Electronic Interactions in the Expanded Metal Compound Li-NH_3

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Inelastic x-ray scattering was used to measure the plasmon as a function of electron density in liquid lithium ammonia as well as the low temperature solid phase. As the electronic density is lowered, electronic correlation effects cause the random-phase approximation (RPA) to break down, requiring more advanced theoretical treatments. The deviation from RPA becomes greatest at the lowest electronic densities. We also see evidence for decreased electronic screening as shown by an increase in the strength of the pseudopotential at lower concentrations. Plasmon behavior in the solid is similar to that of the heavier alkali metals, but surprisingly different than in the liquid.

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It has been known for almost 200 years that certain elemental metals dissolve in liquid ammonia, creating a solution of positively charged ions and unbound electrons. At low metal concentrations, these systems are liquid electrolytes, but, as the concentration is increased, they undergo a metal insulator transition (MIT) and become liquid metals up to their saturation point. These materials are interesting because electron interactions play a large role in their properties. The electron density is usually described by the parameter $r_s = (\frac{4}{3}\pi n)^{-1/3}/a_0^*$, where n is the free electron concentration, and a_0^* is the effective Bohr radius. r_s is proportional to both the distance between electrons and the ratio of the Coulomb to the kinetic energies of the electrons. The metal ammonia systems, often called expanded metal compounds, have larger values of r_s than the elemental metals, and this value can be easily altered by varying the amount of dissolved metal. These solutions have been widely studied for over a century by a variety of techniques [1].

For the lithium ammonia system studied here, concentration of up to ~20 mole % metal (MPM) are possible, which corresponds in the simple electron gas picture to a value of $r_s \sim 7.4$. The MIT transition occurs for concentrations somewhere between 2–6 MPM. A true solid compound forms at temperatures below 89 K with $Li(NH_3)_4$ complexes as the basic unit. The solid undergoes a structural phase transition at 82 K, and orders antiferromagnetically below 25 K.

Recent works have shown novel interesting features in these systems. Neutron scattering studies by Wasse *et al.* [2] show evidence for additional long-range ordering at distances comparable to the ion-ion distances. Inelastic x-ray scattering studies [3] of the phonons in a 20 MPM solution have revealed the presence of a strong phonon softening at a wave vector close to twice the Fermi vector, indicating that the system may be near an instability caused by the interplay between electronic and ionic ordering.

On higher energy scales, these systems provide an excellent testing ground for theories of the electron gas in the jellium model. The jellium model assumes the presence of a uniformly smeared out positive background, and therefore ignores the effect of the ions and the band structure. It is generally treated using the RPA, in which the actual interactions between the electrons are taken to be the same as the average interaction. This model becomes exact as the momentum transfer q and r_s go to zero.

The RPA calculation for jellium at $T = 0$ predicts a plasmon energy at zero momentum transfer of

$$E_0 = \hbar\omega_p = \hbar\left(\frac{4\pi ne^2}{\varepsilon m}\right)^{1/2}, \tag{1}$$

where ω_p is the plasma frequency, m is the electron mass, e is the electron charge, ε is the relative dielectric constant, and $\hbar$ is Planck's constant. The dispersion relationship for q less than the cutoff momentum $q_c \approx \omega_p/v_F$ is

$$E(q) = E_0 + \frac{\hbar^2}{m}\alpha q^2, \tag{2}$$

where $\alpha = (3E_F)/(5\hbar\omega_p)$, v_F is the Fermi velocity, and E_F is the Fermi energy. Above q_c, the plasmon can decay into electron hole pairs, and so becomes strongly damped and is no longer a well-defined excitation. If the medium has a relative dielectric constant ε that is different from unity, then E_0 is reduced by $\varepsilon^{1/2}$, and the effective value of r_s is decreased by ε.

Historically, tests of the jellium model have involved studies of the alkali metals, since it was thought that these systems provided a close approximation to the ideal electron gas. A detailed examination of the dynamical response of the alkali metals Na, K, Rb, and Cs was carried out using electron energy loss spectroscopy (EELS) by vom Felde and co-workers [4]. They found that, for the lighter alkali metals (low values of r_s), the data agreed well with models beyond the RPA, but the dispersion for the heavier alkali metals showed much larger deviations than predicted.

It is believed that the dispersion seen in the heavier alkali metal is related, at least in part, to band structure effects [5]. However, the fact remains that the RPA is inadequate at low electronic densities, and significant deviations due to electronic correlations are predicted. While the details vary depending on the theory, models beyond RPA are universal in predicting a reduced plasmon dispersion. The lithium ammonia system is an ideal testing ground for these theories, since the electronic concentration can be altered without completely changing the properties of the system.

In the original study of the plasmons in this system, inelastic x-ray scattering was used to measure [6] the properties in a 20 MPM lithium ammonia solution. These measurements found deviations from RPA predictions, but less than expected by many theoretical models. More recently, additional measurements of the plasmon at different lithium concentration were carried out by Hayashi *et al.* [7].

The purpose of the work described here is twofold. First, we wish to follow deviations from the RPA jellium model at low electronic densities by looking at solutions with lower lithium content. Using the increased flux available at a third generation synchrotron source, we are able to obtain much better accuracy than in previous work. Second, we wish to examine the importance of long-range order on the system by examining the plasmons in the solid phase.

In this Letter, we report a decrease in the plasmon dispersion coefficient at lower concentrations indicating a greater deviation from RPA and the growing importance of electronic correlation. The effect of long-range order is much more severe; freezing the liquid results in a substantially reduced plasmon dispersion, in strong contrast to RPA which predicts a small increase in the dispersion. This is the first system to show a significant difference between the plasmons in the liquid and solid phases.

Inelastic x-ray scattering measurements were carried out for Li-NH_3 liquid solutions on beam line ID-16 at the European Synchrotron Radiation Facility (ESRF) in a near backscattering geometry. The energy resolution of the spectrometer was 170 meV and the q resolution was 0.5 nm^{-1}. The sample cell allowed progressive dilution of the sample by addition of ammonia; this eliminated the need to change sample cells and meant the setup was untouched for the different concentrations. A sample of the data from a 16.5 MPM liquid solution at 240 K is shown in Fig. 1 for small momentum transfers. Data have been normalized to the incident photon flux and adjusted to units of approximately counts per second. Representative error bars are shown on one data set.

For the solid, inelastic x-ray scattering measurements were carried out on beam line X21 at the National Synchrotron Light Source (NSLS). The setup and sample preparation are essentially the same as described in [6], except that a closed cycle refrigerator was used to achieve the low temperatures needed to form the solid. Here, the energy resolution was 250 meV and the q resolution was about 0.9 nm^{-1}. Crystals were grown by slowly cooling the liquid through the phase transition. Measurements of the structure factor $S(q)$ showed the samples were polycrystalline.

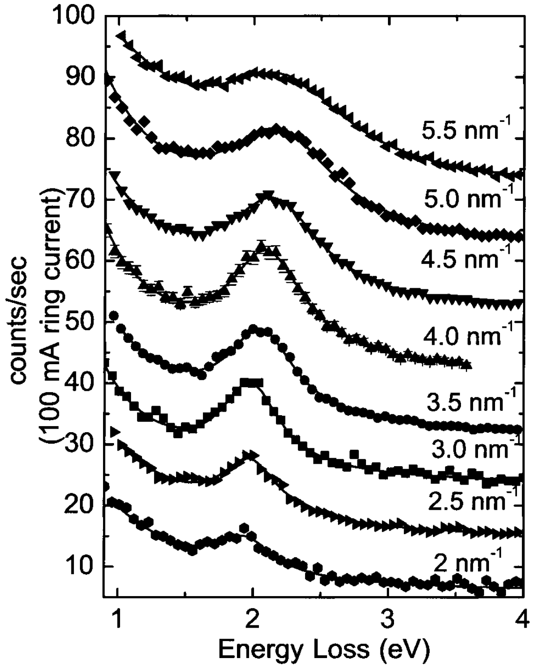

FIG. 1. Plasmon data in 16 MPM lithium ammonia solutions for low q. Solid lines are fit results.

The solid showed evidence of radiation damage. The intensity of the quasielastic peak of the structure factor scaled directly with the x-ray dose. Since the samples were metallic, the most likely cause for the damage is breakdown of some of the NH_3 molecules, and subsequent lattice strain. The damage to the crystal made it necessary to periodically (about once a day) melt and regrow the solid phase to reduce the background from the elastic peak. Inelastic measurements of the plasmon taken before and after the regrowth were indistinguishable. The data shown in Fig. 2 were taken at $T \sim 15$ K, on a sample that was regrown a total of 3 times during the measurements. As a result, different q values show different amounts of elastic background.

As is clearly visible in Figs. 1 and 2, the plasmon broadens and disperses out in energy as we move to larger momentum transfers. The data in the region of the plasmon was fit to a sum of two Lorentzian functions, one for the plasmon, and the other to represent the elastic background. The solid lines in the figures are the fit results. The plasmon energy and width (corrected for

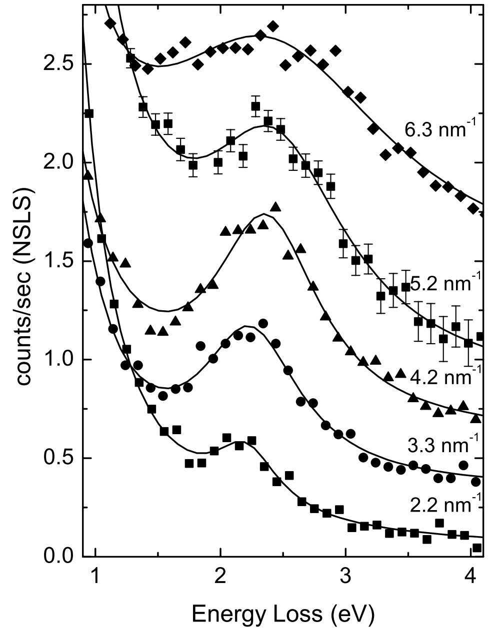

FIG. 2. Data and fits for the plasmon in the low temperature solid phase of Li(NH$_3$)$_4$.

instrumental broadening) are given in Figs. 3(a) and 3(b). The data shown at 20 MPM was discussed in [6].

First, we consider the liquid. The lines in Fig. 3(a) are fits to Eq. (2) for momentum transfers less than q_c, where $q_c = 6.3$, 6.1, 5.9, and 6.5 nm^{-1} for the 20 MPM, 16 MPM, 13 MPM, and solid phases, respectively. E_0 for the plasmon increases as we go to higher concentrations in the liquid and then into the solid phase. This behavior is as expected from Eq. (1) since the electronic density goes up as we add lithium and due to the contraction of the mixture as it freezes. Note that the magnitude of E_0 is reduced by up to 15% from the predicted value; this behavior was previously observed [6] and probably results from polarizability of the ammonia molecules which causes a dielectric constant ε greater than unity. The behavior of the dispersion coefficient is interesting. The decrease in the dispersion coefficient in the liquid as we go to lower concentration is much greater than predicted by RPA, for which the dispersion is only a weak function of the density; $\alpha \sim n^{1/6}$.

Figure 4 shows the liquid dispersion coefficients compared with RPA values and some theories that attempt to take correlations into effect. We have corrected the r_s values of the lithium ammonia system for the effect of a static dielectric constant as described above. The data show a clear decrease in the ratio of the dispersion coefficient to the RPA prediction, indicating the growing importance of correlation at lower electronic densities.

We plot a static local field model consistent with the compressibility sum rule (labeled VS) due to Vashishta and Singwi [8], and three models which are discussed in March and Tosi [9]. The theory labeled CSR is based on a calculation using the compressibility sum rule with Monte Carlo simulations of the ground state of the electron gas as the input. TMSR is a model based on the third spectral moment sum rule for the dynamic structure factor, while GK stands for a local density approximation

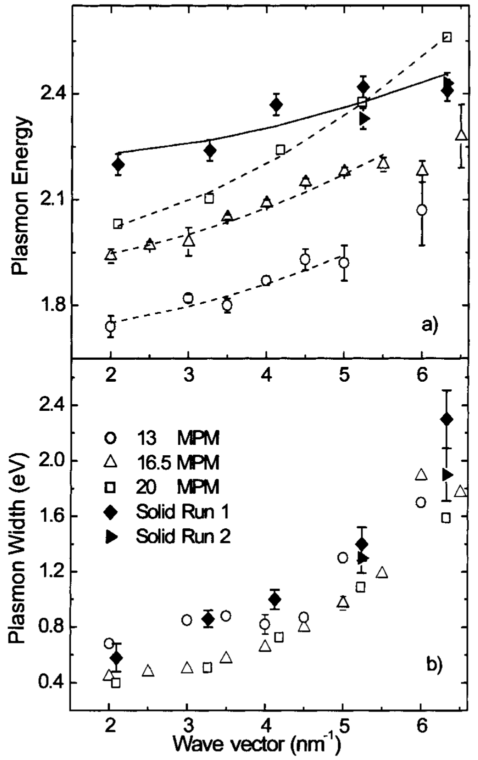

FIG. 3. (a) Plasmon energies plus fits to Eq. (2). Fit lines are drawn only out to the limit of the fitting range (to q_c). (b) Dispersion of plasmon widths.

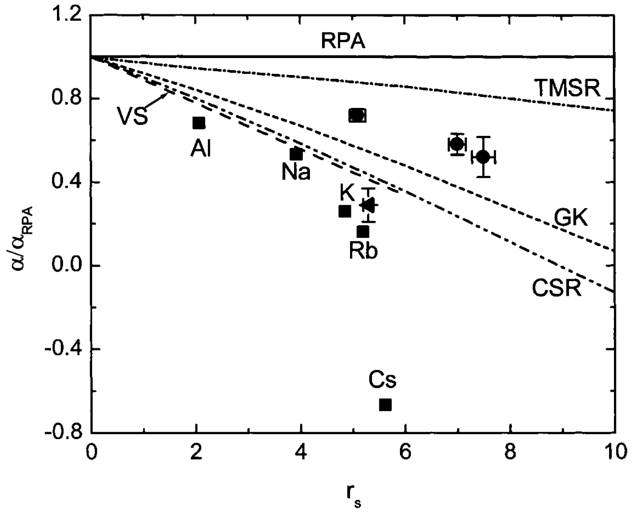

FIG. 4. Dispersion coefficients compared to RPA and other theories. Closed circles are liquid lithium ammonia, the triangle is the solid, and the squares are data for the alkali metals and Al from [4] and [15], respectively. Theoretical models are discussed in the text.

model based on work by Gross and Kohn. Our data show less effect of correlations than predicted by some of the theories, but the same overall trend.

RPA predicts that the plasmon width should be zero up until q_c. Models that take into account the formation of two electron hole pairs predict a value for the decay about an order of magnitude smaller than has been found [10]. Even at zero momentum transfer, the width is not zero due to excitations such as interband transitions that permit decay of the plasmon. In the nearly free electron model (NFE), the width of the plasmon at $q = 0$ is proportional to the square of the Fourier transform of the pseudopotential [11]. Strum and Oliveira [12] have used this to determine linewidths for Li, Na, and K using the NFE model and models for the band structure. In our data, we see that the widths are increasing as we go to lower concentration, implying that the pseudopotential is becoming larger. This is consistent with the fact that, as we approach the MIT, the screening of the electrons becomes less effective so the system becomes less free electronlike and so the pseudopotential becomes larger.

From Fig. 3, it is clear that the dispersion coefficient is substantially reduced in the solid. However, RPA predicts that the higher density of the solid should result in an increase in the plasmon dispersion coefficient. Other workers have looked at plasmon properties in the liquid and solid for lithium and sodium [13] as well as aluminum [14]. The plasmon width and dispersion are identical in these different systems (except for the slight change completely attributable to the difference in the densities), indicating that, if band structure plays a role, the local structure in the liquid mimics that of the solid. Our solid data lies much closer to the plasmon dispersion for elemental metals. An interesting question is whether the heavier alkali metals would also show a difference between the liquid and the solid states; that is, if the difference is a general feature at low electronic densities or specific to this system.

In the solid, there are several possible reasons for the larger bandwidths. The widths do not increase over time, so we do not believe they are related to radiation damage in the solid. Since we are looking at a polycrystalline sample, we are averaging over different crystalline orientations, and, if the plasmon has a different dispersion along different directions, this will give a larger apparent width. The larger width could also indicate a greater degree of coupling to lattice excitations than in the liquid. However, we lack sufficient information to draw any definitive conclusions.

In conclusion, we have carried out inelastic x-ray scattering measurements of the plasmon in the model system lithium ammonia as a function of electron concentration. We have also studied the plasmon in the low temperature solid phase. As we go to lower concentrations, we find evidence for the breakdown of the RPA and the growing influence of electronic correlation. The solid shows evidence of strong interaction of the plasmon with the band excitations.

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