electrons, and the electron potential, much reduced in the core-state region of the ion. This is true in molecules also, and it was assumed to be true in ammonia molecules [13]. The conduction electrons, by their mobility, diminish the net potential by screening the field of positively-charge ions and diminishing the total effective potential.

In the pseudopotential method, the electron-ion interaction is described by a local pseudopotential, and the wave function for a valence level, being expressed as a linear combination of orthogonalized planed waves [14]. In the metal ammonia solutions, where the field of the ion polarizes the ammonia molecules, forming the lithium-ammonia complexes, by orthogonalization the free conduction electrons are excluded from the interior of the complexes and, therefore, do not screen out the ion-ammonia bond [13].

The basic scatterers are the solvated ions and the dipolar ammonia molecules. The resistivity of the system, in the Born approximation can be written as

$$\rho = \left(\frac{m}{n_e e^2} \right) \left(\tau_i^{-1} + \tau_d^{-1} \right)$$

where n_e represents the electron density, τ_i and τ_d represent ion and dipole relaxation times, respectively.

Metal-Nonmetal Transition Models

The two most used models for metal-nonmetal transition are the percolation model of Jortner and Cohen [15], and Mott's model [16]. Jortner and Cohen proposed the percolation model for the metal-nonmetal transition in metal-ammonia solutions in the intermediate concentration range [15, 8]. They proposed that the nonmetallic phase is separated from the metallic phase by a "microscopically inhomogeneous" phase where the concentration is not constant, and it fluctuates about two well-defined values, M_0 and M_1. M_0 and M_1 represent the bounds of the inhomogeneous phase with $M_0 > M_1$, M_0 for the upper, metal phase, and M_1 for the lower, nonmetal phase. Jortner and Cohen defined a percolation problem by which a fraction C of the entire volume is occupied by the metallic region with concentration M_0, the rest being occupied by the lower concentration M_1. The volume fraction C has a linear dependence upon M. The limits of the inhomogeneous region were determined for lithium-ammonia at 223K, and sodium-ammonia at 240K, with $M_0 = 9$ MPM for the metallic phase, $M_1 = 2\ 1/3$ MPM for the nonmetallic phase, and $C = \dfrac{M - 2\frac{1}{3}}{6\frac{2}{3}}$.

Using effective medium theory (EMT) [8], tailored for scattering from the boundary of the metallic clusters, and for low conductivity ratio, C was determined to be greater than 0.4 with good fit with the experimental data.

Another theory proposed for the metal-nonmetal transition was Mott's model [8, 16], in which the metal-nonmetal transition is thought to be a consequence of band crossing, or Mott-type, and above the consolute temperature the transition is Anderson-type [16]. Jortner's solvated electron model [6, 7] considers that, for low

concentration, the electron is trapped in cavities formed by the polarized ammonia molecules. As a consequence, Mott considered that:

1. the localized electrons are spin-paired but situated in separate cavities
2. there are two bands, one for the electron and one for the hole in the spin-paired species
3. the transitions across the pseudogap and within the spin-paired species are of small oscillator strength
4. the number of free carriers is large
5. the discontinuity in the number of free carriers produces a phase separation.

Mott stated that metal-nonmetal transition occurs when the pseudogap opens and the electrons are excited to the mobility edge of upper band. Mott differentiated the metal-nonmetal transition in two regions, one from 6-3 MPM (with bands overlapping) and the other from 3-0.3 MPM (where the material exhibits an intrinsic semiconductor behavior.

Properties of Metal-Ammonia Solutions

Electrical conductivity of concentrated metal-ammonia solutions

The electrical conductivity has been measured in metal-ammonia solutions of lithium, sodium, potassium, rubidium and cesium over a wide range of concentration, starting from 8 MPM to saturation, at one temperature or over a range of temperatures [17, 18, 19, 20].

The main characteristic of the conductivity data is that of the dependence of conductivity upon temperature. The electrical conductivity is an increasing function of

temperature with few exceptions, and almost linear [17]. The electrical conductivity of solutions having concentrations up to saturation limit depend linearly on temperature, but for concentrated solutions of lithium in liquid ammonia, around 22 MPM [21], the electrical conductivity displays a maximum, and then a decreasing conductivity with increasing temperature. Solutions of cesium, which is miscible in all proportions, have a decreasing electrical conductivity dependence with temperature. The electrical conductivity increases with concentration approximately as the cube of metal content [8].

Hall effect

Solutions of alkali metals in ammonia exhibit electronic conduction when metal concentration exceeds a certain value above 8 MPM. Data on lithium-ammonia solutions indicate metallic electric conductivities, mobilities and free-electron Hall coefficients, and approximately free-electron Lorentz numbers [22]. The Hall effect experiments in metal-ammonia solutions primarily led to the conclusion that concentrated solutions represent liquid metals. It was determined that the carrier density in concentrated (concentration of metal content >5MPM) metal-ammonia solutions is equal to the density of metal valence electrons, and it is independent of temperature [23]. From comparison of observed Hall coefficients with free-electron theory, it was established that for lithium, sodium and potassium the assumed carrier per atom is one electron [24].

Density

The density has been measured in solutions of lithium [25], sodium [26], potassium [27], and cesium [28]. From the data it was established that the density is a decreasing function of concentration. For lithium-ammonia solutions it was determined that their densities are less than the density of any other liquid (0.48 g/cm^3) [21], except for the cryogenic liquids. The volume of the solution varies roughly linearly with metal concentration, and can be parameterized in two ways: by the effective volume of ammonia molecules in solution, and by the effective volume of metal ions in solution. From these studies, it can be seen that there is a gradual increase in the effective volume of the metal with increasing concentrations, and that is further increased with increasing temperatures.

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III. EXPERIMENTAL PROCEDURES

Electrical transport measurements

AC Electrical transport measurements were used to determine the resistivity of Li-NH_3 samples with Li concentrations of 20 MPM, 10MPM and 5MPM. Samples were measured as function of temperature, ranging from 210K to 240K.

Values were determined using the equations $\sigma = 1/\rho$ and $\rho = RS/L$ where σ represents the electrical conductivity, ρ is electrical resistivity, R is resistance of sample, S is the cross sectional area and L is the length between leads. Determinations of electrical conductivity versus temperature were made for all the lithium ammonia samples.

The resistance of the material being measured determines which of two different measuring techniques is suitable for determining the resistance. These methods are two-lead and four-lead measurement methods as follows:

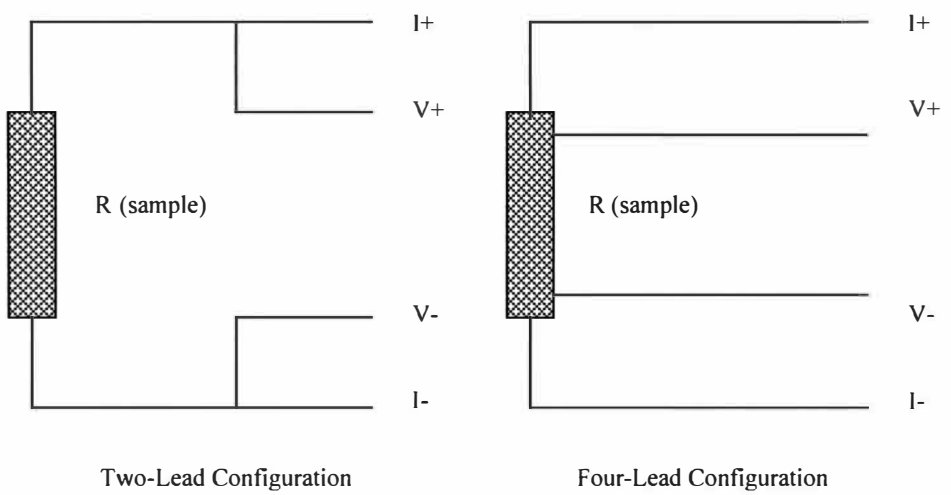

Fig.3.1. Two-lead versus four-lead configuration

In the two-lead measurement configuration, the leads used to measure the voltage are the same as the current carrying leads. For the four-lead configuration, the current travels through a pair of current leads and the sample voltage is measured across a separate set of the voltage leads. The four-lead method is used to measure low values of resistance by eliminating the resistance of the current leads and the contact resistance between the sample and the leads, so this method is more accurate than the two-lead method. For high resistances this is not needed, and so the two lead method can be used.

In the four-lead resistance measurement method, the sample with resistance R is supplied a known current I from a current source and the voltage drop V generated across the sample is measured. The four-lead method was used in this experiment.

The current should be constant during the experiment and it is sent through the outer most wires. The voltage was measured between the inside wires.

The resistivity measurement set-up uses a Stanford Research (SR) 830 lock-in amplifier, a Hewlett Packard 34401A multimeter, a Stanford Research (SR) 554 transformer preamplifier and a variable resistance box.

The SR 830 lock-in amplifier supplies a constant AC voltage, the input voltage needed for the system. The output voltage is applied to the variable resistance box, which is connected in series with the sample. The variable resistance box contains a 100 Ω resistance, the voltage drop across it is used to determine the current flowing through the circuit. This resistance is connected in series with one of the following possible resistances, 400 Ω, 900Ω and 1.9 kΩ, as shown in Fig. 3.2.

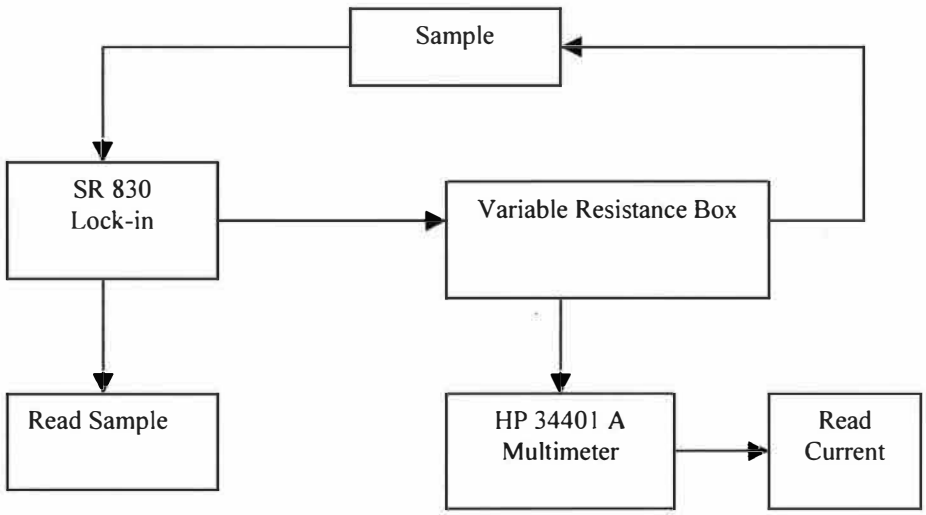

Fig.3.2. Block diagram of resistivity set-up

These other possible resistances are used to adjust the current flowing through the circuit and along the sample, the bigger the additional resistance introduced, the smaller the current flowing through the circuit. In this experiment the 100 Ω resistance was connected in series with 400Ω resistance. The changes in the sample resistance are very much smaller than the resistance of this circuit, so the current flow stays approximately within ±1% constant during the experiment.

The 34401A multimeter indirectly determines the current flowing through the circuit by reading the voltage drop along the 100 Ω resistance in the circuit. Using Ohm's law for electrical circuits, the current flowing in the circuit is given by $I=V/R$, where V represents the voltage drop along the 100Ω resistance and R = 100Ω. The input voltage for the electrical circuit was specifically chosen so that the current through the circuit would be small, from a fraction of a mA up to 10 mA. In our

experiments, the current flowing through the circuit was chosen to be 0.1 mA ±1%. Such a small value is required to avoid heating of the sample due to Joule heating of the stainless steel pin contacts. The simplified electrical circuit used to determine the resistance of the sample is shown below,

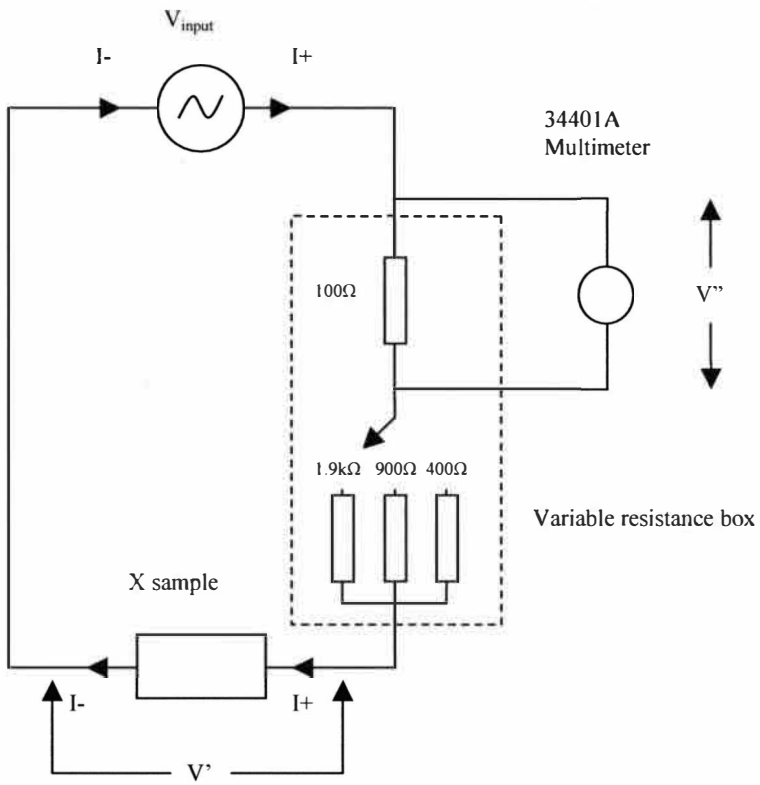

Fig.3.3. Simplified electrical circuit

where V_{input} represents the lock-in amplifier input voltage

V' represents the drop voltage across the sample

V'' represents the voltage across the 100 Ω resistance.

A constant and small value of the current flowing through the circuit and sample is needed. To acquire a constant value for the current in the circuit, the SR 830 lock-in amplifier was used, which supplies a constant voltage.

The lock-in amplifier detects and measures very small AC signals down to nV. Such small signals can be measured even with noise 10^3 times bigger. Using phase–sensitive detection, the lock-in amplifier singles out the component of the signal at the specific reference frequency and phase. The sample is excited at the chosen reference frequency by the SR 830's internal oscillator and the response from the sample at the required reference frequency is detected. All components having a signal with a frequency ω_{sig} different from the reference frequency ω are removed. To minimize any interference from external electrical signals in particular. 60 Hz, the wall frequency, the value of frequency was chosen to be prime number to the wall frequency. The fundamental frequency in this experiment was 23 Hz.

Temperature control and measurement

The metal ammonia solutions investigated were metal ammonia solutions of 20 MPM, 10 MPM and 5 MPM concentration with temperatures ranging from 210K to 240K.

The nylon cell containing the lithium ammonia solution was kept in an insulated container, a dewar filled with non-freezing fluid. The cooling fluid used in the experiment was denatured ethyl alcohol 95% purity. The temperature was controlled by an immersion cooler, in this experiment Thermo NESLAB CC-100 CryoCool Series Immersion Cooler.

The immersion cooler is equipped with a Thermo NESLAB Cryotrol Temperature Controller which is an analog temperature device designed to control the cooling, in 10 °C increments. To cool the fluid to a selected temperature, with both the F (flexible) cooling probe and the sensing probe immersed in the alcohol bath, the control dial of the Cryotrol unit was set to the desired temperature. A schematic of the temperature control and measurement is presented below:

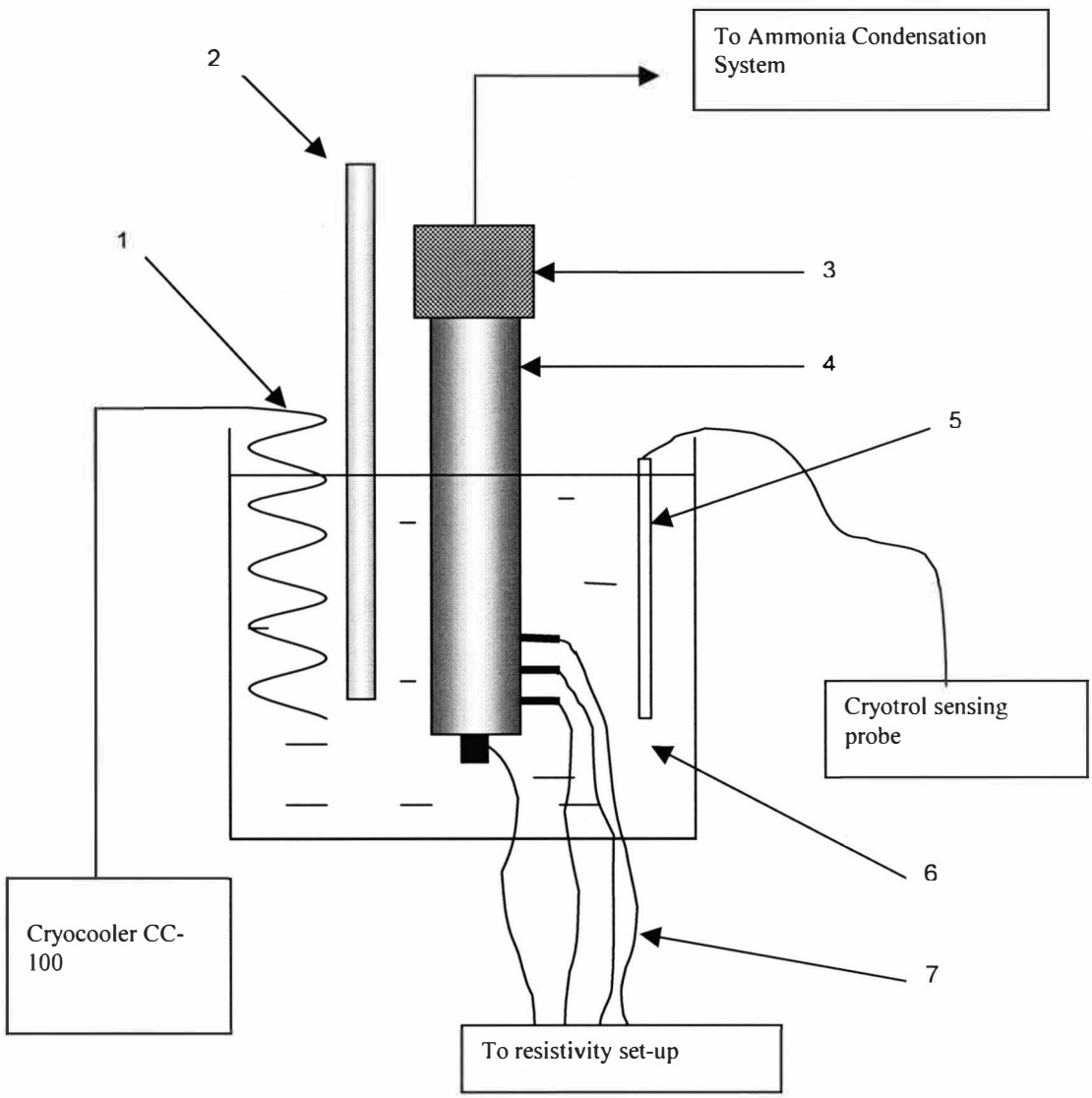

Fig.3.4. Temperature control and measurement system

In the figure (1) represents the flexible cooling probe, (2) thermometer, (3) Swagelok fitting, (4) nylon container cell, (5) sensing probe, (6) alcohol bath and (7) insulated copper wires.

The refrigeration system reduces the temperature of the cooling fluid in the work area, around the sample, to the lowest achievable temperature under the existing heat load conditions. The temperature range depends on the capabilities of the immersion cooler or cold bath being controlled, here from room temperature to around 200-210K. Since the electrical conductivity of the sample is temperature dependent, the temperature gradient should be minimized and temperature nearly constant and uniform in the area of interest. Cooling capacities are reduced and the work area shows temperature layering if the alcohol bath is not uniform, so it is stirred. The cooling fluid was periodically replaced as it collects water vapor from the air when operating at low temperatures. As the concentration of water in the cooling fluid increases, the performance is adversely affected. The ice build up on the cooling probe was removed on regular basis as the ice acts as insulation and reduces the cooling capacity.

The temperature was measured using an alcohol-filled low-temperature thermometer and conductivity measurements taken at one degree increments. To contain the cold and to have a slow rate of heat flow from surrounding area to (from) the sample, a lid made of foam insulating material was used to thermally separate the sample and alcohol bath from exterior environment.

The Cryotrol controls the temperature in the sense that it sets the lower and upper temperatures for the cooling and warming parts of the measurement, rather than maintaining the temperature at a selected value, not being sufficiently precise to maintain the temperature to the desired degree of accuracy. The change in temperature was carried out by turning off and on the cooler. The temperature of the sample changes when it absorbs heat from alcohol bath or provides heat to the bath. The cooling/warming process should take a long period of time to have the temperature steady enough for stabilized values of conductivity. For this purpose the dewar was chosen to have a large heat capacity making warming gradual, of the order of 10° C per hour. The rate of cooling is a function of the immersion cooler, the total heat capacity of the dewar, and the immersion depth of the sample. The depth of the sample and the portion of the cooling probe immersed are adjusted so the rate of cooling of the sample is on the same order as the rate of warming, approx. 10° C per hour. The time needed to read the voltage drop along the sample from the resistivity setup is on the order of 1 sec. The temperature change during such an interval is much less than the tolerance of the thermometer, so the temperature can be considered constant for each such measurement.

Sample Preparation Details

Solutions of lithium in anhydrous liquid ammonia were prepared for 20±0.73%MPM, 10±0.73%MPM and 5±0.73%MPM metal concentration. Metal-ammonia preparation presents experimental challenges. Lithium is highly reactive, reacting with H_2, O_2, H_2O, CO_2, and it rapidly reacts upon contact with air. Because

lithium must be kept chemically isolated, it is stored in mineral oil. Additionally, all the handling, weighing and placing of lithium in the container cell must be done in inert gas atmosphere glove box or under vacuum.

Pure ammonia is a highly toxic and corrosive gas and it reacts with many materials; some exceptions are stainless steel and several plastics. As a result, the ammonia condensation system contains only parts made of stainless steel.

The lithium metal used for the lithium ammonia solution was 3.2 mm diameter lithium wire at 99.9% purity. The lithium wire was cut and trimmed in mineral oil and, after cutting, washed in xylene to remove all traces of mineral oil.

The entire handling and weighing process was done under a closed inert gas atmosphere, helium or argon. One of the glove boxes used in this experiment was MBraun GmbH Unilab Glove box.[†] The working gas is Argon high purity 99.9 % delivered at 80 psi and the regeneration gas an Argon/Hydrogen mixture (90 to 95% Ar with 5 to 10% H_2 portion) delivered at 5 psi. Both working and regeneration gases were provided by AirGas Great Lakes[‡].

The MBraun glove box is equipped with an automatic pressure control system. The glove box is run by a Programmable Logic Controller PLC which maintains the box pressure within a fixed range. This is necessary since while working in the glove box the motion of the gloves into and out of the box changes the volume of the system and therefore the pressure in the box.

The pressure control system principle is illustrated in the following figure.

[†]MBraun, Inc., 14 Marin Way, Stratham, NH 03885 www.mbraun.com
[‡] AirGas Great Lakes, 2475 W. Dickman, Battle Creek, MI 49015 www.airgas.com

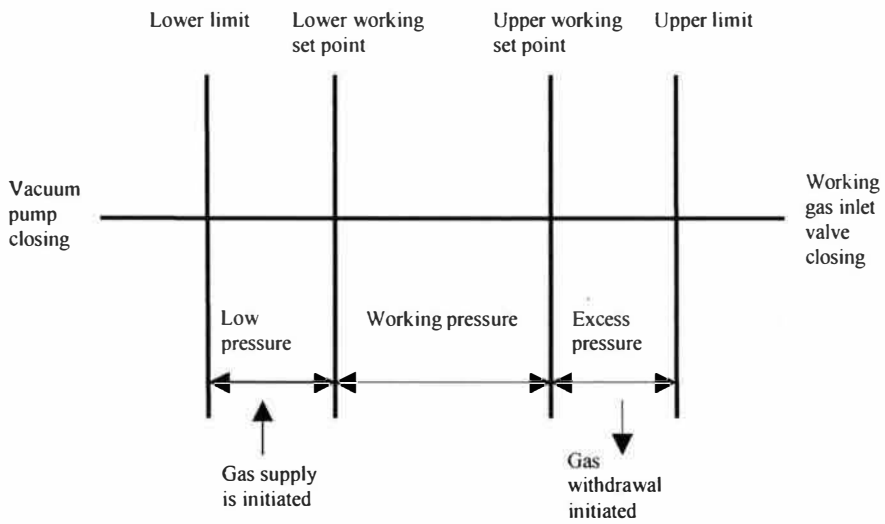

Fig.3.5. Diagram of pressure control system principle

Each time the pressure inside the glove box is not within the set chosen operating pressure parameters, i.e. the working range, the box PLC will call for gas or vacuum until the box pressure is restored to the working pressure. The operating pressure parameters were set to 12 mbarr for the upper pressure limit and 9 mbarr for the lower pressure limit. During operation, the pressure travels between the upper and lower setpoints under automatic control. If the box pressure is below the lower working setpoint, the vacuum pump is closed and working gas Ar is supplied until the box pressure is restored. If the pressure inside the glove box is above the upper working setpoint, the working gas supply is stopped and gas withdrawal is initiated by vacuum pump until the box pressure is within the working range. During operation, the box pressure can be controlled manually by a foot switch, and the pressure is changed within the working range by actuating the foot switch.

To control the oxygen and moisture levels in the box atmosphere, the glove box is equipped with a purification unit, the working gas being permanently circulated between the glove box and the H_2O/O_2 gas purification system. The H_2O/O_2 levels in the box atmosphere were previously reduced to 100 ppm[§] by purging the glove box so that the glove box purifier unit can bring down the oxygen and moisture levels to below 1 ppm.

The purification process works on the principle of gas circulation. The working gas is permanently circulated between the glove box and the H_2O/O_2 purification system. The circulation mode should be permanently activated during operation to have the working gas purified to oxygen and moisture levels to below 1 ppm. The circulation mode is operated and displayed via the OP 17 Operation Panel.

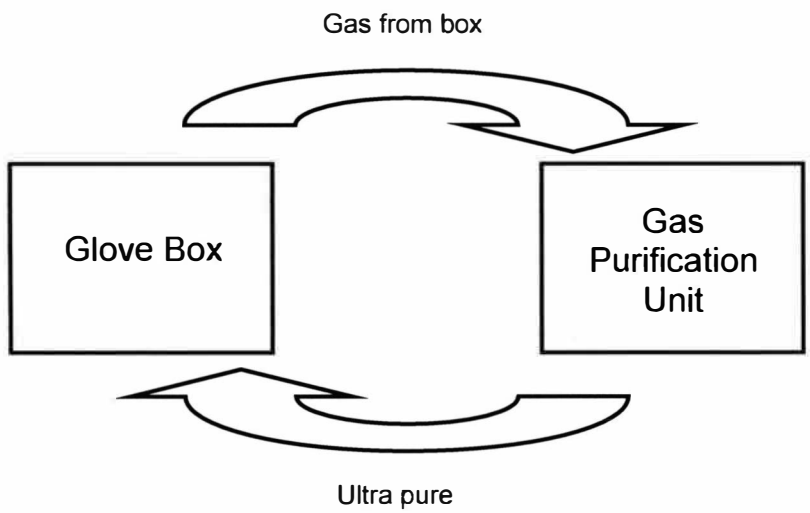

Fig.3.6. Purification system

[§] ppm= parts per million concentration

The lithium is introduced in the Nylon conductivity cell container attached to a vacuum connector with PTFE valve plug HI-VAC and sealed under the Argon atmosphere of the glove box. The conductivity cell container was made out of an insulating material, Nylon 6/6 with a cylindrical shape. Nylon was chosen for this purpose because of its poor electrical conductivity and non-reactivity to the samples.

The method used for supplying the electrical contacts was the four-wire method, the purpose here being the elimination of the resistance of the wires. The four electrical contacts needed for the current and voltage in and out were 18-8 Stainless Steel taper pins attached on the bottom and sides of the cell as shown.

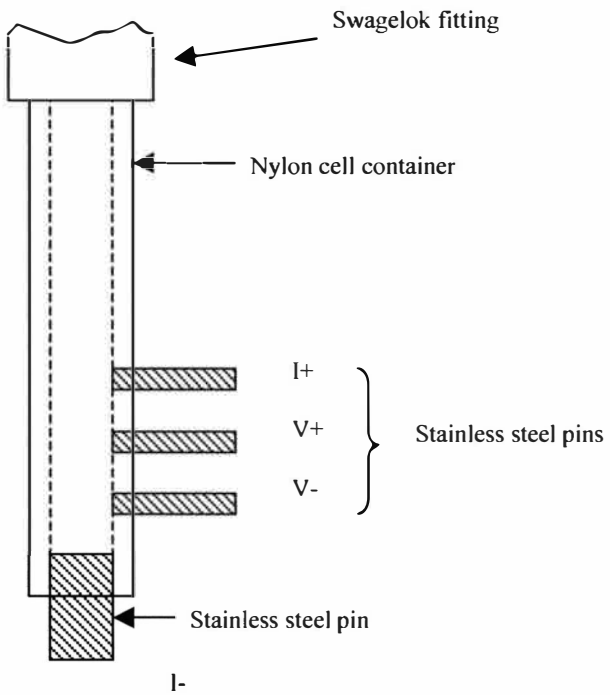

Fig.3.7. Design of the conductivity cell

The sealed cell containing the lithium is then attached to the ammonia system. The valve is opened and the system is vacuumed down to <100 mtorr to remove the Ar from the preparation.

The ammonia used for the experiment was anhydrous ammonia, grade 4.0, liquid phase, kept under its own vapor pressure of 114 psig at 70 °F, provided by AirGas Great Lakes. The purity was 99.99%.

The ammonia condensation system is composed of a glass manifold connected to the ammonia tank, one high pressure tank (cylinder) and two vacuum pumps. A picture and a block diagram of the ammonia condensation system follows.

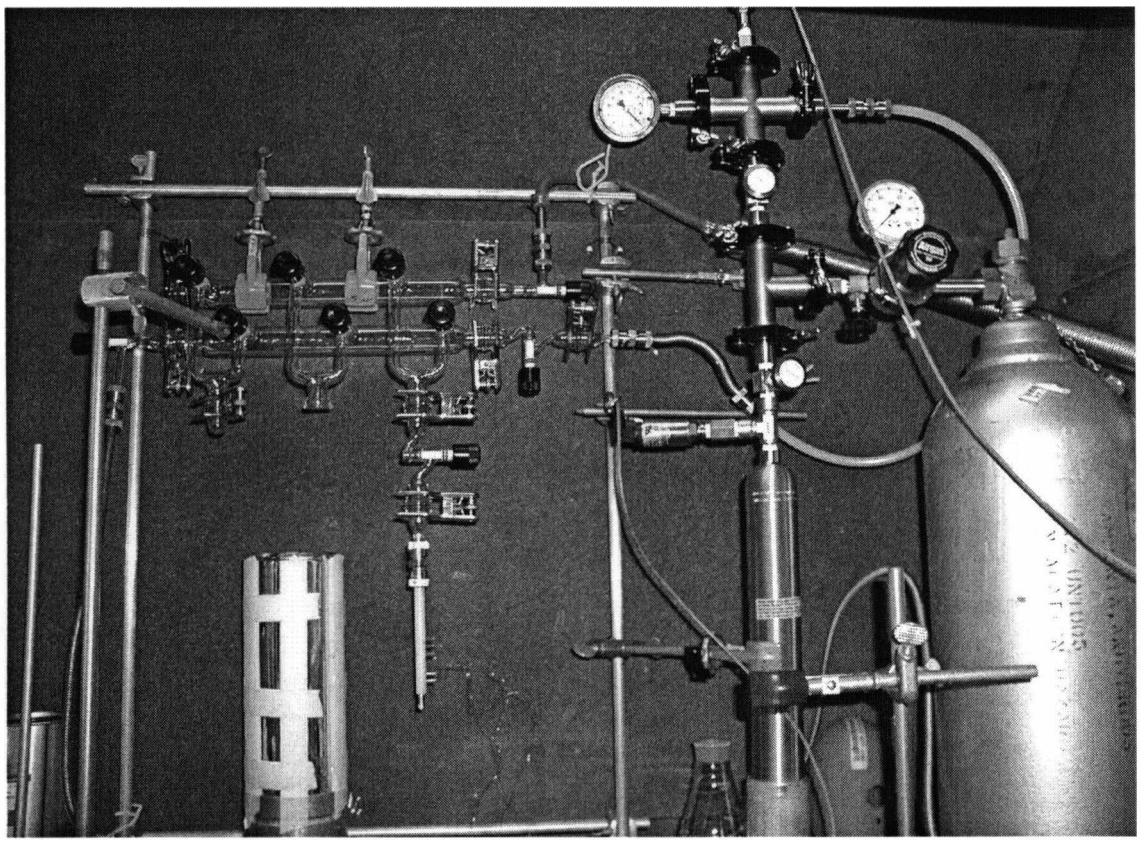

Fig.3.8. Picture of the ammonia condensation system with sample cell attached

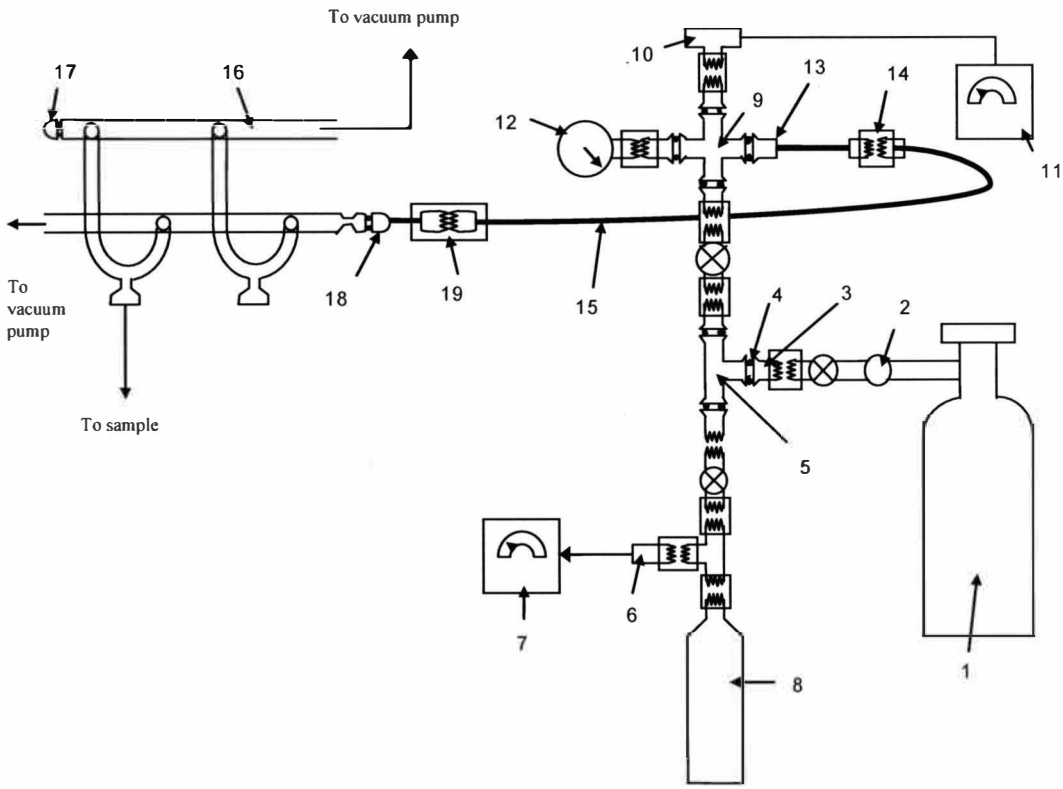

Fig.3.9. Block diagram of ammonia condensation system

1) AirGas ammonia supply tank
2) AirGas ammonia pressure regulator 50 psi
3) SS female pipe adapter NW25 1/4"NPT
4) Centering rings NW25
5) SS tee NW25
6) PX 215-060 AI pressure transmitter 60 psi
7) DP 24-E panel meter
8) Swagelok 316L-HDF4-500
9) SS 4-way cross NW25
10) 531 thermocouple gauge tube 1/8"NPT
11) 801 thermocouple gauge controller
12) 30"Hg/30 psi Noshok pressure gauge
13) Unbored stub NW25
14) Swagelok fitting
15) Nalgene 489 polyethylene tubing
16) HI-VAC vacuum double manifold
17) HI-VAC vacuum end cap
18) HI-VAC vacuum adapter
19) Swagelok fitting

The high pressure tank connected to the Omega pressure gauge controls the amount of ammonia obtained within an accuracy of) 0.5%. We use the equation of state for an ideal gas (which holds very well for ammonia in the pressure temperature range)

$$PV = nRT$$

where P is pressure of ammonia gas in the high pressure tank

V=0.567 L is volume of the high pressure tank

R=0.0821 L·atm/mol·K the universal gas constant, and

T is room temperature,

the amount of ammonia needed for each sample is calculated within 1%.

The volume of pressurized tank V, the universal gas constant R and the room temperature T being constants at equilibrium, the amount of ammonia needed can be determined with:

$$\Delta n = \Delta P(V/RT)$$

where ΔP represents the change in pressure in cylinder and Δn represents the change in amount of ammonia in cylinder, number of ammonia moles transferred from the pressurized tank into the system.

Based upon the consideration that the gas leaving the cylinder will be in the same as the gas entering the rest of the system,

$$(\Delta n)_{\text{cylinder}} = (\Delta n)_{\text{system}} = \rho V/M$$

where ρ represents the density of liquid ammonia and M molar mass of ammonia, by controlling the pressure in the cylinder, the desired amount of ammonia can be obtained. The procedure of obtaining the condensed ammonia follows.

The glass manifold is sealed, allowing only gaseous ammonia to enter the cylinder. The cylinder is filled with pressurized gaseous ammonia to a pressure $P>\Delta P$. To avoid breaking the seals the ammonia in the manifold must be less than 1 atm. Thus, to ensure the transfer of ammonia from the cylinder into the system (manifold), the cylinder has to be of higher pressure than the system at all times. The system will be pressurized with ammonia from the ammonia tank supply (not from the cylinder) to a specified value < 1 atm. First, the cylinder is pressurized to a value:

$P_{initial} \geq \Delta P + 1$ atm.

This ensures that ammonia will flow into the system from the cylinder, and that the excess, ΔP, is transferred. The ammonia supply in cylinder is then sealed and $P_{initial}$ recorded. After this, the system is then pressurized to the value < 1 atm, as determined above. With the previously prepared alcohol bath (below the 240K temperature required to condense ammonia), the condensation of ammonia in the cell container can begin.

The cell container is slowly dipped into the cold alcohol bath (around 210 K) causing the ammonia to condense. This causes the ammonia in the system to be depleted, and the pressure drops. Simultaneously, ammonia is slowly released from cylinder to replenish the ammonia in the system as the liquid is formed, and to allow the temperature in the system to stay at equilibrium. Sharp changes in pressure have to be avoided to prevent seals from leaking, and allow temperature to remain constant. The pressure in the system is monitored, so that it will be maintained at a constant level as ammonia is slowly released from the cylinder. Final pressure in the manifold needs to be the same as the initial pressure to insure the correct amount of ammonia is

liquefied and none of the ammonia transferred remained gaseous in addition to gas already in system. The transfer is continued until the pressure in cylinder reaches the value:

$$P_{final} = P_{initial} - \Delta P.$$

With the system having the same initial and final pressure, the change in pressure of the cylinder corresponds only to the ammonia now condensed in the cell container. Since the cell container already had lithium, the ammonia condensed in it dissolves the lithium to create the lithium-ammonia solution. It is now ready for the conductivity measurements. While still connected to the manifold and immersed in the coolant, it is sealed by closing the PTFE valve plug HI-VAC, and the wiring from the SS pins is connected to the resistivity setup. Conductivity versus temperature is now measured.

Alternative Sample Preparation and Preliminary Work

An alternative procedure was used earlier, as follows.

The other glove box used early on was Plas-Labs 818 GB glove box filled with compressed helium of high purity 99.9%, provided by AirGas Great Lakes.

In the procedure for making the sample, an important step is cleaning out the glove box. Having this in mind, besides the helium tank, the glove box was connected to a vacuum pump, a cold trap and a laboratory gas drying unit.

The laboratory gas drying unit uses drierite, (anhydrous $CaSO_4$) as a desiccant. The air in the glove box is partially pumped out and filled with helium repeatedly until the glove box is cleaned out. The cold trap cleans approximately 10% of the inside

atmosphere of the main chamber for one run so for a dry glove box atmosphere it is necessary to use the cold trap at least 10 times. The use of the laboratory gas drying unit and the cold trap was demanded by the fact that dry air is imperative to obtain a clean environment. The glove box contains a Denver electronic analytical balance in the main chamber, A-series model 250, necessary to weigh the desired mass of lithium for the solution. After the trimmed lithium wire was weighed in the desired amount, it is introduced into the sample container and sealed. The design of the conductivity cell container is the same with the previous one, made out of an insulating material, Nylon, with a cylindrical shape.

After the lithium was introduced in the Nylon conductivity cell container and sealed under the helium atmosphere the next step of the procedure follows. The sealed sample containing the metal is attached to an ammonia condensation system, where the liquid ammonia needed for the metal-ammonia solution is prepared.

The condensation system used for obtaining the liquid ammonia is composed of a glass manifold connected to the ammonia tank and two vacuum pumps. The conductivity cell container is also attached to the manifold, but cannot measure the volume of the liquid ammonia. To determine the volume of liquid ammonia, a pipette is attached to the manifold as well. After the required volume of ammonia is condensed into the pipette, it will be restored to gas phase to be condensed again in the cell container by a similar process. The pressure inside the system is monitored by two pressure gauges. After a reasonable vacuum was obtained (around 10 mtorr), the ammonia, in gas phase, is let into the system. The pressure inside the system should be no more than the atmospheric pressure to avoid breaking the seals and having air

leak in, which would have negative effects on obtaining the desired liquefied ammonia.

One of the pipettes, now filled with ammonia gas, is lowered in a dewar containing a mixture of dry ice and alcohol. The reason for doing so is that ammonia goes from gas phase to liquid phase in the right conditions of temperature and pressure.

If we observe the phase diagram for ammonia, the normal boiling point for ammonia is T_c= 240 K at P=760 torr and we need the temperature of dry ice-alcohol mixture to be less than this value. The temperature of the mixture depends on the type of alcohol used due to the specific heat values of each type of alcohol involved. For the experiment in question we used ethyl alcohol and the temperature reached was T= 213 K at P=760 torr.

As the ammonia condenses, the pressure decreases while the temperature is kept constant by adding more dry ice. More ammonia gas is let into the system to condense in cycles until the desired volume of liquid ammonia is obtained. With the desired volume of liquid ammonia in the pipette, the ammonia now needs to be transferred to the cell container by converting the liquid back into the gas, and then condensing it again in the cell container, which must be done at constant pressure P. The ammonia tank is closed, and the cell container is opened to the manifold.

The pipette is removed gradually from the dry ice-alcohol mixture so that ammonia slowly warms and vaporizes. If done too quickly, the liquid ammonia will boil and the pressure will rise too rapidly, breaking the seals. Simultaneously, the cell container is immersed in the dry ice-alcohol mixture to lower the temperature below

the boiling point of the ammonia in the system, causing the gaseous ammonia to condense in the cell container. The pipette is gradually lifted from the dry ice-alcohol mixture to control the amount of liquid vaporized, and to monitor the pressure in the system (keeping it below 760 torr). The amount of ammonia transferred is determined by the drop in the volume of the liquid in the pipette, the remainder maintained as liquid by keeping it in the dry ice-alcohol mixture. Once the transfer is complete, the cell is sealed and removed from the manifold.

The ammonia remaining in the system needs to be safely removed. The manifold is sealed, and the pipette is detached from the manifold. The liquid ammonia then boils away under the hood. To remove the ammonia vapor from the manifold, a flask attached to the manifold is immersed in liquid nitrogen (77 K) to solidify the remaining ammonia. The flask is then removed to allow the ammonia to boil away.

IV. EXPERIMENTAL RESULTS

In the present measurements, electron transport was considered in the non-metallic and metallic range of metal-ammonia solutions, specifically, lithium-ammonia solutions. The dependence of conductivity upon temperature was analyzed for solutions of lithium-ammonia having concentrations of particular interest for the study of metal-ammonia solutions; that is, 5 MPM to characterize the dilute range of solutions, 10 MPM for concentrated range of solutions, and 20 MPM for near saturation.

Drude's model was used to determine the relaxation time and mean free path of electrons in solution for the different concentrations of lithium-ammonia solutions. Mean free path is a measure of the frequency of collisions, and hence, the conductivity.

For concentration of 5 MPM we find the conductivity $\sigma = 2.74 \times 10^2\ \Omega^{-1}cm^{-1}$ at 223 K compared to reported values of $\sigma = 2.00 \times 10^2\ \Omega^{-1}cm^{-1}$ for the same temperature [1]. For a concentration of 10 MPM we find $\sigma = 1.7 \times 10^3\ \Omega^{-1}cm^{-1}$ compared to reported values of $\sigma = 1.5 \times 10^3\ \Omega^{-1}cm^{-1}$ [2]. For concentration of 20 MPM we find $\sigma = 11.5 \times 10^3\ \Omega^{-1}cm^{-1}$. We found reported values of $\sigma = 15 \times 10^3\ \Omega^{-1}cm^{-1}$ for 21 MPM [3] and so the expected conductivity for concentration of 20 MPM should be smaller than $15 \times 10^3\ \Omega^{-1}cm^{-1}$.

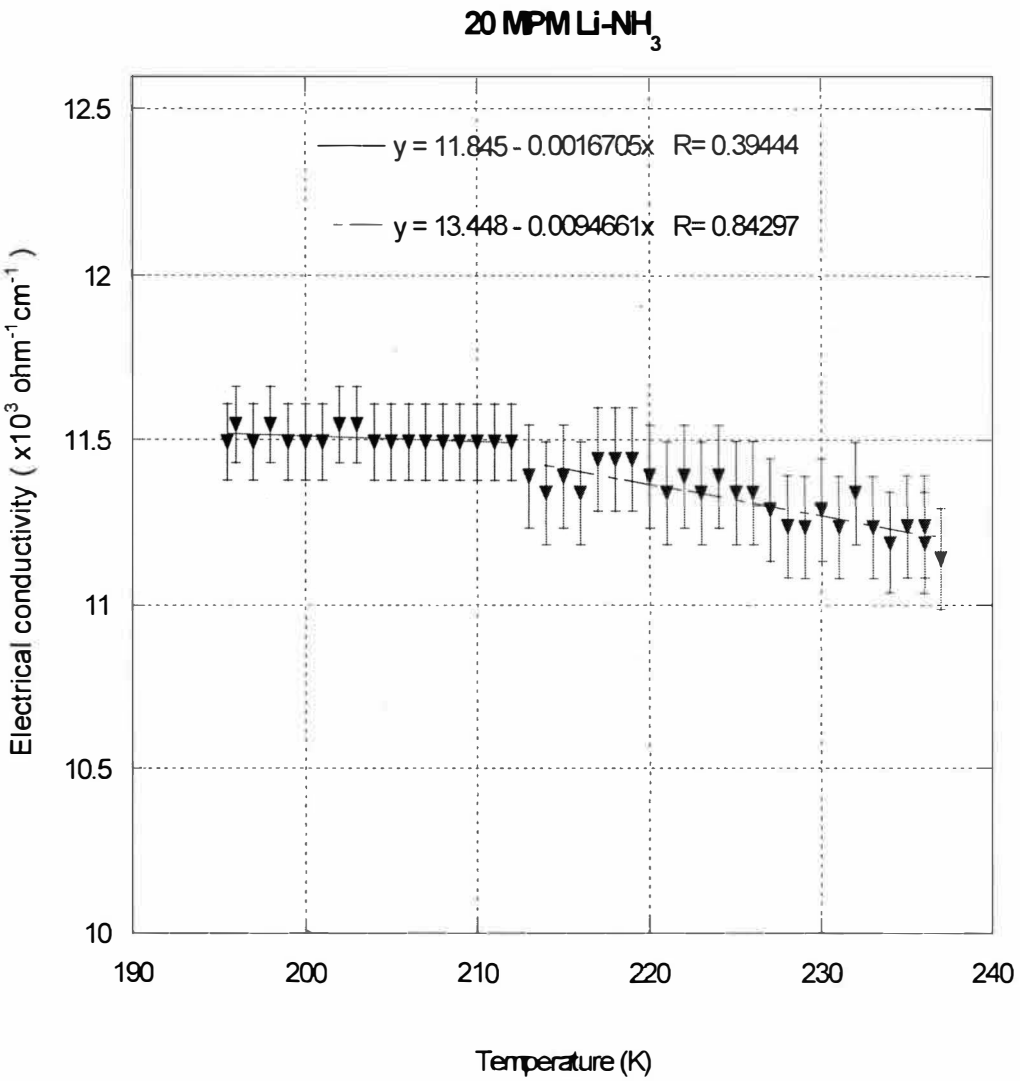

Fig.4.1.Temperature-dependence of conductivity for Li-NH_3 of concentration 20 MPM

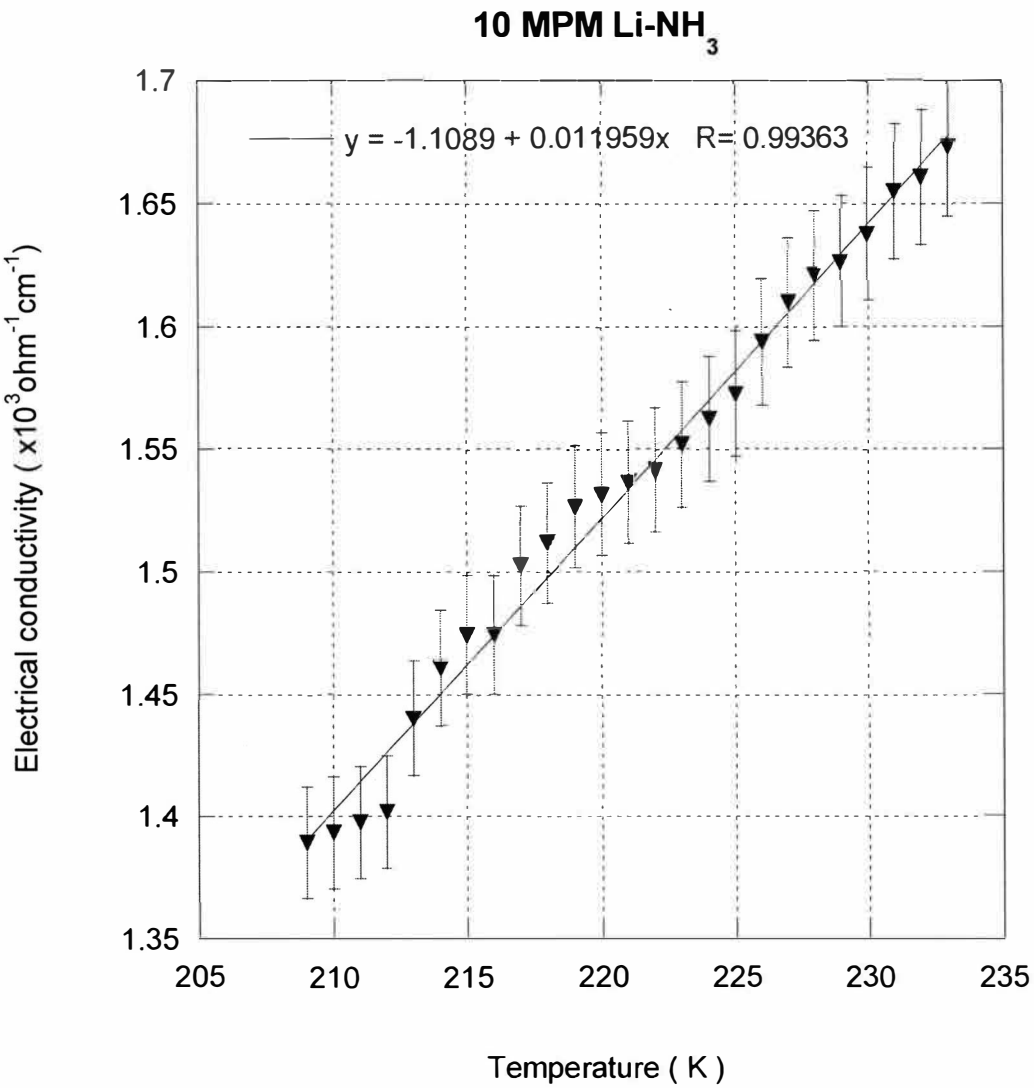

Fig.4.2.Temperature-dependence of conductivity for Li-NH_3 of concentration 10 MPM

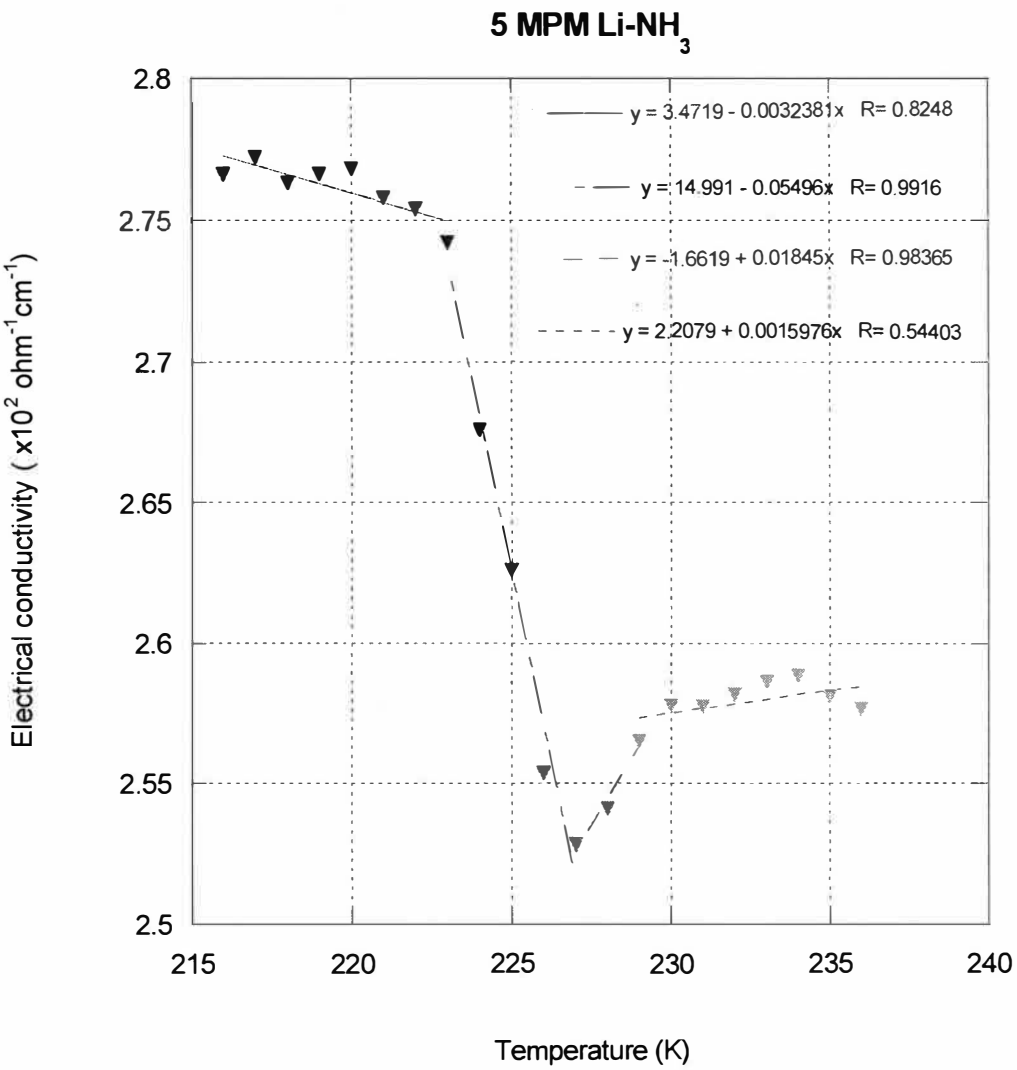

Fig.4.3. Temperature-dependence of conductivity for Li-NH_3 of concentration 5 MPM

As a first approximation for treating our data, we consider the Drude model for electrical transport. While this model does not take into account the electronic correlations, it provides a starting point for the treatment of the electrical transport. The approximate mean free path for the electrons in the liquid has been determined using this theory. Drude applied the kinetic theory of gases to a metal and considered the metal as being a gas of electrons. In the kinetic theory the electrons are treated as identical solid spheres moving in straight lines until they collide with one another. The ions of the metallic atoms represent the immobile heavier positive particles with electrons of mass *m* moving against the background of the heavy immobile ions.

The following approximations were made[**]

1. Between collisions, the electron-electron interaction and electron-ion interaction are neglected. In the absence of external electromagnetic fields, the electrons are assumed to move uniformly in straight line. In the presence of an external field, the electrons are assumed to move following Newton's laws of motion in the presence of those fields, but neglecting the additional complicated fields produced by other electrons and ions.

In the case of lithium-ammonia solutions, the constituent particles are lithium ions, ammonia molecules and electrons, which interact with each other. The solvent molecules interact through an effective pair potential, a 12-6 potential[††] of each pair of nitrogen atoms plus electrostatic interaction between the charges on each molecule [6].

[**] These approximations are standard to Drude theory, but here are cited from N. W. Ashcroft, N. D. Mermin, *Solid State Physics*, Holt, Reinhard and Winston, 1976

[††] potential of the form $\beta\left(\frac{1}{R^{12}}-\frac{1}{R^{6}}\right)$

The electron interacts with the ion through a Coulomb interaction and the electron scattering by the ammonia potential is modeled by a point-dipole potential. The electrons are scattered by ions and oriented ammonia dipoles, either free or bound in solvated ions.

2. Drude collisions represent instantaneous events which abruptly alter the velocity of an electron. This is attributed to the electrons being scattered by the impenetrable ion cores, rather than electron-electron collision.

3. An electron experiences a collision with a probability per unit time $1/\tau$. That is, the probability of an electron collision in any time interval dt is just dt/τ. The time τ represents the relaxation time, the collision time, or, the mean free time.

4. Electrons are assumed to achieve thermal equilibrium with the environment only through collisions. This is done by each electron's recoil velocity being unrelated to its impact velocity, but rather randomly determined and appropriate to the prevailing temperature at the collision site. The hotter the region in which the collision occurs, the faster the electron emerges from the collision.

One measure of the conduction electronic density is r_s defined as the radius of a sphere with volume equal to the volume per conduction electron,

$$r_s = \left(\frac{3}{4\pi n}\right)^{1/3} = \left(\frac{3A}{4\pi Z\rho N_A}\right)^{1/3}$$

where $n = \frac{N}{V} = N_A \frac{Z\rho}{A}$ represents the conduction electron density.

Z = number of electrons the atom contributes

ρ = mass density (g/cm^3)

N_A = 6.0221367x10^{23} mol^{-1} = Avogadro's number

A = atomic mass of the element.

The electronic density for each Li concentration is given in table 4.1 and computed using $n = N_A \frac{Z\rho}{A}$. The mass density values for concentrations in the range of 0 MPM to 21 MPM were taken from [8].

Concentration (MPM)	Mass density (g/cm^3)	Z (charge per mole)	A (g/mole)	n (10^{22} cm^{-3})
1	0.7125	0.01	16.93	0.0251
2	0.7000	0.02	16.83	0.0500
3	0.6700	0.03	16.73	0.0724
4	0.6620	0.04	16.63	0.0959
5	0.6500	0.05	16.53	0.1184
6	0.6375	0.06	16.43	0.1385
7	0.6250	0.07	16.32	0.1614
8	0.6125	0.08	16.22	0.1819
9	0.6000	0.09	16.12	0.2017
10	0.5900	0.10	16.02	0.2218
11	0.5800	0.11	15.92	0.2413
12	0.5700	0.12	15.82	0.2604
13	0.5600	0.13	15.72	0.2789
14	0.5500	0.14	15.62	0.2969
15	0.5420	0.15	15.52	0.3155
16	0.5334	0.16	15.42	0.3334
17	0.5250	0.17	15.32	0.3509
18	0.5200	0.18	15.21	0.3705
19	0.5125	0.19	15.11	0.3879
20	0.5050	0.20	15.01	0.4051

Table 4.1. Free electron densities for lithium-ammonia solutions

A way of measuring atomic distances is the ratio of r_s and a_0, where $a_0 = \frac{\hbar^2}{me^2}$ = 0.529x10^{-8} cm, the Bohr radius, and the dependence of this ratio upon concentration is as follows:

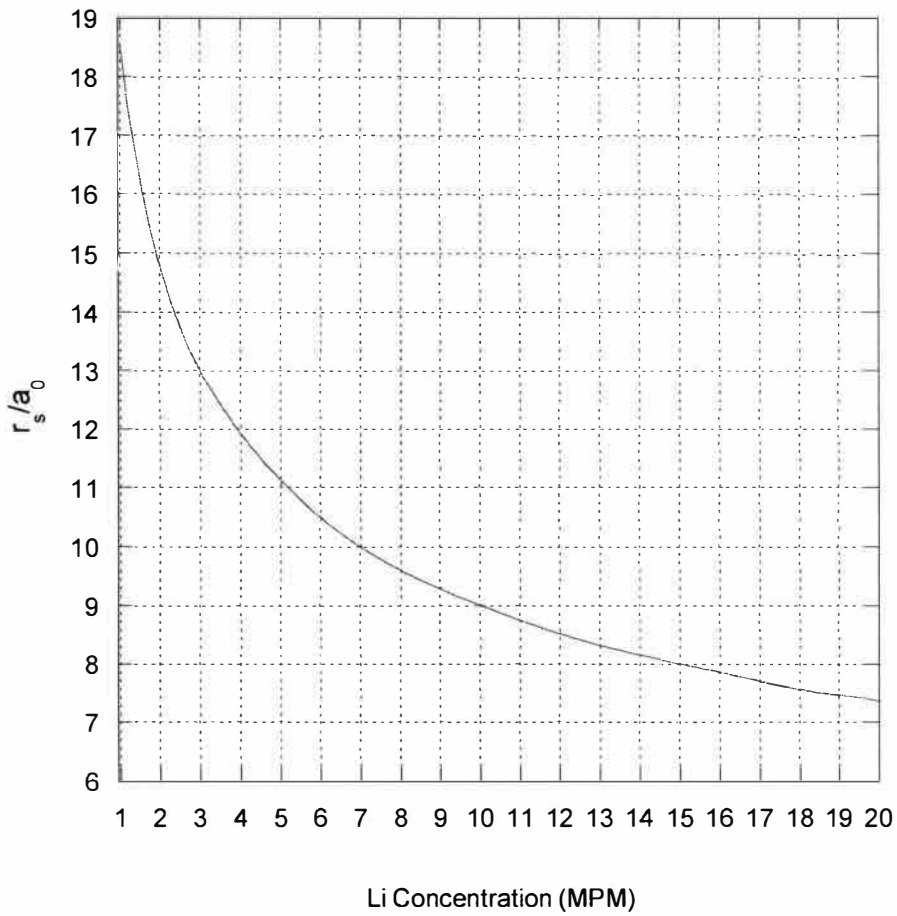

Fig.4.4. Dependence of r_s/a_0 upon Li concentration

According to Ohm's law, the current I flowing in a wire is proportional to the potential drop V along the wire, $V = IR = \rho l/S$. The resistivity, ρ, is defined as the proportionality constant between the electric field $\boldsymbol{E}$ at a point in the metal, and $\boldsymbol{j}$ the current density induced

$$\boldsymbol{E} = \rho \boldsymbol{j}$$

where $\boldsymbol{j} = -ne\boldsymbol{v}$ is the current density, and $\boldsymbol{v}$ is the average electronic velocity.

In the absence of a field, $\boldsymbol{v}$ averages to 0 and there is no net electric current density. In the presence of a field $\boldsymbol{E}$ there will be a mean electronic velocity opposite to the field,

$$\boldsymbol{v} = -e\boldsymbol{E}\tau/m$$

where τ is relaxation time, the average time between collisions.

Substituting $\boldsymbol{v}$ in $\boldsymbol{j}$:

$$\boldsymbol{j} = ne^2\tau\boldsymbol{E}/m = \sigma\boldsymbol{E}$$

with $\sigma = ne^2\tau/m = 1/\rho$, the electrical conductivity, which represents DC electrical conductivity.

To compute the AC electrical conductivity of a metal we use the equation of motion for momentum per electron:

$$\frac{d\boldsymbol{p}}{dt} = -\frac{\boldsymbol{p}}{\tau} - e\boldsymbol{E}$$

The time dependent field $\boldsymbol{E}$ is:

$$\boldsymbol{E}(t) = \mathrm{Re}\left(\boldsymbol{E}(\omega)e^{-i\omega t}\right)$$

and momentum $\boldsymbol{p}$:

$$\boldsymbol{p}(t) = \mathrm{Re}\left(\boldsymbol{p}(\omega)e^{-i\omega t}\right)$$

Substituting the complex $\boldsymbol{E}$ and $\boldsymbol{p}$ in the equation of motion, we find that $\boldsymbol{p}(\omega)$ must satisfy:

$$-i\omega\, \boldsymbol{p}(\omega) = -\frac{\boldsymbol{p}(\omega)}{\tau} - e\,\boldsymbol{E}(\omega)$$

since $\boldsymbol{j} = -\frac{ne\boldsymbol{p}}{m}$ it results:

$$\boldsymbol{j} = \frac{ne^2}{m}\cdot\frac{\boldsymbol{E}(\omega)\tau}{1-i\omega\tau} = \sigma(\omega)\ \boldsymbol{E}(\omega)$$

where

$$\sigma(\omega) = \frac{ne^2}{m}\cdot\frac{\tau}{1-i\omega\tau} = \frac{\sigma_0}{1-i\omega\tau}$$

The conductivity $\sigma(\omega)$, at zero frequency, represents the DC electrical conductivity of a metal. Relaxation time is $\tau = m/\rho ne^2$ or using $n = \frac{3}{4\pi r_s^3}$, is $\tau = \frac{4\pi m r_s^3}{3\rho e^2}$ or using the $\frac{r_s}{a_0}$ ratio,

$$\tau = \left(\frac{0.22}{\rho}\right)\left(\frac{r_s}{a_0}\right)^3 x10^{-14}\ \text{sec.}$$

Since the relaxation time is of order of 10^{-14} sec compared to $\sim 10^{-2}$ sec for one cycle (23Hz source voltage) for our apparatus, the AC voltage doesn't change appreciably during one collision and can be considered constant. The SR830 lock-in pre-amplifier from the resistivity setup used to read the voltage drop across the sample displays voltage signals in volts rms (root mean square), so, we can treat the electrical conductivity as DC conductivity with the rms voltage.

The mean free path l represents the average distance an electron travels between collisions. Also, $l = v_0 \tau$, where v_0 represents average electronic speed.

The free mean path is determined with the Fermi velocity, v_F:

$$v_F = \left(\frac{\hbar}{m}\right) k_F = \frac{4.20}{r_s / a_0} x10^8 \, cm/\sec$$

where k_F represents Fermi wave vector [9].

Concentration (MPM)	r_s / a_0	τ (10^{-14} s)	l (Å)
5	11.09	0.059	2.20
10	8.99	0.240	11.20
20	7.36	1.051	59.9

Table 4.2. Dependence of free mean path upon concentration of solution at 210K

In the table the free mean path is computed for the solutions of 5MPM, 10MPM and 20MPM, with conductivity values measured at 210K. For the concentrated solutions, as the concentration of metal content increases, more $Li(NH_3)_4^+$ complexes are created and there are fewer unbound NH_3 molecules. The $Li(NH_3)_4^+$ complexes have a net positive charge and they repel each other resulting in a increase of volume and decrease in density. For the dilute solutions, the increase in volume is also due to the cavities with the radius r=3-3.2Å [7] in which the electrons reside and so an additional decrease in density.

The non-metallic state contains solvated electrons (electrons in cavities), solvated metal ions (ions surrounded by the layer of oriented solvent molecules) and isolated (non-solvating) NH_3 molecules. The metallic state (>5MPM) contains free electrons, solvated metal ions and isolated NH_3. At low concentrations there are sufficient NH_3 molecules, beyond the number needed to solvate the Li ions, to trap the electrons in at least one layer each, and the liquid is non-metallic. As the concentration increases, there are progressively fewer NH_3 molecules unassociated with Li ions, until the point that there are no free NH_3 molecules at saturation.

In the low concentrations, the electrons are localized to cavities in the ammonia, which lowers the overall density of the solution. As electron concentrations increase with metal concentration, these electrons begin forming bipolarons, and higher concentrations result in more complex structures, and lowering the density further. In the metallic phase, these electron structures result in total delocalization of the electrons, as well as more ammonia bound to lithium-ammonia complexes, and a further decrease in density.

At any given concentration, increasing temperatures causes thermal expansion of the solution, and weakening of the dipole-electron interaction causing the cavities. Other work by R. E. Lo [8] indicate a linear decrease in density with respect to temperature.

For the 20 MPM concentration work has been reported according to which a shallow peak in conductivity around 200 K is expected and a slight decrease of the conductivity with temperature [4]. Our data reflect the decrease of the conductivity for temperatures greater than 213 K but the peak in conductivity around 203 K is not significant within our accuracy.

At 5 MPM and T<210K, the solution is in the immiscibility region (see fig.1.2. phase diagram), and there is a separation of the denser, nonmetallic solution into the bottom and the less dense metallic solution to the top. The sensing electrodes were only in the upper, metallic zone of the solution, and so higher, metallic conductivities were measured. When the temperature exceeded the critical value of 210K, the solution becomes miscible, and the nonmetallic properties were distributed to the location of the electrodes. The graph reflects the gradual lowering of the conductivity $\frac{d\sigma}{dT} < 0$, $\frac{d\sigma}{dT} = -0.05496$. While separate, the non-metallic portion of solution, settled on bottom, has surplus of unbound NH_3 molecules. Above *Tc* (see phase diagram fig.1.2) they mix, redistributing the surplus of NH_3 molecules in the entire volume of sample and hence a decrease in conductivity.

After redistribution, the unbound ammonia molecules (initially on the bottom from the nonmetallic part) react with the delocalized electrons (from the metallic portion, on top) and restrict the electronic freedom, while still remaining in the

metallic state. At lower concentrations (below 4 MPM) this would instead contribute enough ammonia to cause localization, and even cavities, returning the combined solution to a uniformly non-metallic state. The Cohen and Jortner model [10] describes this as microscopically inhomogeneous, with zones of metallic (9 MPM) and non-metallic (2.3 MPM) solutions distributed throughout, with a net effect of the measurable macroscopic results. The conductivity for 5 MPM was too low to correspond to the strict separation suggested by this model, however, so some mixing of the states must be occurring even in the liquid-liquid phase.

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V. CONCLUSION

In summary, we have performed measurements of electrical conductivity versus temperature of lithium-ammonia solutions with the lithium content of 5 $\pm$0.73% MPM, 10 $\pm$0.73% MPM and 20 $\pm$0.73% MPM over a range of temperatures from 210K to 240K. These particular concentrations were chosen to study the behavior of lithium-ammonia solutions over a wide range of concentrations, from dilute to near saturation. The solution of lithium-ammonia with 5 MPM lithium content was chosen to study the metal-nonmetal transition, the 10 MPM to study the metal-liquid phase, and the 20 MPM for the concentrated solution.

The sample was made from lithium of 99.9% purity combined with ammonia of 99.99% purity. The lithium was placed in a nylon sample cell under controlled atmosphere (Ar) in a glove box. A measured amount of ammonia was condensed in the sample cell through a vacuum tight glass manifold. To avoid degradation, the lithium-ammonia solution is kept in an alcohol bath and temperature varied from 210K to 240K.

AC electrical transport measurements were used to measure the resistivity of each sample and, hence, electrical conductivity. The resistance of the sample was determined using the four-lead measurement method. We found values matching the literature for the electrical conductivity for 5 MPM and 10 MPM solution at 211K.

The scope of this thesis was to obtain electrical conductivity measurements using four wire measurements to eliminate the contact resistance. We have shown how it is possible to carry out accurate measurements of the electrical conductivity in these systems with the four wire measurements.

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