

Collective Excitations in Lithium Ammonia as a Function of Electron Density

A. H. Said,^{1,2} C. Burns,² H. Sinn,¹ E.E. Alp¹

¹Advanced Photon Source, Argonne National Laboratory, Argonne, IL, U.S.A.

²Department of Physics, Western Michigan University, Kalamazoo, MI, U.S.A.

Introduction

Alkali metal dissolved in liquid ammonia results in a free electron and an alkali metal ion. A saturated lithium ammonia system has the lowest density ($\sim 0.477 \text{ gm cm}^{-3}$) of any known liquid at room temperature. Because this system has a low electron density when compared to that of typical metals, we expect the electron-electron interactions of the properties to play an important role. Usually the electron density is described by the dimensionless parameter r_s , which is 2 to 6 in typical metals and >7.4 in the Li-NH₃ system. We carried out high-resolution ($\sim 2 \text{ meV}$) inelastic x-ray scattering (IXS) measurements of a Li-NH₃ mixture at different concentrations (13, 16, and 20 mole percent metal [MPM]) at a temperature of 240K.

Methods and Materials

The experiments were carried out at beamline 3-ID-C at the APS. A synchrotron beam of 21.657 keV was monochromatized by a diamond monochromator, which was further monochromatized by two silicon channel-cuts and focused by a total-reflecting mirror to a spot size of 0.2 mm^2 at the sample. A temperature-controlled, spherically bent and diced Si (18 6 0) analyzer was used to reflect the scattered x-rays into a cadmium zinc telluride (CZT) detector 6 m away from the analyzer and offset 3 mm from the scattered beam. The total experimental energy resolution was 2 meV. The setup for the experiment is shown in Fig. 1.

Stainless-steel cells with two thin (0.014-in.), flat beryllium windows were used as a sample container. The 99.9%-pure lithium was cut in a helium-filled glove box, weighed, and placed into the sample cell. A measured volume of high-purity 99.99% anhydrous ammonia was condensed in the cell at a temperature of $\sim 200\text{K}$. The cell was sealed off and placed in a helium flow cryostat and kept at 240K.

Results

The dispersion of the phonon $\Omega(Q)$ and linewidth $\Gamma(Q)$ are shown in Fig. 2. At low Q , a linear dispersion in $\Omega(Q)$ was observed for the three concentrations, as is expected from the soundlike mode.

The speed of sound for these modes is shown in Fig. 3. The ion-acoustic velocity was obtained from fitting the linear low- Q region. It is close to the measured sound

velocity. The modes disperse to a maximum energy around Q_0 , which is half the position of the first maximum of the static structure factor. However, the first peak in $S(Q)$ shifted to a lower Q value when the lithium concentration was lowered, as shown in Fig. 4.

At around $Q = 2K_F$, a mode softening occurs that becomes stronger at 20 MPM solution. As the concentration goes down, the phonon goes to a higher energy around $Q = 10 \text{ nm}^{-1}$. We expect such a change in this behavior below 8 MPM, where the system is not a good metal any more. The fast change in the measured sound velocity below 8 MPM, as shown in Fig. 3, lets us predict a change in the dispersion at low Q as well. The

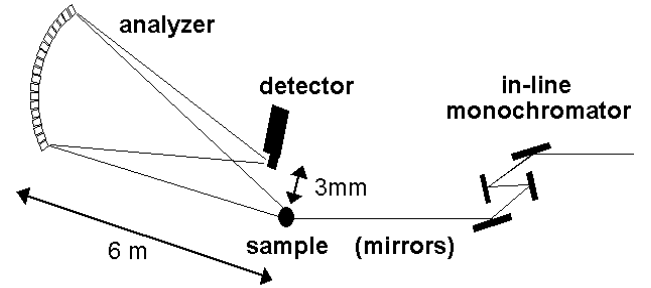


FIG. 1. The setup at beamline 3-ID-C.

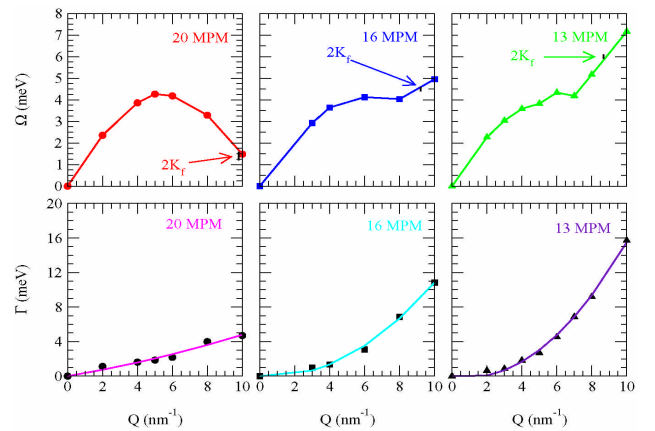


FIG. 2. The dispersion of the energy and width of the acoustic mode. We used the damped harmonic oscillator (DHO) model to fit our data.

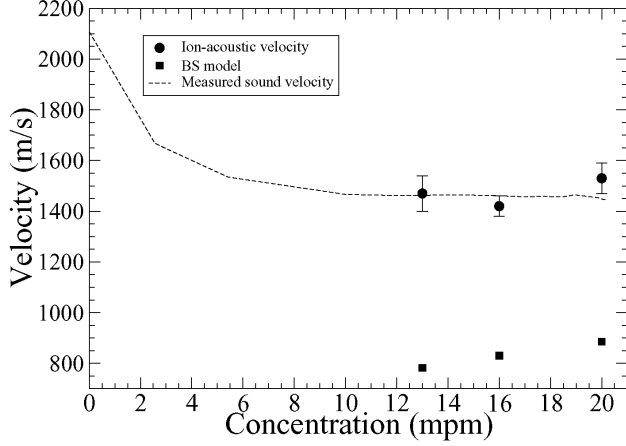


FIG. 3. Sound velocity.

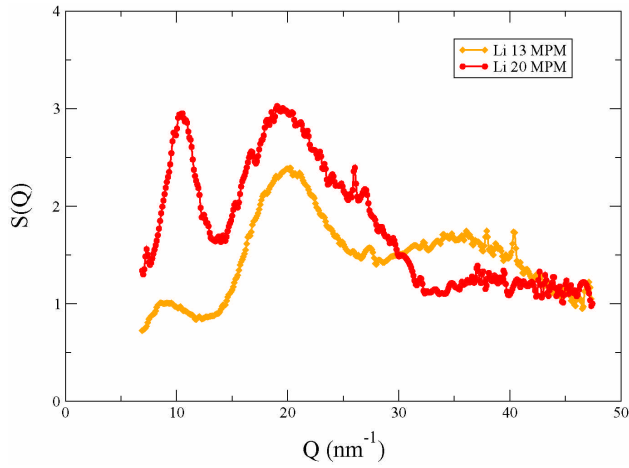


FIG. 4. The static structure factor $S(Q)$ for two concentrations.

damping of the acoustic modes becomes stronger as the concentration gets lower, as shown in Fig. 2.

Discussion

We consider the Bohm-Staver (BS) model [1], which looks at the metal as a gas of pointlike ions interacting through the Coulomb potential screened by the electron gas. As a result of the screening, the long-wavelength frequency of the longitudinal collective excitations Ω_p is reduced by $1/\epsilon(Q,0)$:

$$\omega^2(Q) = \Omega^2/\epsilon(Q,0),$$

where ω = the plasma frequency of the ion gas and $\epsilon(Q,0)$ = the electron dielectric constant. As $Q \rightarrow 0$ [2],

$$\lim_{Q \rightarrow 0} \epsilon(Q) = 1 + \frac{q_{TF}^2}{Q^2} \frac{K}{K_F},$$

where q_{TF} = the Thomas-Fermi screening length, K = the compressibility of the system, and K_F = the free electron compressibility. In the random-phase approximation (RPA), $K/K_F = 1$; therefore, the sound velocity is

$$v_s = \lim_{Q \rightarrow 0} \sqrt{\frac{\Omega_p^2}{\epsilon(Q,0)Q^2}} = \sqrt{\frac{mZ}{3M}} v_F,$$

where m = the electron mass, M = the ion mass, and v_F = the velocity of the electron at the Fermi surface. By applying this model to our system, as shown in Fig. 3, we found that the calculated values of the sound velocity do not agree with either the measured sound velocity or the ion-acoustic velocity.

In conclusion, we carried out IXS measurements of collective excitations in lithium ammonia as a function of electron concentration and found a deviation in the dispersion from pure alkali metals. The BS and RPA model are not valid in our system, which indicates that electron-electron interaction and band structure effects are important in understanding this system.

Acknowledgments

This work was supported by the U.S. Department of Energy (DOE), Division of Materials Science, Grant No. DE-FG02-99ER45772, and by sector 3-ID of the Synchrotron Radiation Instrumentation Collaborative Access Team (SRI-CAT). Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

References

- [1] N. H. March, *Liquid Metals, Concepts and Theory* (1990).
- [2] G. D. Mahan, *Many-Particle Physics* (1981).