

Evidence for an Instability Near Twice the Fermi Wave Vector in the Low Electronic Density Liquid Metal $\text{Li}(\text{NH}_3)_4$

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(Received 10 August 2000)

We report high-resolution inelastic x-ray scattering measurements in the metallic liquid $\text{Li}(\text{NH}_3)_4$, which to a good approximation can be treated as a dilute alkali metal. We see a well-defined excitation out to large momentum transfers. This excitation shows a strong softening at wave vectors near the first peak in the structure factor, which occurs near twice the Fermi momentum.

DOI: 10.1103/PhysRevLett.86.2357

PACS numbers: 63.50.+x, 61.25.Mv, 78.70.Ck

Solutions of alkali metals in ammonia have been investigated for over a century due to their many interesting properties. In these systems, the outermost electron of the alkali metal separates from the ion, resulting in a free electron and an alkali metal ion. At the solubility limit, about 20 mole % metal (MPM) for lithium $\text{Li}(\text{NH}_3)_4$, the system is a good liquid metal down to its freezing point, $T_F = 89$ K, but it has a low electronic density compared to most good metals.

Conventionally, the electron density is described by the dimensionless parameter,

$$r_s = \frac{(\frac{4}{3}\pi n)^{-1/3}}{a_0^*}. \quad (1)$$

Here, n is the free electron concentration, $a_0^* = \hbar^2 \epsilon / m^* e^2$ is the effective Bohr radius, ϵ is the static dielectric constant, m^* is the effective mass of the electron, and e is the electric charge. For jellium at $T = 0$, r_s is the “only” parameter, and it is approximately the ratio of the Coulomb to kinetic energies for the electrons. Systems with large values of r_s are of interest since the electronic interactions play a more important role in their properties. Most metallic elements have r_s between 2–6. For a saturated solution of $\text{Li}(\text{NH}_3)_4$, $r_s \cong 7.4$. By decreasing the amount of dissolved metal, r_s can be increased to any desired value, although for $r_s \sim 11$ (~ 5 MPM) the $\text{Li}(\text{NH}_3)_\beta$ system undergoes a metal-insulator transition (MIT) [1]. At 20 MPM, the lithium ion dissociates, leaving a free electron and a large, spherical complex, where each lithium ion is surrounded by four ammonia molecules.

The ease of changing the electron density, the importance of electronic correlations, and the strong coupling to the polar NH_3 molecules make $\text{Li}(\text{NH}_3)_4$ a very interesting strongly interacting many-body system. In addition, the extremely low atomic number of the constituents makes this an ideal system to study with inelastic x-ray scattering (IXS) techniques. We describe here high-resolution (~ 2 meV) IXS measurements at $T = 240$ K of the low energy excitations of $\text{Li}(\text{NH}_3)_4$. The system has a Fermi energy $E_F \cong 0.93$ eV and a Fermi momentum $k_F \cong 0.49 \text{ \AA}^{-1}$.

Samples were made using 99.9% pure lithium and high purity (99.99%) anhydrous ammonia. The sample cell had thin (0.013 cm), flat beryllium windows with a path length of 1.3 cm. Lithium was introduced into the cell in a helium atmosphere, and the ammonia was condensed in the cell at $T \sim 210$ K. The cell was sealed and placed in a vacuum can. The sample was kept at $T \sim 240$ K by a Peltier cooler. Measurements of the inelastic spectrum and structure factor taken at the beginning and at the end of the experiment were identical, indicating no alteration in the sample quality over time. The empty cell background signal was found to be small (less than 1%) at the momentum transfers discussed here.

These experiments took place at beam line 3ID at the Advanced Photon Source (a detailed description of the instrument is given in Ref. [2]). A diamond monochromator provided 21.65 keV x rays which were further monochromatized by a four bounce monochromator and focused onto a $150 \times 350 \mu\text{m}^2$ spot. Scattered x rays were reflected by a temperature controlled, spherically bent, diced Si (1860) analyzer crystal 6 m from the sample in a near backscattering geometry. The experimental energy resolution was determined using the elastic scattering from Plexiglas and found to be 2.4 meV.

In IXS scattering an x ray with a well-defined energy, wave vector, and polarization, $(\omega_i, k_i, \hat{e}_i)$ scatters into a new state described by $(\omega_f, k_f, \hat{e}_f)$. An energy $\omega = \omega_f - \omega_i$ and a momentum $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ is transferred by the x ray to the system. Figures 1 and 2 show the low energy ($|\omega| < 8$ meV) IXS spectra in $\text{Li}(\text{NH}_3)_4$ for different values of q . The data have been normalized for comparison. The dotted curve is the measured instrumental resolution.

The series of low momentum data in Fig. 1 ($0.2 \leq q \leq 1.0 \text{ \AA}^{-1}$) displays a dramatic effect. There is clearly a well-resolved collective mode at $q = 0.4, 0.5,$ and 0.6 \AA^{-1} . At $q = 0.2$ and 0.8 \AA^{-1} , the spectra are significantly wider than the resolution function, indicating that there is an unresolved low energy peak. At $q = 1.0 \text{ \AA}^{-1}$, which is very close to $2k_F$, the measured spectra are very close to the resolution function. Since the raw data are symmetric about 0.5 \AA^{-1} , we can, without any

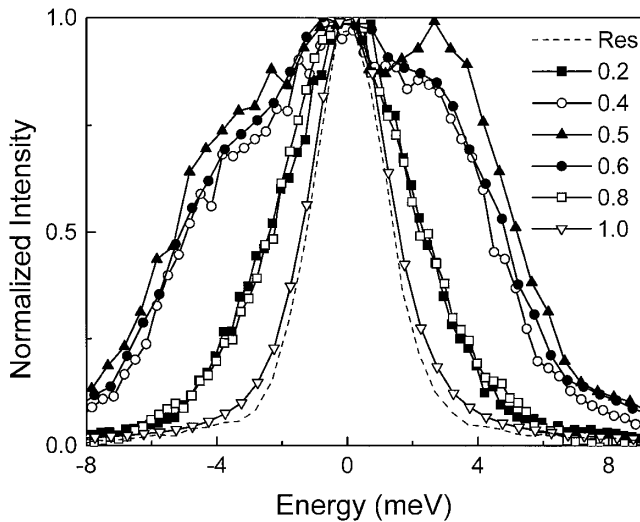


FIG. 1. Low energy excitations in $\text{Li}(\text{NH}_3)_4$ at low momentum transfers ($q = 0.2\text{--}1.0 \text{ \AA}^{-1}$). The phonon modes increase in energy, but then soften to near 0 as the wave vector approaches 1 \AA^{-1} .

deconvolution, safely say that the observed collective mode increases to a maximum near $q = 0.5 \text{ \AA}^{-1}$ and then collapses towards “zero” near $q = 2k_F \cong 1.0 \text{ \AA}^{-1}$.

The high momentum data, Fig. 2, show significant broadening (unresolved at $q = 1.2, 1.4 \text{ \AA}^{-1}$) which increases as q increases.

We fit the data using a damped harmonic oscillator (DHO) model convolved with our experimental resolution function. The fitting function F was defined as

$$F(q, \omega) = I_o(q) \frac{\Gamma_0(q)}{\Gamma_0(q)^2 + \omega^2} + [n(\omega) + 1] \times I(q) \frac{4\omega\Gamma(q)\Omega(q)}{[\Omega(q)^2 - \omega^2]^2 + 4\Gamma(q)^2\omega^2}. \quad (2)$$

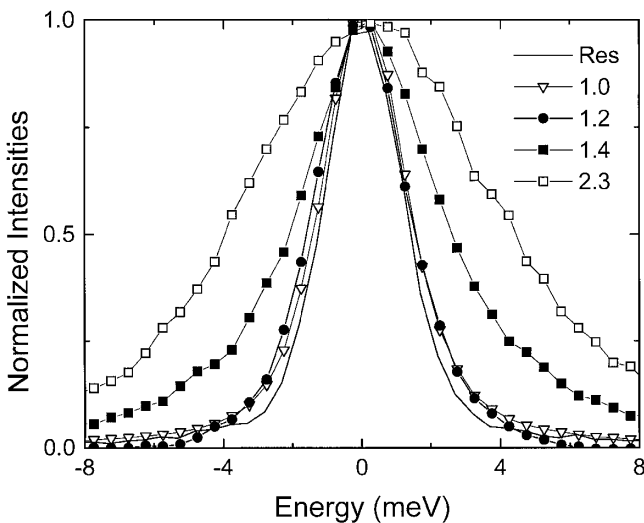


FIG. 2. Low energy excitations in $\text{Li}(\text{NH}_3)_4$ at higher momentum transfers of $q = 1.0\text{--}2.3 \text{ \AA}^{-1}$.

The second term gives the scattering from a pair of Lorentzian-like modes, I is the intensity of that peak, Γ its half-width, Ω is the energy of the peak, and $n(\omega)$ is the thermal factor. The subscript 0 corresponds to the same factors for the central peak; $T \gg \Gamma_0$ is assumed.

Figure 3 shows the results of the fit. At low q , the phonons disperse to higher energies, as is expected for a soundlike mode, and the intensity of the mode increases. The mode position and intensity have maxima near $q = 0.5 \text{ \AA}^{-1}$ and then are reduced dramatically as q goes to $2k_F$. At $2k_F$ and higher momentum transfers, it is unclear if the collective mode still exists or if the central peak has simply become very broad. The inset of Fig. 3 shows $\Gamma_0(q)$ (central peak width) which narrows near 1 \AA^{-1} ; our fit values for $\Gamma(q)$ yield half-widths substantially smaller than the instrumental resolution (1.2 meV), and so the exact values are probably not reliable.

If the observed phononlike mode has softened only due to its interaction with the electrons, the minimum in the dispersion curve is perhaps a hint that we may be close to an instability of the ground state. But if the mode truly goes to zero energy, then it would imply a new ground state. Our resolution is too low to know if we have a real static charge density wave.

Figure 4 shows the structure factor for $\text{Li}(\text{NH}_3)_4$ and pure ammonia measured with a $\sim 1 \text{ eV}$ incident beam (therefore integrating over the inelastic cross section). The data have been corrected for known factors such as the polarization and geometrical effects, which are fairly large (50%) at higher angles. The large very narrow first peak position is at $q \cong 1.0 \text{ \AA}^{-1}$, while the second peak is close to $q \cong 1.8 \text{ \AA}^{-1}$. The resolution of the data is about 0.1 \AA^{-1} because the bent crystal analyzer collects a

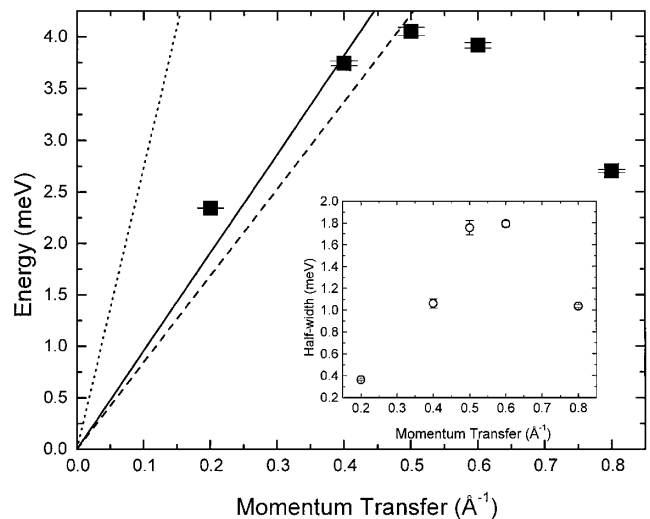


FIG. 3. Fits of the DHO model to the data peaks shown in Fig. 1. The central peak width is shown in the inset. Lines are for the ion-acoustic velocity for bare lithium ions (dotted), for a $\text{Li}(\text{NH}_3)_4$ complex vibrating as a unit (dashed), and for the measured acoustic sound velocity (solid).

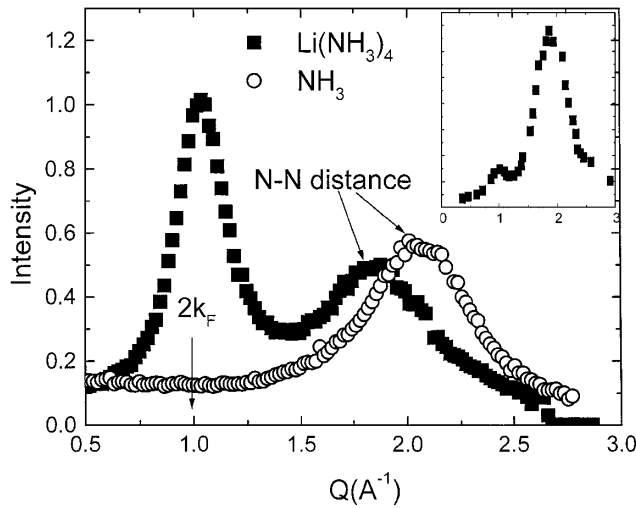


FIG. 4. The structure factor in pure NH_3 and $\text{Li}(\text{NH}_3)_4$. The inset shows neutron measurements on $\text{Li}(\text{NH}_3)_4$.

$d\Omega = 0.01$ sr on the output. The large first peak occurs within error at the same momentum transfer where our data in Figs. 1 and 2 showed an extremely soft collective mode.

Our results for peak positions and width are consistent with the small angle x-ray scattering data of Knapp *et al.* [3] in the region of overlap (they measured only to 1 \AA^{-1}). Neutron scattering measurements of the structure factor taken by Chieux and Bertagnoli [4], as well as more recent work by Wasse *et al.* [5], show both peaks in the same position as we observe, but the relative sizes are different (inset of Fig. 4, data taken from Ref. [4]).

Neutron scattering data [4] and our own work show that the peak in ammonia near 2 \AA^{-1} is due to the mean nitrogen spacing in the system, and as lithium is added to ammonia it continuously evolves to the peak at 1.8 \AA^{-1} in $\text{Li}(\text{NH}_3)_4$. The interesting feature is the first peak, which occurs close to $2k_F$, and is very strong compared to the nitrogen peak. This is counterintuitive, since there are 4 times as many nitrogen atoms as Li^+ , and each nitrogen has roughly 5 times as many electrons. On this basis, one would expect the x-ray scattering from the Li ions to be a few percent of the scattering from the NH_3 complexes. To explain the greater height of the first peak, we must assume some reasonable degree of long-range spatial ordering of the coupled lithium ion-free electron systems. This could occur because the collective modes of this complex have softened strongly near $2k_F$, or due to a real static charge density wave, with some finite coherence length. The peak width of 0.3 \AA^{-1} is larger than the instrumental resolution and is consistent with both possibilities.

Based on the average spacing a_s between Li ions in $\text{Li}(\text{NH}_3)_4$, we might expect a peak near $(2\pi/a_s)$, which occurs just above $2k_F$. Of course, any solid is more open than the mean sphere radius a_s , so that some Bragg peaks in the solid phase would be at significantly smaller q . A

preliminary experiment shows several Bragg peaks very near $q = 1 \text{ \AA}^{-1}$ for all three solid phases of $\text{Li}(\text{NH}_3)_4$; i.e., the natural length scale for the structure in the system is close to $2k_F$.

A number of neutron and x-ray scattering experiments have measured the excitations in the pure liquid alkali metals [6]. These systems show qualitatively similar behavior to what is observed here—the excitations disperse linearly at low momentum, reach a peak, and then show a minimum. For liquid Rb, there is a strong minimum just above T_F that becomes very small as the temperature increases to twice T_F (Ref. [7]). Our data are quite different in that we see a very strong minimum (zero within our resolution) at $T \sim 2.5T_F$. Preliminary data show no temperature dependence for the excitation properties.

Well-defined excitations have also been observed in other systems: liquid H_2 [8], liquid NH_3 [9], liquid Ni [10], liquid Al [11], and liquid Ge [12]. In the systems with well-defined excitations at large q , there is a dip at the same wave vector as the first peak in the structure factor. The surprising feature of the Li- NH_3 system is the depth of the dip even far from T_F .

As a first approximation of the Li- NH_3 system, we take the two component ion-electron jellium model of Bardeen and others [13], where the strongly interacting electrons are coupled only by the Coulomb interaction to mobile monovalent ions. (Of course, the interaction becomes more complex at small enough distances.) In this case, for the small energy losses discussed here, the IXS cross section [14] is

$$\frac{d^2\sigma}{d\Omega d\omega_f} \sim S(q, \omega) = \sum_f \sum_i |\langle f | \hat{\rho}_q | i \rangle|^2 \delta(\omega_f - \omega_i - \omega), \quad (3)$$

$$\hat{\rho}_q = \sum_{i,j} F_A(q) e^{i\mathbf{q}\mathbf{R}_i} + e^{i\mathbf{q}\mathbf{r}_j}. \quad (4)$$

Roughly speaking, $\hat{\rho}_q$ is the total electron density operator, and $F_A(q)$ is the atomic form factor of the Li ion-ammonia complex. $r_j(R_i)$ are the nuclear coordinates of the mobile electrons (Li^+). In this case, it can be shown that $S(q, \omega)$ has peaks where $\text{Re}[\varepsilon_T(q, \omega)] = 0$. Here, $\varepsilon_T(q, \omega)$ is the total dielectric function for the Coulomb coupled ion-electron system.

The zeros of ε_T (for $\omega \ll E_F$) are the low lying excitations of the jellium model, given by

$$\omega^2(\mathbf{q}) = \frac{\Omega_p^2}{\varepsilon_e(\mathbf{q}, \omega)}. \quad (5)$$

Here, Ω_p is the ion's plasma frequency, and ε_e is the dielectric function for the electron gas. In the low frequency long wavelength limit and for weak coupling ($r_s \rightarrow 0$), $\varepsilon_e(q, \omega) = k_{\text{FT}}^2/q^2$, $\omega \rightarrow 0$, $q \rightarrow 0$, where k_{FT} is the Thomas-Fermi screening length. Such static screening

leads to excitations with a linear dispersion. The velocity using Eq. (5) with Thomas-Fermi screening is plotted on Fig. 3. The higher dotted line is the velocity expected for bare Li ions, while the lower dashed line is for the vibration of a unit where each Li^+ is bound with four NH_3 , which is much closer to the measured results. At higher momentum transfer, weak coupling approximations such as the Lindhard dielectric function predict weak singularities in derivatives of the dielectric function at $2k_F$. Such nonanalytic behavior can result in so-called Kohn anomalies, i.e., softening in the phonon spectrum as well as a periodic variation, the so-called Friedel or Ruderman-Kittel oscillations, in the real space pair potential between Li ions. For spherical Fermi surface systems, there has been no reported experimental evidence of Kohn anomalies in the phonon spectrum. However, we should point out that a Lindhard or RPA treatment of $\epsilon_e(k, \omega)$ near $2k_F$ may be completely inadequate. In our case, it is clear that a dramatic reduction in the phonon frequency implies that, in this model, there must be, at least, a strong peak in the dielectric function near $2k_F$. How this relates to freezing, if it does, is related to how the ground state of the Li ions depends on temperature as well as Coulomb coupling, as reflected in Eq. (5).

There has been an enormous amount of work on the theory of the behavior of the strongly interacting electron system. Numerical simulations (see, for instance, Ceperley [15]) have shown that the jellium model the electron gas becomes ferromagnetic at $r_s \sim 20$ and forms a Wigner solid for $r_s \sim 100$. These electronic densities are too low to be relevant to our experiments.

In the early 1960s, Overhauser, using a Hartree-Fock description, argued [16] that the ground state of jellium at any r_s might include spin and charge density waves (CDW) at even multiples of $2k_F$. In the jellium model, the formation of a charge density wave is energetically unfavorable due to substantial Coulomb energy that would result. However, in the two component plasma, the ions can readjust their positions to reduce this increase of Coulomb energy. Overhauser also proposed that many of the anomalous properties of the alkali metals could be explained by the formation of a CDW. Although this conclusion remains quite controversial, some systems, such as the spin density wave state in chromium metal, are probably related to the Overhauser ground state. We believe that the structure in $\text{Li}(\text{NH}_3)_4$ may be driven by the tendency of the electrons to order at $2k_F$.

In conclusion, we have carried out high-resolution inelastic x-ray scattering measurements of the low energy excitations and the structure factor in pure liquid ammonia and in the liquid metal $\text{Li}(\text{NH}_3)_4$ system. In the metal, we find well-defined excitations that strongly soften, perhaps go to zero, in the vicinity of the first peak in the structure factor which occurs very close to $2k_F$. Future

literature [17] will discuss these excitations at higher momentum transfers, as a function of temperature, and as a function of lithium concentration to try to establish how this instability depends on r_s , how it relates to the MIT, and whether it is some type of precursor to the freezing of low density monovalent metals.

We thank E. Isaacs and A. Shukla for interesting discussions. This work was supported by the DOE, Division of Materials Science Grant No. DE-FG02-99ER45772 and by DOE, Basic Energy Sciences under Contract No. W-31-109-Eng-38.

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