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Structure and Excitations in Metal Ammonia Compounds

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STRUCTURE AND EXCITATIONS IN METAL AMMONIA COMPOUNDS

by

Xue Wang

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Submitted to the
Faculty of The Graduate College
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requirements for the
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Xue Wang
This work has two parts. In the first part, inelastic x-ray scattering was used to measure the plasmon excitations in liquid lithium ammonia systems. The measurements were carried out for different metal concentrations, 8 mole per metal (MPM), 10 MPM, 11 MPM, 16 MPM and 20 MPM of temperature 200K. The data were analyzed to determine the plasmon energy and the linewidth as a function of momentum for each metal concentration. Deviations from the random phase approximation (RPA) in the jellium model increase as the concentration is lowered.

In the second part of this work, elastic x-ray scattering was used to measure the structure of quenched sodium ammonia mixtures at different concentrations (0 MPM, 3 MPM, 6 MPM, 9 MPM, 12 MPM and 15 MPM). An amorphous structure is found in quenched sodium ammonia systems and its properties are discussed.
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CHAPTER I

INTRODUCTION

The first experiment reported about metal ammonia systems was from Weyl (1864). A couple of years later (1871), Seely [18] recovered Na from a sodium ammonia solvent. He concluded that the metal did not react with ammonia and the solution was similar to salt in water or sugar in tea. In 1898, ammonia became commercially available, and the research on this topic was accelerated.

In these systems, the outermost electron dissociates from the atom, leaving a free electron and an ion in the solvent. But the electron density is very low, therefore, the interactions between electrons play a large role in their properties. The electron density is usually described by a parameter \( r_s = \frac{\frac{3}{2} \pi n}{a_0^2} \), where \( n \) is free electron density, and \( a_0^* \) is the effective Bohr radius. Typical metals have the value of \( r_s \) between 2 and 6. For lithium ammonia systems, \( r_s \geq 7.35 \) and when the concentration goes to zero, \( r_s \rightarrow \infty \). For
20 mole % metal (MPM) lithium ammonia, the electron density is about $4 \times 10^{21} e^-/cm^3$. By changing the metal concentration in the systems, the electron density varies too, therefore the systems can be an insulator, metal or semiconductor.

Recently, studies [2, 3] of the plasmon in liquid and solid lithium ammonia as a function of momentum transfer have been carried on 20 MPM, 16.5 MPM and 13 MPM. In the present thesis, the high resolution inelastic x-ray scattering (IXS) technique was used to measure the plasmon peaks as a function of momentum transfer for several concentrations of the lithium including much lower concentrations than that measured before. Also the results are compared with Random Phase Approximation (RPA) in the jellium model. Strong deviations from the RPA were found, with the greatest deviations at the lower electronic densities.

For sodium ammonia, we studied the metallic glass using elastic x-ray scattering. If we freeze the sodium ammonia fast enough, the atoms in the system are frozen before they can re-orient to a lower energy structure. This is first measurement of the structure of the metallic glasses.
2.1 X-ray and Its Applications

About one hundred years ago, Wilhelm Conrad Röntgen (1845-1923) discovered x-rays. He was awarded the Nobel prize for physics in 1901, six years after his discovery "in recognition of the extraordinary services he has rendered by the discovery of remarkable rays subsequently named after him" [1].

X-rays are part of transverse electromagnetic spectrum between ultraviolet light and gamma radiation and have an approximate range of wavelengths of 0.1 - 100 Å. As visible light, x-rays can be explained as wave or particle (wave-particle duality), depending on the experiment. They are usually produced by rapidly decelerating fast-moving electrons and converting their energy of motion into a quantum of radiation. However, at Advanced Photon Source (APS) in Argonne National Laboratory (ANL), 7-GeV electrons
are injected into 1104-\(m\)-circumference storage ring which consists of more than 1,000 electromagnets and associated equipment, located in a concrete enclosure. Therefore a narrow beam of electrons can be formed by a powerful electromagnetic field and can be bent to give out x-rays. Bending magnets (BM) and insertion devices (ID) are the two main ways to create x-rays at APS.

The energy of photons is

\[ E_{\text{photon}} = h\nu = \frac{hc}{\lambda} = \eta ck \]  

(2.1)

In 1906, Charles Barkla discovered that each element had a characteristic x-ray, and x-rays could be scattered by gases [4]. The diffraction of x-rays by crystals was first observed by Max von Laue, Paul Knipping and Walter Friedrich in 1912 [4]. Major John Hall-Edwards pioneered in developing x-rays technology in medical use (radiation therapy) in Birmingham, England [4].

Since Röntgen's discovery that x-rays can identify bony structures, x-rays have been developed for their use in medical imaging. And x-rays have also been used in crystallography, astronomy, microscopic analysis, x-ray
fluorescence, etc. Paintings are often x-rayed to reveal the underdrawing and pentimenti or alterations in the course of painting, or by later restorers. Many pigments such as lead white show well in x-ray photographs.

2.2 Bragg’s Law and Elastic X-ray Scattering

Bragg’s law was derived by Sir W. H. Bragg and his son Sir W. L. Bragg in 1913 [2]. Although it is simple, Bragg’s law confirmed the existence of real particles at the atomic scale which was very important at that time. Bragg’s law also provides a powerful tool for studying crystals in the form of x-ray and neutron diffraction.

When x-rays hit an atom, the electronic cloud starts to move as an electromagnetic wave at same frequency (blurred slightly due to variety of effects). The re-emitted wave fields interfere with each other either constructively or destructively, producing a diffraction pattern on a detector or film. Both neutron and x-rays wavelengths are comparable with the inter-atomic distances, so they are very good probe for this length scale.

Bragg’s law (Figure 1) is written as

\[ n\lambda = 2d \cdot \sin \theta \] (2.2)
Figure 1. X-rays are reflected by atoms plane. \((AB + BC) = n\lambda,(AB) = (BC) = d \sin \theta\), therefore, \(n\lambda = 2d \cdot \sin \theta\) (Bragg’s law) [4].

where \(n\) is an integer, \(\lambda\) is the wavelength of x-rays, moving electrons, protons and neutrons, etc, \(d\) is the spacing between the planes in the atomic lattice, and \(\theta\) is half of the angle between incident beam and scattered beam (scattering angle in Figure 2).

2.3 X-ray Absorption

When a beam of x-rays passes through matter, it will be absorbed partly or totally. The coefficient of mass absorption \(\mu\) of a piece of material is defined as follows [2]. Consider a beam of monochromatic x-rays of intensity \(I\) incident perpendicularly on a thin sheet whose mass per unit is \(dp\). The intensity of the transmitted beam is \(I + dI\), where \(dI < 0\). \(dI\) is proportional
Figure 2. A schematic of general scattering experiment. $E_i$, $k_i$ and $e_i$ are, respectively, the energy, the wave vector and the polarization vector of the incident beam. $E_f$, $k_f$ and $e_f$ are, respectively, the energy, the wave vector and the polarization vector of the scattered beam. $d\Omega$ is the solid angle and $Q$ is the momentum transfer, $2\theta$ is the scattering angle [4].

both to $I$ and to $dp$.

$$dI = -\mu Idp$$

(2.3)

where $\mu$ is the mass absorption coefficient of the material. It is easy to derive:

$$\frac{I}{I_0} = \exp(-\mu p) = \exp(-\mu \rho x)$$

(2.4)

where $I_0$ is the intensity of incident beam, $\rho$ is the density, $x$ is the thickness.

The coefficient $\mu\rho$ is called the linear absorption coefficient. And when $x = \frac{1}{\mu\rho}$, $I = I_0 e^{-1}$, So $1/\mu\rho$ is called attenuation length. For a given material, the coefficient $\mu$ increases in general with the wave length [3], but this increase is not continuous.
2.4 X-ray Diffraction

When a beam of x-rays hits an atom, two processes may occur, (a) the beam may be scattered without energy change, (b) the beam can be absorbed, and (c) the beam may be scattered with energy gain or loss.

The first process is called elastic x-ray scattering, and the second, x-ray absorption, and the third, inelastic x-ray scattering. As it is shown in Figure 2, if the energy does not change ($E_i = E_f$), it is elastic scattering, otherwise, inelastic scattering. When the incident x-rays interact with matter (gas, liquid, and solid) and the frequency of x-rays is shifted higher or lower, this is called Raman scattering [5]. And when a high energy photon collides with a free electron and transfers energy, this process is Compton scattering [6].

2.5 Inelastic X-ray Scattering

Figure 2 is valid for all probes, including neutrons, photons, and electrons. The incident beam is defined by the energy $E_i$, momentum $k_i$ and the polarization $e_i$. The scattered beam is defined by the energy $E_f$, momentum
\( k_f \) and the polarization \( e_r \). The energy transfer and momentum transfer are

\[
\hbar \omega = E_i - E_f \tag{2.5}
\]

\[
Q = k_i - k_f \tag{2.6}
\]

For x-rays, the momentum transfer, compared with the initial momentum, is very small. Therefore, \( k_i \approx k_f \), and the value of momentum transfer can be written as

\[
Q = 2k_i \sin(\theta), \tag{2.7}
\]

where \( 2\theta \) is the scattering angle (Figure 2).

In an inelastic x-ray scattering experiment, we measure the double differential cross section,

\[
\frac{d^2\sigma}{d\Omega d\omega_f} \tag{2.8}
\]

which is proportional to the probability that an x-ray is scattered into a solid angle \( d\Omega \) around the direction defined by \( k_f \) and a bandwidth \( d\omega_f \) around \( \omega_f \). The cross section can be calculated by considering the interaction Hamiltonian between the scattering system, in this case, the electromagnetic
field and the scattering electrons. When the x-ray energy is small compared with the electron rest energy, the relativistic effects can be ignored. Then the interaction Hamiltonian \cite{7,10} can be written as

\[ H_{\text{int}} = H_{\text{int}}^{\text{charge}} + H_{\text{int}}^{\text{spin}}, \]  

(2.9)

where

\begin{align*}
H_{\text{int}}^{\text{charge}} &= \sum_i \left( \frac{e^2}{2mc^2} \mathbf{A}(\mathbf{r}_i, t) \cdot \mathbf{A}(\mathbf{r}_i, t) - \frac{e}{2mc} (\mathbf{P}_i \cdot \mathbf{A}(\mathbf{r}_i, t) + \mathbf{A}(\mathbf{r}_i, t) \cdot \mathbf{P}_i) \right) \\
H_{\text{int}}^{\text{spin}} &= \sum_i \left( -\frac{e \hbar}{mc} \mathbf{s}_i \cdot \nabla \cdot \mathbf{A}(\mathbf{r}_i, t) - \frac{e \hbar}{(mc)^2} \frac{e^2}{c^2} \mathbf{s}_i \cdot (\dot{\mathbf{A}}(\mathbf{r}_i, t) \times \mathbf{A}(\mathbf{r}_i, t)) \right)
\end{align*}

(2.10)

(2.11)

where, \( m \) is the mass of the electron, \( c \) is the speed of light, \( \mathbf{P}_i \) is the momentum operator of the electrons, and \( \mathbf{A} \) is the vector potential operator of the electromagnetic field, which can be written as a linear combination of the creation and annihilation operators for photons as \cite{11}

\[ \mathbf{A}(\mathbf{r}_i, t) = \sum_k \left( \frac{\hbar c^2}{2\omega V} \right)^{1/2} \left( a_k \mathbf{e}_k e^{i\mathbf{Q} \cdot \mathbf{r}} + a_k^\dagger \mathbf{e}_k^* e^{-i\mathbf{Q} \cdot \mathbf{r}} \right) \]

(2.12)

where \( \mathbf{e}_k \) is the polarization vector of the electromagnetic field, \( a_k \) and \( a_k^\dagger \) are photon creation and annihilation operators.
In the absence of magnetic interactions, and when the initial photon energy is much higher than the atomic binding energy, the partial cross section can be reduced to

\[
\frac{d^2\sigma}{d\Omega d\omega} = r_0^2 \frac{\omega_f}{\omega_i} |\mathbf{e}_i \cdot \mathbf{e}_f|^2 N \sum_{i,f} |<i| \sum_j e^{i\mathbf{Q} \cdot \mathbf{r}_j} |f>|^2 \delta(E_f - E_i - \hbar\omega)
\]

(2.13)

where \(r_0(=\frac{e^2}{m c})\) is the classical electron radius, and \(N\) is the number of atoms in the scattering volume. Equation (2.13) can be written as

\[
\frac{d^2\sigma}{d\Omega d\omega} = N\left(\frac{d\sigma}{d\Omega}\right)_{Th} S(Q, \omega)
\]

(2.14)

where

\[
\left(\frac{d\sigma}{d\Omega}\right)_{Th} = r_0^2 \frac{\omega_f}{\omega_i} |\mathbf{e}_i \cdot \mathbf{e}_f|^2
\]

(2.15)

is the Thomson scattering cross section, and

\[
S(Q, \omega) = \sum_{i,j} |<i| \sum_j e^{i\mathbf{Q} \cdot \mathbf{r}_j} |f>|^2 \delta(E_f - E_i - \hbar\omega)
\]

(2.16)

is the dynamical structure factor.
2.6 High Resolution X-ray Scattering

Plasma excitations are low-energy excitations. The energies are typically of the order of 1 eV. Compared with the incident beam energy, the energy transfer is very small, so the magnitude of the x-ray wave vector does not change significantly during the scattering process. According to Figure 2 and equation (2.6) it can be written as [14]

\[ Q = 2k_i \sin \theta = \frac{2E_i}{\hbar c} \sin \theta \quad (2.17) \]
\[ Q(\text{Å}^{-1}) = 1.013E_i(\text{keV}) \sin \theta \quad (2.18) \]

From equation (2.1), we can derive the energy resolution as a simple expression

\[ \frac{\delta E}{E} = \frac{\delta k}{k} \quad (2.19) \]

where \( \delta E \) and \( \delta k \) are the bandwidth in energy and in wave vector, respectively. And Bragg's law can be written as
\[ d_{hkl} \sin \theta = \lambda \]  \hspace{1cm} (2.20)

\[ 2k \sin \theta = G \]  \hspace{1cm} (2.21)

where \( k \) is the value of wave vector \( (k = |k| = \frac{2\pi}{\lambda}) \) and \( G \) is the reciprocal lattice vector \( (G = |G| = \frac{2\pi}{d_{hkl}}) \), \( d_{hkl} \) is the distance between atomic planes for a given reflection. In these equations (2.20, 2.21), \( G, \theta \) and \( k \), have uncertainties \( \delta G, \delta \theta \) and \( \delta k \), respectively. So \( \delta G \), in achieving high energy resolution, is specified as crystal contribution. The momentum transfer can be changed by adjusting the scattering angle \( (2\theta) \) and it is independent from the energy transfer. Since the entire \((Q, \omega)\)-space is accessible with practically the same resolution in momentum and energy [14], this is very useful. By adjusting the slits position, we can define the divergences of the incident and scattered beam. \( \delta \theta \) is, therefore, called the geometric contribution.

The energy resolution depends on many things. The major contributors are the quality of monochromator and analyzer crystals (crystal contributions) and on Bragg angle variation in these crystals (geometry contribution). If the Bragg angle is very close to the backscattering angle, the intrinsic en-
nergy resolution is independent.

2.7 Jellium Model

Jellium is the model of interacting electrons in a smeared background of positive charge. In this model, the system properties depend only on the charge density of electrons at 0 K. The model works with atoms as if they were actually blobs of jelly, this is how it gets the name. The Hamiltonian of the system has three parts [15]:

$$H_{electrons} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j=1}^{N} \frac{e^2}{|r_i - r_j|}$$  \hspace{1cm} (2.22)

where $N$ is the number of electrons in the jellium, $p_i$ is the momentum of the $i$–th electron, $m$ is the mass of electron and $e$ is the charge of the electron.

When the electron gas shifts by $x$ relative to the positive background, an electric field

$$E = n e x / \varepsilon_0$$  \hspace{1cm} (2.23)

is created. Here $n$ is the electron density. The force on electron created by
the electric field will be \(-eE\). The equation of motion is

\[
 nm \frac{d^2 x}{dt^2} = -neE = - \frac{n^2 e^2 x}{\varepsilon_0}
\]  

(2.24)

or it can be written as

\[
 \frac{d^2 x}{dt^2} + \omega_p^2 x = 0
\]  

(2.25)

where \(\omega_p = (\frac{ne^2}{m\varepsilon_0})^{1/2}\) is plasmon frequency. Equation (2.25) is the special situation when wave vector \(q \to 0\). For a more general situation, electronic density can be written as

\[
 \rho(r) = \sum_i \delta(r - r_i) = \sum_q \sum_i e^{iq(r-r_i)} = \sum_q \rho_q e^{iq\cdot r}
\]  

(2.26)

So we get

\[
 \rho_q = \sum_i e^{-iq\cdot r}
\]  

(2.27)

and

\[
 \rho_0 = n
\]  

(2.28)
If we take the derivative on both side of equation (2.27),

\[ \dot{\rho}_q = -i \sum_i (q \cdot \nu_i) e^{-iqr} \]  

(2.29)

where \( \nu_i = \frac{dr_i}{dt} \) is the velocity of the \( i^{th} \) electron. If we take another derivative on both sides of equation (2.29)

\[ \ddot{\rho}_q = - \sum_i [(q \cdot \nu_i)^2 + i(q \cdot \dot{\nu}_i)] e^{-iqr} \]  

(2.30)

If we use Hamilton’s equation (2.22) and Fourier transform, after simplification [16], we get

\[ \ddot{\rho}_q = - \sum_i (q \cdot \nu_i)^2 e^{-iqr - \frac{ne^2}{m\varepsilon_0} \rho_q} \]  

(2.31)

or

\[ \ddot{\rho}_q + \omega_p^2 \rho_q = - \sum_i (q \cdot \nu_i)^2 e^{-iqr} \]  

(2.32)

when \( q \to 0 \),

\[ \dot{\rho}_q + \omega_p^2 \rho_q = 0 \]  

(2.33)

so

\[ \omega_p = \left( \frac{ne^2}{m\varepsilon_0} \right)^{1/2} \]  

(2.34)
when $q > 0$, the dispersion relationship can be derived from equation (2.32) [16]

$$\omega_q^2 = \omega_p^2 + \frac{3}{5} v_F^2 q^2$$  \hspace{1cm} (2.35)

or

$$\omega_q = \omega_p + \frac{2v_F^2}{10\omega_p} q^2$$ \hspace{1cm} (2.36)

Therefore, we expect to see the plasmon energy increase with $q$. 
CHAPTER III

METAL AMMONIA SYSTEM

3.1 History

The earliest published experiments in which a metal was observed to dissolve in ammonia were those reported by Weyl (1864). He studied sodium and potassium in ammonia and concluded that ‘ammoniums’ (NH$_4$) were being formed. By evaporating the sodium ammonia solvent, Seely (1871) recovered Na only seven years later. So he realized that the metal did not react with ammonia and the solution was similar to salt in water and sugar in tea [17]. He said: "The solid disappears in the liquid and on evaporating the liquid, the solid reappears in its original form" [18]. After 16 years (1873-1889), ammonia became commercially available in 1898 and this accelerated the research.

Beginning in 1895 and continuing into the 1930s, the ‘Kansas group’ of H.
P. Cady, E. C. Franklin, and C. A. Kraus provided the world with much of the available information (phase diagrams, vapor pressures, and conductivities etc) on metal-ammonia solutions [19, 20].

In 1963, a series of conferences with the name Colloque Weyl was begun with the goal of bringing together research on metal-ammonia solutions. M. Sienko made an extraordinary contribution by studying transitions, conductivity, surface tension, the metal-nonmetal transition, etc. While at Cornell, in the same year, Sienko was led to the startling discovery that the two layer coexistence curves for Li-NH$_3$, Na-NH$_3$, and K-NH$_3$ were almost the same in exhibiting parabolic dependencies, however all other critical phenomena (and the theoretical models) corresponded to cubic coexistence curves. By his study, we know that liquid-liquid phase separation in metal ammonia solutions was related to the metal-nonmetal transition [36].

In 1946, Jr. Richard A. Ogg reported the theory and the experiment for the superconductivity in metal ammonia system in two papers [22, 23]. He stated that “the liquid-liquid phase separation which occurs on slow cooling (upper consolute temperature 232 K) is the device adopted by the systems to avoid the Bose-Einstein condensation, with its unfavorable free energy change.” [22] But, “by sufficiently rapid cooling, it appears that the liquid-
liquid phase separation is prevented, and that the system becomes frozen and hence metastable in the ‘forbidden’ concentration region, which is thus characterized by the Bose-Einstein condensation of trapped electron pairs.” [23] He predicted that this kind of systems should be superconducting according to London’s theory [24]. In another paper [23], he reported that he successfully measured the resistance of Na-NH$_3$ systems in seven cases out of two hundred trials with different concentrations and field strengths. The resistance measured is of the order of $10^{-13}$ $\Omega$ or smaller. “In view of the fact that the liquid samples possessed resistances of the order of thousand ohms, the solids in question may fairly be said to be superconducting.” [23] In the same year, J. W. Hodgins watched the persistent currents in frozen metal-ammonia solutions [9]. The resistance of the ring is indicated to be in the order of $10^{-12}$ $\Omega$.

However, there is no other confirmation of superconductivity of metal ammonia from other groups. And we did not find any superconductivity in metal ammonia system in our experiments either. We used a nylon tube (3.175 mm O. D., 2.362 mm I. D., 0.4064 mm wall) and sealed one end. Then put correct amount of sodium in the tube in the glove box (see Appendix A for details), and connected to the ammonia condensation system (Figure
After the ammonia was condensed in the tube, we sealed the other end, leaving the sample length equal to 2.54 cm. Then we put the tube in liquid nitrogen to freeze the sample quickly (quench process). We made a couple of samples at different concentrations. Samples were taken to Material Science Division at Argonne National Laboratory and measured by Superconducting Quantum Interference Device (SQUID) down to 5 K. No evidence was found for superconductivity in the samples.

3.2 Structure and Properties

3.2.1 Phase Diagram

Figure 3 and Figure 4 are phase diagrams for lithium ammonia and sodium ammonia, respectively. Both of them have an insulator phase at low concentration, and when the concentration increases, there is liquid-liquid phase separation. Both of them become metallic at higher concentrations. Lithium ammonia is saturated at 20 MPM, and sodium ammonia, 16 MPM. The colors of the mixtures vary from deep blue to golden yellow from low concentrations to high concentrations for both lithium ammonia and sodium ammonia.
Figure 3. Li-NH₃ phase diagram (from C. A. Burns [12]).

Figure 4. Na-NH₃ phase diagram (from A. Said [13]).
3.2.2 Structure

Solid metal-ammonia compounds characteristically retain the golden color of the concentrated liquid solutions. The lithium compound has the lowest melting point (89 K) of any metal as well as a wide variety of striking transport properties. The europium compound, Eu(NH₃)₆, also has a rich variety of physical properties associated with it [17].

Not all of the metals known to dissolve in liquid ammonia form stable solids and the composition of the solids that do form is limited. Sodium and potassium are known to precipitate as metals when the solution is frozen. Lithium, calcium, strontium, barium, europium, and ytterbium form solid compounds and the lattice structure and unit cell dimensions are known [17].

Early structural studies on lithium ammonia compounds have been reported by Mammano and Sienko (1968) and by Kleinman, Hyder, and Thompson (1970) [17]. They conclude that there were two crystalline solid phase below 90 K. Phase I [25] (stable between 82 K and 89 K) is a cubic phase with \( a = 9.55\,\text{Å} \); and phase II is stable between 25 K and 82 K. Chieux et al. [26] performed several low-temperature neutron powder diffraction (NPD) data collections on both Li(NH₃)₄ and Li(ND₃)₄ over the temperature range 3 K - 85 K using the D1B spectrometer at the Institute Laue-Langevin. They
found out that the protonated compound changed according to cooling from 85 K to 60 K from phase I to phase II. The diffraction patterns indicated that both phases were body-centered cubic (bcc), with $a = 15.03\,\text{Å}$ at 85 K and $a = 14.93\,\text{Å}$ at 60 K. Below 25 K (phase III), the diffraction patterns show the formation of a superstructure having a period $2a$. Stacy and Sienko’s work [27] showed that the space group of phase I and phase II are $I\overline{4}3d$, Young et al. [55] give more details on the structure of Li(ND$_3$)$_4$ which is shown in Figure 5.
3.2.3 Some Properties

At $T = 0K$, the properties of the electron liquid are determined by the electron density $r_s$ which is

$$r_s = \left(\frac{\pi}{3}n\right)^{-1/3} a_0^*$$

(3.1)

where $n$ is the free electron concentration (Table 1), $a_0^*$ is the effective Bohr radius, $a_0^* = \frac{\hbar^2}{m^* \varepsilon}$, where $m^*$ is the effective mass of the electron, and $\varepsilon$ is the static dielectric constant.
Table 1. Some calculations for different concentration in lithium ammonia systems. Densities are from [33].

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<th>density (MPM)</th>
<th>$Q_c$</th>
<th>$w_i$</th>
<th>$v_i$</th>
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<th>electron density ($n \times 10^{22}/cm^3$)</th>
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At very low concentration (below $10^{-3}$ MPM), the electrons are believed to reside in isolated cavities surrounded by polarized ammonia molecules (Figure 6). At higher concentration ($\approx 10^{-3}$ $\rightarrow$ 0.5 MPM), electrons form bipolarons. As concentration increases (below 4 MPM), the bipolarons begin to cluster together and eventually form a multichannel structure. At the concentration near 4 MPM, the systems undergo a metal insulator transition (MIT). The systems stay metallic up to saturation, which is about 20 MPM for lithium.

3.3 Plasmon

The plasmon is the quasiparticle resulting from the quantization of plasma oscillations just as photons and phonons are quantizations of light and sound waves, respectively. A plasma oscillation in a metal is a collective longitudinal excitation of the conduction electron gas. To excite a plasmon, we can pass an electron or a photon through a thin metallic film. The reflected or transmitted electron or photon will show an energy loss equal to integral multiples of the plasmon energy.

If electron interactions are treated using the random phase approximation
(RPA) in the jellium model, it is easy to get the plasmon energy at zero momentum transfer from equation (2.34) [29],

\[ E(0) = \hbar (\frac{4\pi ne^2}{\varepsilon m^*})^{1/2} \quad \text{(CGS)} \]  
\[ E(0) = \hbar (\frac{ne^2}{\varepsilon m^*})^{1/2} \quad \text{(SI)} \]  

where \( \omega_p \) is plasma frequency.

For momentum transfer is smaller than some cut-off momentum \( q_c \approx \frac{\omega_p}{\nu_F} \) (where \( \nu_F \) is Fermi velocity, the value for \( q_c \) see Table 1), RPA predicts the plasmon dispersion relationship at \( T = 0K \)

\[ E(q) = E(0) + \frac{\hbar^2}{m} \alpha q^2 \]  

where \( \alpha = \frac{3E_F}{5\hbar \omega_p} = \frac{3\hbar(3\pi^2)^{2/3}(me_0)^{1/2}}{e} \cdot n^{1/6} \propto n^{1/6} \), where \( n \) is electron density, \( E_F \) is Fermi energy, \( \hbar \) is Planck’s constant, \( e_0 \) is electric constant, \( m \) is the mass of electron, \( e \) is the charge of an electron.

An example is shown in Figure 7, at momentum transfer \( q = 4.2nm^{-1} \). It shows that there is a well-defined plasmon which energy is about 2 eV.
Figure 7. Inelastic x-ray scattering signal from a 20 MPM lithium ammonia mixture at $Q = 4.0\,nm^{-1}$, solid lines are the fitting of the peaks.

## 3.4 Metallic Glasses

Metallic Glasses, also called Glassy Metals, are amorphous materials. In these materials, there is no long range order of the positions of the atoms as in crystals (see Figure 8). Most classes of solid materials can be prepared in some amorphous form. For instance, window glass is an amorphous ceramic, many polymers are amorphous, and even foods are amorphous solids.

Amorphous material are often prepared in a couple of different ways, such as ion implantation, thin-film deposition, and rapid cooling. Ion implantation is a process by which ions of a material can be implanted into another solid,
Figure 8. A sketch of a two dimensional crystal structure with long range order (left) and a two dimensional amorphous material without long range order [60].

d therefore, changing the structure and physical properties of the solid. Thin-film deposition is a technique for depositing a thin film of a material onto a substrate or onto previously deposited layers.

Metallic glass or glassy metals are usually prepared by rapid cooling. The cooling reduces the mobility of the material’s molecules before they can pack into a more thermodynamically favorable crystalline state, especially when the viscosity of the material is high. Metals are difficult to transfer to an amorphous state, so the cooling process has to be extremely rapid. The material changes from a supercooled liquid state to a solid state as the cooling is performed. The temperature at which this transition occurs is called the glass transition temperature or $T_g$. Figure 9 shows the volume versus tem-
temperature for insulating (dashed line) and metallic (solid line) materials [30].

$T_g$ is glass transition temperature, and $T_M$ is the melting point.

In amorphous materials, there is no long range order. To describe the structure, the radial distribution function (RDF) is one of the methods to be introduced. RDF tells how many atoms we can expect at a distance between $r$ to from one chosen atom. The idea is demonstrated in Figure 10.

If the atoms are not correlated, then the expected number of atoms at the distance between $r$ and $r + dr$ will simply be the average number of atoms per unit volume, times the shell of radius $r$ and thickness $dr$. In a 3-dimensional space, it will be

$$N_{ideal} = \frac{N}{V} \times V_{shell}(r) = \rho \times 4\pi r^2 dr \quad (3.5)$$
where $\rho$ is the number density of atoms. In a correlated amorphous system, we will use [31]

$$G(r) = 1 + \frac{1}{2\pi^2 \rho} \int_0^\infty [S(q) - 1] \frac{\sin qr}{qr} \cdot q^2 dq$$

(3.6)

where $G(r)$ is RDF, $S(q)$ is the structure factor which can be measured by elastic x-ray scattering or neutron scattering.

When $r \to 0$, $g(r) \to 0$, see Figure 10, since no atom can overlap with another atom. When $r \to \infty$, $g(r) \to 1$, since when $r$ increase, the number of atoms in the shell will be closer to the average number of molecules per unit volume times the volume of the shell, which after the normalization, will approach 1.
Figure 10. Schematic explanation of the radial distribution function. The atom at the origin is highlighted by a black sphere. The shaded regions indicate the 1st and 2nd coordination shell, respectively [32].
CHAPTER IV

EXPERIMENT AND DATA ANALYSIS FOR LI-NH$_3$ PLASMON

4.1 Preparation of Samples

Alkali metals have to be cut very carefully in an inert gas (such as Ar in this experiment), since they are very reactive. For the same reason, the cutting tools and the sample cells have to be made of the materials which do not react with alkali metals or ammonia, such as stainless steel, beryllium (Be), etc.

Metal ammonia samples have to be stored at low temperature (193.15 K in this experiment), since the mixtures have high vapor pressure at room temperature. Figure 11 shows what the sample cell looks like. Different sample cells are designed for different concentrations of lithium ammonia. The concentrations are not allowed to change after the samples are made. The details about how to prepare lithium and how to cut it in the Argon
filled glove box are in Appendix A. After the sample cell is filled with lithium in the glove box, it is attached to the ammonia condensation system (Figure 12, and Figure 13). The amount of ammonia condensed is determined by the volume of the system and the pressure of the gas. Samples are made by using 99.9% pure lithium and high purity (99.99%) anhydrous ammonia.

Here are the steps we used to prepare our samples.

1. Cut and weigh the required amount of lithium in glove box filled with the inert gas (Ar) and put it in the sample cell. (see Appendix A and B for details about how to use the glove box and how to calculate the weight of lithium)
2. Seal the sample cell by closing valve V in Figure 12
3. Attach the sample cell to the ammonia condensation system (Figure 13, and Figure 14)
4. Valve V1, V2 and V3 are closed, open Valve V4, Valve 8, 5 and 3
5. Pump the system until the pressure is under 100 millitorr
6. Open Valve V (Figure 12) until the pressure in the system is under 100 millitorr
7. Close the valve between the pump and the system
8. Close valve 8
9. Open valve 2 until we get the pressure somewhere around 12 psi (any value under 14.7 psi is good)

10. Close valve 2

11. Open valve 8 and record the pressure

12. Put a Dewar of ethanol under the sample cell

13. Cool the ethanol to about -50°C by Thermo NESLAB cc-100

14. Repeat step 9 to sept 11 until we get the required amount of ammonia in the sample cell

15. Seal the sample cell by heat (Figure 15), Set the heat gun to "lo" and heat the pliers about 10 seconds, then heat seal the nylon tube on the top of the sample cell

16. Put the sample cell in a container filled with dry ice

In Figure 14:

1. AirGas Ammonia supply tank

2. AirGas ammonia pressure regulator

3. Valve 3

4. Stainless Steel tee NW25

5. Valve 5

6. OMEGA pressure gauge (psi)
Figure 11. Sample cell for lithium ammonia, left (side view), middle (side view), right (top view). Be Windows will be glued to the stainless steel sample cell, and stainless steel window mount support will be mounted on top of Be windows by Hysol Epoxy to secure the vacuum inside sample cells. Since the thermal expansion coefficients of stainless steel and Be are slightly different from each other, the window mount support is very necessary.
Figure 12. Sample cell with Valve V. After lithium was put in the sample cell, the valve V will seal the system to prevent the reaction between lithium and air.

Figure 13. Picture of metal ammonia condensation system with sample cell attached.
Figure 14. Schematic diagram of ammonia condensation system.

7. 1/2 liter tank (Swagelok 316L-HDF4-500)
8. Valve 8
9. Nylon tube
10. Varian 801 TC vacuum gauge
11. HI-VAC vacuum end cap
12. HI-VAC vacuum double manifold

*V₁, V₂, V₃, and V₄ are vacuum valves.
Figure 15. Heat sealing the sample cell. Set the heat gun to “lo” and heat the plier about 10 second, then heat seal the nylon tube on the top of the sample cell.

Figure 16. Schematic view of inelastic x-ray scattering experiment set-up at Sector 30 of the APS.
Figure 17. Analyzer and the rectangular aluminum momentum slot.

Figure 18. Schematic explanation of observation angle of the analyzer.
4.2 The Experimental Dynamic Structure Factor of Li-NH₃

These experiments took place at Sector 30 at the Advanced Photon Source (APS) at Argonne National Laboratory. The dynamic structure factor of lithium ammonia systems were measured with lithium concentrations of 10 MPM, 11 MPM, 16 MPM at temperature T = 200 K. The 20 MPM sample was measured at 200 K at Sector 9 ID, which has a similar set up to Sector 30. The sample cells were measured more than once at different times and the signal did not change, which shows the stability of the samples.

Figure 16 shows the schematic view of the inelastic x-ray scattering experiment set-up at Sector 30, APS. X-rays come from an undulator, then pass through a pre-monochromator (two crystals), high-resolution monochromator (four crystals), and a focusing mirror (the little rectangle), before they hit the sample. The scattered x-ray is focused by the analyzer to the detector.

Figure 17 shows the analyzer we used for taking the data on Sector 30 at APS. There was a rectangular aluminum momentum slot in front of the analyzer to improve the accuracy of the dispersion measurement. The slot size (d) is one inch. The distance (r) between the analyzer and the sample is one meter. Figure 18 shows the schematic view of the rectangular aluminum
momentum slot. The angle $\theta$ can be calculated by $\theta = d/r$, which is 1.45°C. So from the center to the edge, it will span a angle 0.725°C which corresponds to 0.6 nm$^{-1}$ momentum transfer.

The structure factor $S(Q)$ results are shown in Figure 19. The structure factor $S(Q)$ measured here is the integration of the $S(Q, \omega)$ over $\omega$ at constant $Q$. The experimental value of $S(Q)$ is $S(Q) = \int_0^\infty S(Q, \omega)d\omega$. There are two peaks in measured $S(Q)$. The peak on the right is around 20 nm$^{-1}$ or lower which agrees with other IXS measurements [34, 35]. Neutron measurements show similar results [36, 37].

The right peak is related to the mean nitrogen spacing in the system, and when more lithium is added into the system, it evolves to the peak at 18 nm$^{-1}$ at saturation point (20 MPM) which is measured at Sector 9 at APS.

The first peak occurs close to $2k_F$ at lithium concentration of 20 MPM. It is believed that there is some degree of long-range spatial ordering of the coupled lithium ion-free electron systems [34]. And it can occur because the collective modes of the mixture have softened strongly near $2k_F$ [34,35]. The wave vectors at the Fermi surface have a magnitude of

\[ k_F = (3\pi^2 n)^{1/3} \]  

(4.1)
Calculated values of $k_F$ at 10 MPM, 11 MPM, 16 MPM and 20 MPM are $4.0 \, \text{nm}^{-1}$, $4.1 \, \text{nm}^{-1}$, $4.6 \, \text{nm}^{-1}$ and $4.9 \, \text{nm}^{-1}$, respectively, at this temperature. At lower concentration, for example 10 MPM, the intensity of the first peak, decreases by a factor of five. This decrease is because lower density of electrons and the ionic correlations are not that strong which affect the molecules’ position much less. And the first peak position is not close to the $2k_F$ position as in the 20 MPM sample.

4.3 The Inelastic X-ray Scattering Data

The inelastic scattering data for lithium ammonia were measured in the $Q$ range between $2.5 \, \text{nm}^{-1}$ and $6.5 \, \text{nm}^{-1}$ and the energy range between $-0.5 \, \text{eV}$ and $4 \, \text{eV}$. We found well-defined plasmon peaks at different lithium concentrations, and the peaks broaden as the momentum transfer increases. The experiments were carried on Sector 30 and Sector 9 at Advanced Photon Sources (APS) in Argonne National Laboratory.

Figure 20 shows the data taken at Sector 9 for 20 MPM lithium ammonia mixture at 200 K. The plasmon clearly moves to higher energy when momentum transfer increases. And the peak width increases with momentum
Figure 19. Structure factor $S(Q)$ for lithium ammonia.
transfer too. The plasmon broadens out at high Q value, which is the same result as [34].

Figure 21, Figure 22 and Figure 23 are the data taken at Sector 30 at APS, and they are for 16 MPM, 11 MPM and 10 MPM lithium ammonia, respectively. The plasmon behavior is similar at lower concentration to the plasmon in 20 MPM lithium ammonia, except that it is broader and weaker.

Figure 22 and Figure 23 show the data at different Q values with fitting lines, since it is difficult to compare the plasmon by just looking at them, we add the fitting peaks too.

4.4 Data Analysis

4.4.1 Fitting Function

The instrumental resolution function is a combination of Gaussian and Lorentzian peak functions. When it is closer to zero energy loss, it is closer to Gaussian peak function, further away from zero position, it is more like Lorentzen peak function. Plasmon peaks are far from the center in our experiment, therefore, Lorentzian peak function was used for fitting the data
Figure 20. The momentum dependence of the plasmon of lithium ammonia (20 MPM).
Figure 21. The momentum dependence of the plasmon of lithium ammonia (16 MPM).
Figure 22. IXS data for Li-NH$_3$ 11 MPM at different $q$. The vertical axis is intensity (counts/second) and horizontal axis is energy loss (eV).
Figure 23. IXS data for Li-NH\textsubscript{3} 10 MPM at different \( q \). The vertical axis is intensity (counts/second) and the horizontal axis is energy loss (eV).

In this experiment,

\[ y = y_0 + \frac{2A}{\pi} \cdot \frac{w}{4(x - x_0)^2 + w^2} \]  

(4.2)

where \( y_0 \) is baseline offset, \( A \) is total area under the curve from the baseline, \( x_0 \) is the center of the peak and \( w \) is the full width of the peak at half height (FWHM).

In our data fitting, we use a sum of two Lorentzian functions, one for the elastic background, the other one, plasmon peak. The equation is similar to
equation (4.2).

\[ y = y_0 + \frac{2A_1}{\pi} \cdot \frac{w_1}{4(x - x_{10})^2 + w_1^2} + \frac{2A_2}{\pi} \cdot \frac{w_2}{4(x - x_{20})^2 + w_2^2} \]  

(4.3)

The parameters here are similar as equation (4.2), second term is for the elastic background and the last term is for the plasmon peak.

4.4.2 Plasmon Energy

We compare our data with the jellium model, and in this model we treat the electron interactions by using the random phase approximation (RPA).

So the plasmon energy at zero momentum transfer is given by equation (2.34)

\[ E(0) = \hbar \omega_p = \hbar \left( \frac{4\pi ne^2}{\varepsilon n} \right)^{1/2} \]

(4.4)

For momentum transfer \( q < q_c \), RPA predicts the plasmon dispersion relationship

\[ E(q) = E(0) + \frac{\hbar^2}{m} \alpha q^2 \]

(4.5)

where \( \alpha \) is a coefficient that depends only on the electron density\( (\alpha = \frac{3E_F}{\hbar^2 \omega_p} \propto n^\frac{1}{6}) \).
At lower concentrations, the plasmon peak is small and hard to locate the position. But we can use the longitudinal current spectrum [38] which is defined as

\[ C_L(Q, \omega) = \left( \frac{\omega^2}{Q^2} \right) S(Q, \omega) \]  

(4.6)

where \( Q \) is the momentum transfer, \( \omega \) is the frequency of photons, and \( S(Q, \omega) \) is the dynamic structure factor of the material measured. The factor \( \omega^2 \) wipes out the low frequency portion of the structure factor, and emphasizes the real inelastic features of dynamic structure factor \( S(Q, \omega) \). In this method, it is easy to locate the peak position in \( S(Q, \omega) \). We double-checked our fitting with this technique, the difference is less than 100 meV.

Figure 24 shows the plasmon energies at different concentrations and the fitting data to equation (4.5). For 20 MPM lithium ammonia, the best fit yields \( E(0) = 1.85 \pm 0.0199 \) eV, and the quadratic dispersion coefficient \( \alpha = 0.195 \pm 0.013 \). For this electron density (\( T = 200 \) K), RPA predicts 

\[ E(0) = \hbar \omega_p = \hbar \left( \frac{ne^2}{\varepsilon m} \right)^{\frac{1}{2}} = 2.36 \text{eV} \text{ and } \alpha = \frac{3E(0)}{5\hbar \omega_p} = 0.24 \].

The reduction of \( E(0) \) may be due to polarizability of the lithium ion cores and the ammonia molecules [34]. The reduction is about 22% from RPA value \( \left( \frac{2.36-1.85}{2.36} \times 100\% = 22\% \right) \). Assuming \( \varepsilon = 1.62 \) makes the RPA value for \( E(0) \) match the measured value. This value also increase the RPA dispersion coefficient,
Figure 24. Plasmon energies at different concentrations and the fitting to equation (4.5). Fit lines are drawn only out to the limit of fitting range (to $q_c$).

yielding $\alpha = 0.30$.

For the lower concentrations, we did a similar fitting and the results are in Table 2. From Table 2, we can tell, that when the concentration decreases, $E(0)$ decreases less from the RPA value. At the same time, the decrease in the dispersion coefficient from the value RPA predicts is greater, which has been observed before [34, 35]. This is very interesting since the dispersion is only a weak function of the density according to equation $\alpha = \frac{3E_F}{5\mu_d} \propto n^{1/6}$.

Figure 25 shows the dispersion of plasmon energy. The solid lines are the best fit to a quadratic dispersion equation (4.5), and the dashed lines are
Figure 25. Plasmon energies plus fits to equation (4.5) for different concentrations. Fit lines are drawn only out to the limit of the fitting range (to $q_c$).
Table 2. Fitting result of plasmon peaks at different concentrations.

<table>
<thead>
<tr>
<th>MPM</th>
<th>$E(0)$</th>
<th>$E(0)_{RPA}$</th>
<th>%diff</th>
<th>$\alpha$</th>
<th>$\alpha_{RPA}$</th>
<th>%diff</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.85±0.0199eV</td>
<td>2.36eV</td>
<td>22%</td>
<td>0.195±0.013</td>
<td>0.24</td>
<td>18.8%</td>
</tr>
<tr>
<td>16</td>
<td>1.83±0.013eV</td>
<td>2.14eV</td>
<td>14.5%</td>
<td>0.11±0.01</td>
<td>0.23</td>
<td>52.2%</td>
</tr>
<tr>
<td>11</td>
<td>1.677±0.03eV</td>
<td>1.82eV</td>
<td>7.9%</td>
<td>0.053±0.023</td>
<td>0.22</td>
<td>75.9%</td>
</tr>
<tr>
<td>10</td>
<td>1.605±0.026eV</td>
<td>1.75eV</td>
<td>8.3%</td>
<td>0.046±0.021</td>
<td>0.21</td>
<td>78.1%</td>
</tr>
</tbody>
</table>

the RPA fit to equation (4.5) where $\alpha$ value is only determined by electron density ($n$). As what we see in Table 2, the Figure 25 shows the measured dispersion decrease from RPA dispersion and the decrease becomes much greater when the concentrations decrease.

There are two aspects of RPA treatment of the jellium model that might not be adequate for this mixture. One is the RPA does not properly treat electron-electron interactions at low electron densities and high momentum transfers. The other is that the jellium model does not treat inhomogeneities in the charge distribution, which might be very significant [34]. Substantial deviations in the dispersion coefficient from RPA predictions are also found in other systems, such as Al [39], Li [40], Rb, Cs [41,42], etc.

All the data are fitted up to some cutoff momentum transfer ($q_c$). The values are, 6.3 $nm^{-1}$, 6.1 $nm^{-1}$, 5.8 $nm^{-1}$, and 5.7 $nm^{-1}$, for the 20 MPM,
16 MPM, 11 MPM and 10 MPM, respectively. However, in Figure 25, 16 MPM lithium ammonia, even 6.0 $nm^{-1}$ is smaller than cutoff momentum transfer 6.1 $nm^{-1}$, the plasmon energy is still lower than the one at momentum transfer 5.5 $nm^{-1}$. And 11 MPM lithium ammonia data, we see similar phenomena. To explain this, we need to discuss the analyzer we used to take our data (Figure 17, Figure 18).

In Figure 25, 16 MPM lithium ammonia data, while 6.0 $nm^{-1}$ is smaller than the cutoff momentum transfer 6.1 $nm^{-1}$, and the analyzer has a width of 0.6 $nm^{-1}$ in momentum transfer, so part of the analyzer is seeing momentum transfer bigger than cutoff momentum transfer. It is the same in Figure 25, 11 MPM lithium ammonia data. Since $5.5 + 0.6 = 6.1$ $nm^{-1} > 5.8$ $nm^{-1}$ (cutoff momentum transfer for 11 MPM lithium ammonia), the last point (5.5 $nm^{-1}$) is lower than the previous one. Figure 26 shows that at the cutoff momentum transfer ($q_c$), the plasmon decays to electron-hole excitation only at lower energy levels which is why the plasmon energy is much lower at cutoff momentum transfer.

Sternemann et al [38] found a double-plasmon excitation in simple metals using inelastic x-ray scattering. This is predicted by many-body perturbation theory of the homogeneous-electron-gas model beyond the RPA. It is also
believed that electron-ion interaction effects do not affect it. We measured 20 MPM lithium ammonia mixture at high energy and high momentum transfer at Sector 9, APS, but we did not see any peak in this mixture. In theory [38,44], the second plasmon peak is supposed to show up at two times energy position which is 4 eV in this mixture. In Figure 27, we do not see any feature like this. We tried different momentum transfers, and got the same results.
Figure 27. IXS data of 20 MPM lithium ammonia at Q=5nm\(^{-1}\).

4.4.3 The Linewidth of Plasmon Peaks

From Figure 20 to Figure 23, we can see that the width of the plasmon peaks increase as the lithium concentrations decrease. We assume the measured linewidth can be written as

\[ w_m = \sqrt{w_i^2 + w_p^2} \]  \hspace{1cm} (4.7)

where \( w_i \) is the instrumental linewidth and \( w_p \) is the plasmon linewidth.

Figure 28 shows the resolution of the inelastic x-ray scattering experiment. The instrumental linewidth is 0.13 eV. And Figure 29 shows the resolution
Figure 28. Resolution of IXS data at Sector 30 (APS). Solid squares are the data, solid line is the best fit. Resolution is 0.13 eV.

of IXS experiment is 0.1 eV at Sector 9 where 20 MPM lithium ammonia mixture were measured.

After correcting the linewidth of the plasmon peak, Figure 30 shows the dispersion relationship of plasmon linewidth.

The plasmon linewidth has a momentum dependence of $q^2$ in the treatment of jellium model to second order in perturbation theory, which shows that the plasmon can decay into two particle-hole pairs below $q_c$. But from Figure 31, we fit the data to power equation $y = a + b \cdot q^n$ and if we force $a = 0$, the best fit for $n$ yield much lower value than 2. In this case, they
Figure 29. Resolution of IXS experiment at Sector 9 (APS). Solid squares are the data, solid line is the best fit. Resolution is 0.1 eV.

Figure 30. Dispersion of plasmon width after corrected by instrumental linewidth.
Figure 31. Lithium ammonia linewidth and best fit to equation $y = a + b \cdot x^2$ for different concentrations.
Figure 32. Li-NH$_3$ 8 MPM at momentum transfer $q = 3.57$ nm$^{-1}$, no plasmon feature is recognized on graph.

are $1.63 \pm 0.11$, $1.62 \pm 0.16$, $1.60 \pm 0.26$ for 16 MPM, 11 MPM and 10 MPM respectively. Burns et al. have measured 20 MPM lithium ammonia at 220 K and get similar results [34].

The plasmon width is supposed to be proportional to $q^2$ up to the cutoff momentum transfer in RPA theory. However, if we consider the electron-hole pairs effect in the decay, the plasmon width can be larger than some theoretical calculations [45]. Due to interband transitions, the plasmon width may not be zero at $q = 0$. As a matter of fact, the width should be proportional to the square of the Fourier coefficient of pseudopotential [46]. If we fit the
data in Figure 30 to $y = a + b \cdot q^n$ and force $n = 2$, the best fit yields for $a$ are $0.20 \pm 0.028$ eV, $0.256 \pm 0.0491$ eV and $0.263 \pm 0.083$, for 16 MPM, 11 MPM and 10 MPM, respectively. The linewidth of plasmon at zero momentum transfer is getting wider and wider when concentrations are getting lower and lower which might due to pseudopotential or band structure. From Figure 19, we can see the static structure factor for different concentrations, the first peak getting weaker and weaker when the concentration decreases.

By using the nearly-free-electron (NFE) pseudopotential theory, Sturm and Oliveira [46] calculated wave-vector-dependent plasmon linewidth due to interband transitions in lithium, sodium, and potassium and they found that two electron-holes excitations lead finally to an increasing linewidth, in qualitative agreement with experiment. However, the quantitative discrepancies show that interband transitions to empty $d$ bands beyond the NFE model make a contribution to the plasmon linewidth in potassium. In our data, we see the plasmon widths increase as we go lower concentrations too.

At concentrations higher than the metal insulator transition (MIT) (around 4 MPM), the liquid is still metallic and we expected that there would be plasmon peaks until 4 MPM. But our data show that at 10 MPM, the plasmon peaks are pretty wide and small, therefore they are hard to recognize by just
looking at them. We also take some data for an 8 MPM sample (Figure 32), but the plasmon peak is so wide that it is hard to recognize it by eye on the graph. At 10 MPM, \( r_s = 9 \) which is much greater than most metals. It is hard to know what value of \( r_s \) is small enough so that the electrons are sufficiently free for plasma-like behavior, however, it is suggested that the value should be somewhere around 10 [47]. \( r_s = 10 \) at a concentration of 7 MPM. However, since the value is so close to 10 at 8 MPM, the plasma excitation might be too small to be observed at this x-ray flux, or it might take too long to see plasma-like features. With a strong elastic background, the plasmon peak tends to be wide. At large \( r_s \) values, the Coulomb potential energy dominates, therefore, the electrons start to be localized. As a matter of fact, in the limit \( r_s \gg 1 \), it also can form a crystal - the Wigner crystal [48], in which electrons, rather than ions, are the constituents of the lattice. It is believed that when \( r_s \geq 100 \) [49] in three dimensions and \( r_s \geq 35 \) [50] in two dimensions, the Wigner crystal can be formed.
CHAPTER V

EXPERIMENT AND DATA ANALYSIS FOR METALLIC GLASSES

5.1 Preparation of Samples

There are two kinds of samples in this experiment. One is lithium ammonia (20 MPM), the other ones are sodium ammonia (3 MPM, 6 MPM, 9 MPM and 12 MPM).

Figure 33 shows what the sample cells look like. The left one is for sodium ammonia and the right one, lithium ammonia. X-rays will go into the smaller window (x-ray size is 2 by 3 mm) and come out from the bigger window. The bigger windows are for bigger scattering angle. The maximum scattering angle for the sodium ammonia sample cell is 63.4°, and for lithium ammonia, 68.2° (See appendix B for dimensional details). Lithium ammonia samples were prepared in the same way as documented in chapter 4. Sample of lithium ammonia were made by combining 99.9% pure lithium
Figure 33. Sample cells (a) sodium ammonia (left); (b) lithium ammonia (right).
with 99.999% pure ammonia. After the correct amount (see Appendix A for calculations) of lithium was put into the sample cell in the glove box (see Appendix A for details of glove box operations), it was connected to the ammonia condensation system (Figure 13) to make the lithium ammonia samples. After they were done, sample cells were sealed by using the same technique shown in Figure ref16. And they were stored in liquid nitrogen before they were put in the beam line at Sector 12 in APS.

Sodium ammonia samples preparation is a little bit different from lithium ammonia samples. It was made by combining 99.9% pure sodium with 99.999% pure ammonia. We use a glass tube to make the sample. It is shown in Figure 34.

The sodium were delivered in to the glass tube in glove box. The opera-
Figure 35. The end of glassware is broken.

tion in the glove box is the same as the lithium ammonia samples. Then we connect this part (Figure 34) with the ammonia condensation system (Figure 13), and we follow the same steps as chapter 4 to make sodium ammonia sample. Afterward, the bottom end of the glass tube was broken and the sodium ammonia fell down to liquid nitrogen, as shown in Figure 35.

Figure 36 shows what it looks like in liquid nitrogen. Since the action was quick and the liquid nitrogen was close to the glass tube, the vapor of nitrogen was around the glass tube. There was very little possibility for the sodium ammonia to react with $O_2$ or $H_2O$ in the air. The samples were kept
in liquid nitrogen until we put them in the sample cell on the beam line. The temperature of liquid nitrogen is 77.36 K and ammonia was condensed with sodium at -50°C. Since the sample size is not big (0.2 inch diameter, therefore, the volume is $6.54 \times 10^{-8} \text{m}^3$) and the temperature difference was so large (300K-77.36 K = 222.64 K), and the whole process takes about 2-5 seconds. The density is 0.60-0.6565 $g/cc$ for the samples. According to Thompson [17], the heat capacity of Na-NH$_3$ solution is a linearly increasing function of temperature. So we can use the average heat capacity 14 $cal/(K\text{mol})$ to figure out the quench speed, which is about 2.1 $J/\text{second}$. Since the surface and the size of the samples may vary therefore the quench speed may vary accordingly.
From the law of heat conduction (also known as Fourier's law) [51],

\[
\frac{\Delta Q}{\Delta t} = -kA \frac{\Delta T}{\Delta x}
\]  

(5.1)

where \( k = LT\sigma \) according to Wiedemann-Franz law [43], where \( L \) is Lorenz number which is \( 2.44 \times 10^{-8} \, W \Omega K^{-2} \), \( T \) is the temperature, \( \sigma \) is electrical conductivity. For \( \sigma_{Li(NH_3)_4} = 8 \times 10^3 \, \Omega^{-1} cm^{-1} \), and \( C_{Li(NH_3)_4} = 11 \, cal/K \) at 77 K, the heat transfer rate of lithium ammonia is 2.64 \( J/s \). It is comparable with the experimental estimate.

To compare with the quenched sample, we also made one 3 MPM sodium ammonia sample which was frozen slower. The nitrogen vapor creates a temperature gradient and the sample which was in the glass tube was put into the liquid nitrogen slowly (about one minute).

5.2 Experiment

5.2.1 Experiment Set-ups

This experiment was carried at Sector 12 BM, at APS, in Argonne National Lab. The energy of x-rays was 18 KeV. There are two set-ups for this
Figure 37. MAR CCD set-up at 12 BM, APS.

experiment. One is similar to Figure 16 with a NaI detector (elastic x-ray scattering set up). The other one is the same set up with a MAR CCD camera (Figure 37). Instead of using a one inch by one inch NaI detector with a 0.01 inches slit in front of it, we switched to a big screen Mar CCD which diameter is 165 mm for sodium ammonia mixture to save time.

5.2.2 The Elastic X-ray Scattering Data

Figure 38 is the background for the lithium ammonia mixture. Figure 39 and Figure 40 are the data for lithium ammonia at different temperatures. Figure 41-Figure 49 are the CCD pictures for lithium ammonia, sodium ammonia, background and CeO$_2$. We use CeO$_2$ data (exposure time is 140
seconds) to calibrate our measurements. CeO$_2$ [52] is cubic and the space group is $Fm\bar{3}m$, $a=5.4112(1)$ Å. The x-ray diffraction angle information in Figure 55 is from the International Center for Diffraction Data.

In Figure 39, and Figure 40, we can see there are some amorphous features along with many crystalline peaks. The data are plotted with a semi-log scale. The features in the squares are from background. In the CCD pictures, the direct beam was masked to protect the CCD camera and the position is labeled in Figure 41. The spikes in Figure 46 and Figure 49 are due to the Be windows. Since the scatter guards were taken out for these two measurements, the Be windows were not blocked, and therefore show on the CCD pictures.

5.3 Data Analysis

5.3.1 Structure of Lithium Ammonia

Figure 39 and Figure 40 are the elastic x-ray scattering data for lithium ammonia phase I (between 82 K and 89 K) and phase II (25 K - 82 K), respectively. By using software - the General Structure Analysis System (GSAS), we determined that the structure of phase II is body centered cubic
Figure 38. Li-NH$_3$ background.

Figure 39. Li-NH$_3$ phase I.
Figure 40. Li-NH$_3$ phase II.

(bcc) structure (see Figure 5) and space group, $I\bar{4}3d$.

GSAS is set of programs for the processing and analysis of both single crystal and powder diffraction data obtained with x-rays or neutrons [53]. The Rietveld method is the major method that GSAS use for powder diffraction data [54]. The Rietveld method which is named after Hugo Rietveld is a technique to determine the structure of crystalline materials. The x-ray and neutron diffraction of powder samples results in certain pattern characterized by peaks with different intensity, different shape, at different position etc. The Rietveld method uses a least squares approach to refine a theoretical line profile until it matches the measured profile, therefore, to figure out the
Figure 41. Li-NH$_3$ background CCD picture.

Figure 42. Li-NH$_3$ CCD picture at 60K.

Figure 43. Na-NH$_3$ background CCD picture.

Figure 44. Na-NH$_3$ 3 MPM CCD picture at 10 K.
Figure 45. Na-NH$_3$ 6 MPM CCD picture at 10 K.

Figure 46. Na-NH$_3$ 9 MPM CCD picture at 10 K.

Figure 47. Na-NH$_3$ 12 MPM CCD picture at 10 K.

Figure 48. Na-NH$_3$ 15 MPM CCD picture at 10 K.
structure of the crystal. Figure 50 shows lithium ammonia phase II data (x cross), Calculation, background and the difference between the calculation and the observation data.
Figure 50. Phase II of lithium ammonia (GSAS).
The bond lengths and the angles between the bonds (shown in Table 3) agree with other people's approach [55] whose data are shown in chapter 3. And the space group is \( \overline{I}43d \) with \( a = 14.81\pm0.005\text{Å} \). Figure 39 shows the data for phase I. Phase I of lithium ammonia is an antiferromagnetic metal [27]. We tried to determine the structure by using elastic x-ray scattering data (Figure 39), but failed. From Figure 39, we can see, there are not many peaks compared with Figure 40 (phase II). The structure of this phase must be in some special form, so that not many peaks are created. We are unable to determine it.

5.3.2 Metallic Glass

For the CCD data for lithium ammonia and sodium ammonia, we use software fit2D to analyze. The software can be found at [56].

Fit2D is a program for 1 and 2 dimensional data analysis, used on most of European Synchrotron Research Facility beam-lines and by many other crystallography groups around the world too. Fit2D is a very powerful software which can calibrate and correct the detector distortions along with many other data analysis functions.

For powder diffraction (2-D) which is what we use in this experiment,
Table 3. Coordinates for parameters for Li(NH$_3$)$_4$.

<table>
<thead>
<tr>
<th></th>
<th>X(Å)</th>
<th>Y(Å)</th>
<th>Z(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>N(1)</td>
<td>0</td>
<td>0</td>
<td>2.488</td>
</tr>
<tr>
<td>H(1)</td>
<td>0.34606</td>
<td>0</td>
<td>3.354</td>
</tr>
<tr>
<td>H(1)</td>
<td>-0.17303</td>
<td>-0.2997</td>
<td>3.354</td>
</tr>
<tr>
<td>H(1)</td>
<td>-0.17303</td>
<td>0.2997</td>
<td>3.354</td>
</tr>
<tr>
<td>N(2)</td>
<td>1.96272</td>
<td>0</td>
<td>-0.28983</td>
</tr>
<tr>
<td>H(11)</td>
<td>1.96272</td>
<td>0</td>
<td>-0.28983</td>
</tr>
<tr>
<td>H(12)</td>
<td>2.26477</td>
<td>0.52317</td>
<td>-0.67312</td>
</tr>
<tr>
<td>H(13)</td>
<td>2.26477</td>
<td>-0.52317</td>
<td>-0.67312</td>
</tr>
<tr>
<td>N(2)</td>
<td>-1.01228</td>
<td>-1.68153</td>
<td>-0.28983</td>
</tr>
<tr>
<td>H(21)</td>
<td>-1.28341</td>
<td>-2.22281</td>
<td>0.47674</td>
</tr>
<tr>
<td>H(22)</td>
<td>-1.58524</td>
<td>-1.69997</td>
<td>-0.67312</td>
</tr>
<tr>
<td>H(23)</td>
<td>-0.67959</td>
<td>-2.22284</td>
<td>-0.67312</td>
</tr>
<tr>
<td>N(2)</td>
<td>-1.01228</td>
<td>1.68153</td>
<td>-0.28983</td>
</tr>
<tr>
<td>H(31)</td>
<td>-1.28341</td>
<td>2.22281</td>
<td>0.47674</td>
</tr>
<tr>
<td>H(32)</td>
<td>-0.67959</td>
<td>2.22281</td>
<td>-0.67312</td>
</tr>
<tr>
<td>H(33)</td>
<td>-1.58524</td>
<td>1.69997</td>
<td>-0.67312</td>
</tr>
</tbody>
</table>
fit2d can convert the 2-D image data to the equivalent integrated 2-theta scan data with a zero-dimensional detector. From the CCD pictures in 5.2, we can see the rings have the same center which is masked to protect the CCD camera from the direct beam. By choosing more than three points on a ring, fit2d can decide the position of the center. The integration of the 2-D data is equivalent to drawing a line from the center straight up (Figure 51) and projecting all the data onto that line. The equivalent 2-theta scan data is in Figure 52. In the same way, we can get all the equivalent 2-theta scan data from all the CCD images shown in 5.2. Sodium ammonia data are shown in Figure 56. After we emptied the sample cells, the background of lithium ammonia and sodium ammonia were taken, and they are shown in Figure 53 and Figure 54.

By using the software called RAD [57], we can get reduced radial distribution function (RDF) and other structure information from elastic x-rays scattering data. RAD is an interactive computer program for radial distribution analysis of x-ray diffraction data from amorphous materials. It is free and it can be downloaded from [58].

RAD was written by V. Petkov in 1988. The program consists of a main part and four subroutines (SETUPD, DATRED, NORM, and CALCRD),
Figure 51. Li-NH$_3$ CCD picture at 60 K.

Figure 52. Li-NH$_3$ 2-theta data from CCD picture (Figure 51).

Figure 53. Background for lithium ammonia CCD data.

Figure 54. Background for sodium ammonia CCD data.
Figure 55. CeO$_2$ CCD data for calibration purpose.

Figure 56. Equivalent 2-theta scan data for sodium ammonia at different concentrations.
Figure 57. RDF for sodium ammonia at different concentrations.

where separate steps in processing the experimental intensities are performed. SETUPD creates the x-ray diffraction data file which includes scattering angles and a parameter data file, supplied by users. DATRED, Basically, it will subtract the x-ray diffractions data from their background and make some other corrections. NORM will use the corrected data from DATRED, and the parameter data file as input. Then the corrected X-ray diffraction data are scaled into electron units by high-angle method [59]. CALCRD calculates some feature functions, such as radial distribution function \( G(r) \), reduced \( G(r) \), etc. And the RDF \( G(r) \) which is calculated by RAD for lithium ammonia data (Figure 40) is consistent with neutron data [36,37].
Figure 57 shows the RDF for sodium ammonia at different concentrations. At higher r value, which means when the position is far from the center, the RDF tends to be 1 since the atomic density tends to be the average atomic density. According to our knowledge about the structure of sodium ammonia, the first peak in Figure 57 might be the distance between sodium and nitrogen atoms. And the second peak might be nitrogen-nitrogen distance. RDF can give out the length of the bond between atoms and also the angle between the bonds which is described as [60]

\[
\theta = 2\sin^{-1}\left(\frac{r_2}{2r_1}\right)
\]  

(5.2)

Wasse et. al. [36] measured the structure of liquid saturated solutions of sodium ammonia at 200 K and found that the nearest distance between Na and N is about 2.45(2)Å and the nearest distance between two nitrogen atoms is between 3Å and 4.5Å. Our data on the quenched solid show that the Na-N length is slightly larger (2.55Å) and N-N length is about 4.5Å. And the angle between these two bonds is 60.1 ± 0.21° (according to equation (5.2)).

Different models are introduced by many people [61–64], micro-crystallite model is the only one can explain lithium ammonia. This model says that
the disordered phase can be represented by an assembly of microcrystals of \( \text{Li(NH}_3\text{)}_4 \). The differences resulting from an absence of long-range periodicity may be the result of the small size of the well-defined crystals. In Figure 39 and Figure 40, the lithium ammonia data, we can see the crystal peaks with amorphous features. In Figure 39, two points (which have two arrows above) are separated by 2.5 Å (two theta = 12.5°). According to [65], the crystal size is

\[
L = \frac{0.94\lambda}{B(2\theta) \cos(\theta)} \tag{5.3}
\]

where \( 2\theta \) is the scattering angle, \( B \) is the width of the peak (in radian) which is 0.044, and \( \lambda \) is the wavelength of x-rays, for 18 KeV x-ray, the wavelength is 0.69 Å. So the dimension \( L = Na \) is 15.1 Å.

The sodium ammonia phase diagram (Figure 4) shows that the sodium ammonia will separate to two different phases (solid sodium and solid ammonia) at a temperature lower than 160 K. But when the sample was quenched fast enough in the liquid nitrogen, the sodium ammonia mixture will freeze as it was at the temperature higher than 160 K before it can reorient to separate phases. However, micro-crystallite model may not be good to explain sodium ammonia according to our data.

We also take data at different temperatures for sodium ammonia mix-
tures, but they look similar, except the peaks position moves a little bit due to thermal expansion. Based on the standard CCD scan (CeO$_2$ in Figure 55), we can calibrate the peak positions in Figure 56 and other temperature data which are not shown here.

By comparing Figure 52 and Figure 40, we realize that a lot of small peaks are too weak to see in the CCD camera pictures. The resolution in CCD camera is 0.05° according the specifications data from MAR USA Inc. and the experimental setup (Figure 37). But the peak size (half width at half maximum) in Figure 40 is about 0.03°. So we are not so sure if the sodium ammonia is all amorphous phase or amorphous phase mixed with some sodium and ammonia microcrystalline in it.

Figure 58 shows the difference between the quenched sample, slowly (about one minute) frozen sample and pure ammonia. The peak (around 20 nm$^{-1}$) might be due to the solid ammonia, when sodium is added, the peak (around 21 nm$^{-1}$) in pure ammonia shift left a little bit, so do the peaks in the first circle (17 nm$^{-1}$). And the bump at somewhere smaller than 10 nm-1 is corresponding to sodium. Figure 59 shows the difference in RDF ($G(r)$) between pure ammonia, 3 MPM sodium ammonia (slowly frozen sample) and 3 MPM quench sodium ammonia. The first peak (Na-N) dis-
appears in pure ammonia data. However, the slowly frozen 3 MPM sodium ammonia sample has a first peak slightly smaller than the quenched sample which shows the quench process does work in some way. The second peak (N-N) shift left in pure ammonia data. Since we just threw the samples into the liquid nitrogen to quench them, the temperature difference is same, but the sizes of samples vary a little, therefore, the quench speed will be different and it is hard to compare the results at different samples quantitatively. If we can control the quench speed, we can tell how the quench speeds affect the results. Therefore, higher resolution and samples with different quench speeds will help our understanding of these samples.
Figure 58. Comparison between different quench speeds for 3 MPM sample and pure ammonia.

Figure 59. RDF of pure ammonia, slow frozen 3 MPM sodium ammonia and quench 3 MPM sodium ammonia.
CHAPTER VI

SUMMARY

In the first part of present work, the medium resolution inelastic x-ray scattering (MERIX) spectrometer at 30 ID (Advanced Photon Source) is used to measure the plasmon features in 10 (MPM), 11 MPM, 16 MPM lithium ammonia liquid systems. The 20 MPM lithium ammonia system was measured at 9 ID, APS. In the second part of this work, the structure of quenched sodium ammonia systems were measured at 12 ID, APS for different concentrations and different temperatures.

In the first part of this work, well-defined plasmon features were found from high concentrations (20 MPM) to low concentrations (until 10 MPM). For 8 MPM sample, the plasmon peak is too wide to be recognized. By comparing with random phase approximation (RPA) in the jellium model, strong deviations in energy from RPA were found, the lower concentration, the greater deviations.
For the linewidth of the plasmon peak, they are supposed to be proportional to the square of momentum transfer ($q^2$). However, our results show that the power of dependence of momentum transfer is smaller than 2. At zero momentum transfer, the linewidth of plasmon peak is getting wider and wider when the concentrations are getting lower and lower which may be due to interband transitions.

The second part of this work focuses on the structure of lithium ammonia and quenched sodium ammonia systems. Structure of Phase II of lithium ammonia is figured out and it agrees with earlier work. However, the structure of Phase I was not determined, since the structure might be in a special shape so that very few peaks were created, therefore there was not enough information to narrow down the structure. By quenching the sodium ammonia liquid, the atoms or molecules are “frozen” in position before they can re-orient to a lower energy position. Therefore, it forms a metallic glass material. And the quenching process is very critical. We got some qualitative results about the structure of quenched sodium ammonia mixture.
APPENDIX A
PREPARATION OF SAMPLES

Calculations for the mass of the lithium and ammonia for certain (P) mole % metal (MPM): Assume that \( \mu_{metal} \) and \( \mu_{NH_3} \) are atomic weight of metal and NH\(_3\), respectively. P is the concentration of the liquid. \( \rho_{NH_3} \) is the density of the liquid at 200 K, \( V_{samplecell} \) is the volume of the sample cell. And for certain volume \( V_{samplecell} \), the total mass is \( \rho_{NH_3} V_{samplecell} \) which contain \( x \) (mol) metal and \( y \) (mol) NH\(_3\). And \( \frac{x}{x+y} = P \), therefore,

\[
y = \frac{x(1-P)}{P} \quad (A.1)
\]

\[
x\mu_{metal} + y\mu_{NH_3} = \rho_{NH_3} V_{samplecell} \quad (A.2)
\]
Plug (A.1) into (A.2), we get:

\[ m_{metal}(g) = \frac{\mu_{metal}P \cdot p_{MNH_3}V_{samplecell}}{\mu_{NH_3}(1 - P) + \mu_{metal}P} \]  \hspace{1cm} (A.3)

Similarly, we can get the NH₃:

\[ n_{NH_3}(mol) = y = \frac{(1 - P) \cdot p_{MNH_3}V_{samplecell}}{\mu_{NH_3}(1 - P) + \mu_{metal}P} \]  \hspace{1cm} (A.4)

where \( n_{NH_3} \) is the amount of substance of ammonia.

Therefore, the pressure of NH₃ we need is:

\[ p_{NH_3} = \frac{n_{NH_3}RT}{V} \]  \hspace{1cm} (A.5)

where \( p_{NH_3} \) is the pressure we need for ammonia, \( V \) is the volume of the ammonia condensation system, \( T \) is room temperature, and \( R \) is universal gas constant 8.314510 \( J/(mol \cdot K) \).

The procedure of preparing lithium:

1. Immerse the lithium in XYLENE to remove the oil layer, since the lithium is kept in mineral oil

2. Then take lithium out and put it in methanol. Methanol will react
with the black surface of the lithium, it takes about half minute to one minute

3. Then put lithium in acetone

4. Place the lithium back into XYLENE for a few seconds

5. Put lithium in Glove box

Cut lithium by stainless steel knife and weight it in the glove box, then put certain mount of lithium (calculated by equation (A.1)) in the sample cell, seal it (Figure 15, take it out and connect it to ammonia condensation system (Figure 13. The process of putting the sample cells in the glove box and taking out is described in Figure A.1-A.7.

Figure A.1. Schematic explanation of how to put sample cell in/out MBRAUN Glove Box, Step 1.
Figure A.2. Schematic explanation of how to put sample cell in/out MBRAUN Glove Box, Step 2.

Figure A.3. Schematic explanation of how to put sample cell in/out MBRAUN Glove Box, Step 4.

Repeat evacuating / refilling for several times (3-4 times)

Figure A.4. Schematic explanation of how to put sample cell in/out MBRAUN Glove Box, Step 5.
Figure A.5. Schematic explanation of how to put sample cell in/out MBRAUN Glove Box, Step 6.

Figure A.6. Schematic explanation of how to put sample cell in/out MBRAUN Glove Box, Step 7.

Figure A.7. Schematic explanation of how to put sample cell in/out MBRAUN Glove Box, Step 8.
APPENDIX B

SAMPLE DESIGN DRAWING

Figure B.1 shows the sample cells for the structure experiment (chapter 5) of sodium ammonia and Figure B.2, lithium ammonia with all dimensional details. The sapphire windows are transparent, therefore, it is easy to check the samples by just looking through the windows. The thickness of sapphire windows is 0.005 inches which is 127 microns. The attenuation length of sapphire windows is 914 microns for 18 KeV x-rays (Figure C.6), which makes it suitable for the sample cell windows.
Figure B.1. Sample cell with dimensional details for sodium ammonia structure experiment.
Sample Cell
Material: Ni (316 SS for toper insert)
Quantity: 3

4-40 holes (don't break through)

Taper:
Small diameter: 0.100"  
Large diameter: 0.120"

Also need three:
1/4" SwageLoc caps with topped 1/4-20 hole through center
3/4" length Ni 1/4-20 bull, no head

Figure B.2. Sample cell for lithium ammonia structure experiment with dimensional details.
Figure B.3 shows the cold finger and the vacuum can with Kapton windows. Since the original vacuum can leaves very little room for sample cell, a new vacuum can with Kapton windows was designed (right picture in Figure B.3. This vacuum can was used at Sector 30 as well as Sector 9 (for 20 MPM lithium ammonia sample).
Figure B.4. Sample cell dimensions for lithium ammonia plasmon experiment.
Figure B.4 shows the design for the lithium ammonia sample cells for the plasmon experiment. The windows are made of Beryllium (Be). The thickness of Be windows is 0.005 inches, which is 127 microns. But the attenuation length for 9 KeV x-rays is 7312 microns (Figure C.5).
APPENDIX C

ATTENUATION LENGTH OF DIFFERENT MATERIALS IN THIS EXPERIMENT

From Figure C.1 to Figure C.6, we list the attenuation lengths for the windows and some samples we measured in the experiments. Calculations were prepared using Ref. [66].

Figure C.1. Li-NH$_3$ attenuation length at 10 MPM: 4300 microns for 9 KeV x-rays.

Figure C.2. Li-NH$_3$ attenuation length at 5 MPM: 3800 microns for 9 KeV x-rays.
Figure C.3. Na-NH$_3$ attenuation length at 5.2 MPM: 21000 microns for 18 KeV x-rays.

Figure C.4. Na-NH$_3$ attenuation length at 10.7 MPM: 20000 microns for 18 KeV x-rays.

Figure C.5. Be windows attenuation length is 7000 microns for 9 KeV x-rays.

Figure C.6. Sapphire windows attenuation length is 900 microns for 18 KeV x-rays.
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