# Coherent Inelastic Neutron Scattering in $NH_4Cl$†

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Some normal modes of vibration have been measured in undeuterated ammonium chloride by coherent inelastic neutron scattering utilizing a triple-axis neutron spectrometer. The behavior of the low-energy modes near the λ-type order-disorder phase transition at 242°K is correlated with the anomalous behavior of the elastic constants in this region. A splitting of the torsional mode has also been observed above the phase transition.

EXTENSIVE studies in the ammonium halides have been made by many workers[1–4] utilizing *incoherent* inelastic neutron scattering techniques, as well as total cross section measurements.[5] A particular goal has been to elucidate the nature of the various order-disorder transitions as a function of temperature. A knowledge of the lattice dynamics of these compounds combined with the available IR, Raman, NMR, neutron, and x-ray data would be most useful in understanding these transitions. However, for a complete understanding of their lattice dynamical properties, it is necessary to determine the phonon dispersion curves for the acoustical and optical modes, as well as the torsional modes of vibration. This can only be accomplished by *coherent* inelastic neutron scattering from single crystals. It has generally been assumed that the large incoherent-scattering cross section of hydrogen precluded coherent inelastic scattering studies of hydrogenous materials. The purpose of this communication is to report the measurement of some normal modes of vibration in $NH_4Cl$ by coherent inelastic scattering of neutrons and to illustrate some of the advantages over incoherent scattering techniques.

The measurements were made with a single crystal (approximately 20×12×4 $mm^3$) on the triple-axis spectrometers at the Oak Ridge Research Reactor (ORR) and the High Flux Isotope Reactor (HFIR). They were carried out at 78°K, room temperature, and intermediate temperatures. Although the coherent scattering amplitudes of N and Cl are large, the coherent scattering amplitude of H is not negligible, and for some Bragg reflections in $NH_4Cl$ the coherent scattering by the four hydrogen atoms is comparable to or even larger than the scattering from N or Cl. This suggests that even those modes that are predominately due to hydrogen motion can be measured in some cases.

Figure 1 shows the TA(0,0,ζ) phonon branch measured as a function of the phonon wave vector **q** at a temperature of 78°K. Since the frequencies clearly depend on the wave vector **q**, it is obvious they are the result of coherent inelastic scattering. Such measurements are not possible by incoherent scattering techniques. The coherent effects were also confirmed by a

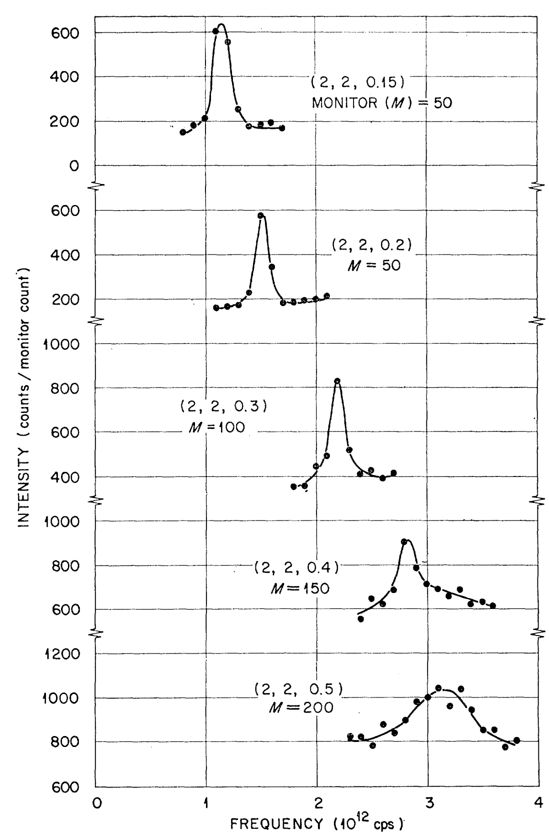


FIG. 1. TA(0,0,ζ) phonon branch in $NH_4Cl$ measured as a function of the phonon wave vector **q** at a temperature of 78°K.

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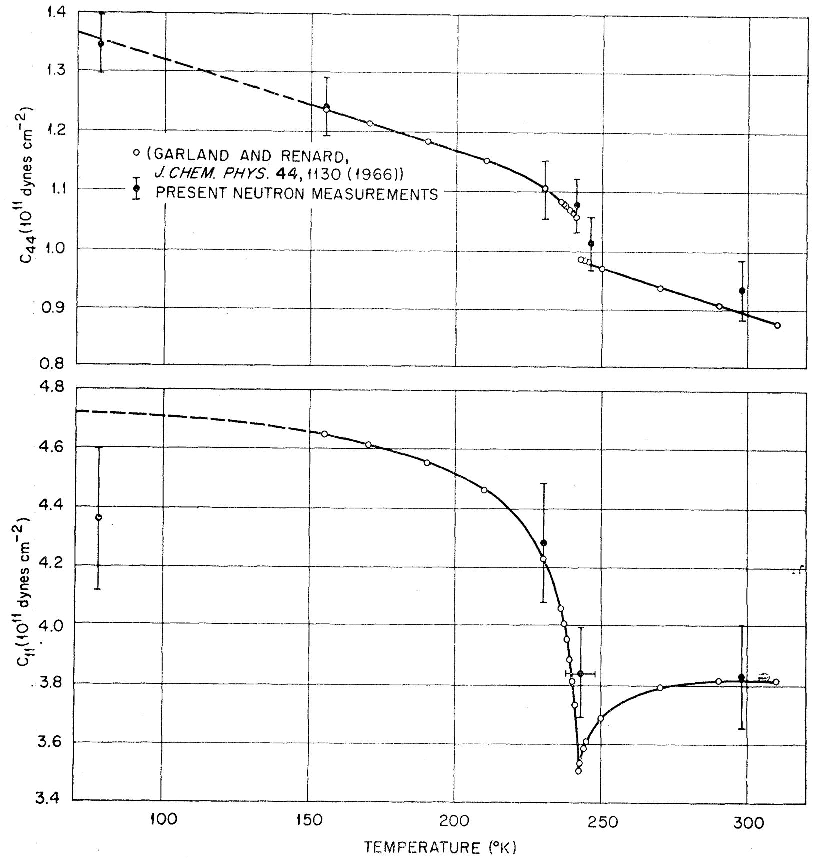


FIG. 2. Comparison of elastic constant measurements of Garland and Renard (Ref. 7) by ultrasonic methods and those obtained in this study.

polarization analysis[6] of the TA(0,0,0.2) phonon on a triple-axis polarized-beam spectrometer.

As is well known, the frequencies of the acoustic phonons at small **q** vectors and in high symmetry directions are simply related to the elastic constants of the crystal. Garland and Renard[7] have measured, by ultrasonic methods, the elastic constants of $NH_4Cl$ as a function of temperature and found pronounced anomalous behavior in the vicinity of the λ-type order-disorder transition ($T_c = 242$°K). Our neutron measurements of the TA$(0,0,\zeta)$ phonon at $\zeta = 0.2$, although not as precise as the ultrasonic measurements, are in substantial agreement with the temperature variation of $c_{44}$ determined by the above workers. This is illustrated in Fig. 2. The LA$(\zeta,0,0)$ phonons, which are related to $C_{11}$, are asymmetrical and much broader than the transverse phonons and it is not possible to determine their frequencies very accurately; nevertheless, from a similar study of the frequency versus temperature dependence of the LA(0.15,0,0) mode, there are indications that they too exhibit unusual behavior in the vicinity of $T_c$. (The neutron measurements have not been corrected for resolution or dispersion effects which would be necessary for a quantitative comparison.)

The longitudinal and transverse optic phonons are relatively flat, which makes it rather difficult to separate the coherent from the incoherent scattering. The optic modes will be discussed in a more complete report on the lattice dynamics of $NH_4Cl$ in the near future; however, the neutron measurements do indicate that the TO and LO modes at $q=0$ are in qualitative agreement with the IR and Raman data.

Since the torsional mode in $NH_4Cl$ is of particular interest, we have studied this mode in some detail. The phonon peak is sharp and very intense at 78°K with an observed frequency of $11.65 \pm 0.10 \times 10^{12}$ cps ($388 \pm 5$ $cm^{-1}$) for all values of **q**. Under these circumstances the coherent and incoherent scattering are completely superimposed. However, from a neutron polarization analysis of this mode, it is estimated that approximately 25% of the scattering in the torsional mode is due to coherent effects. It is not possible to obtain a more quantitative value for the two types of scattering since multiple scattering effects are not negligible in a sample of these dimensions. As the transition temperature is

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approached the single peak broadens considerably and at room temperature three separate peaks are observed. The peak-height-to-background ratio is too unfavorable for a polarization analysis at this time. Further studies on the torsional mode are underway.

Even with its inherent limitations, the measurement of coherently scattered phonons in undeuterated hydrogenous substances should be extremely useful for studying the effects of isotopic substitution by comparing similar phonons measured in the deuterated substances. This technique is also invaluable for those materials where large deuterated crystals are not readily attainable.

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# Effect of Thermal-Neutron Irradiation on the Elastic Moduli of LiF†

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The three elastic-constant changes, and the dilation, of LiF have been measured as a function of neutron flux. The elastic constants all decrease with flux, the change being linear for fluxes less than $10^{16} n/\mathrm{cm}^2$. This is contrary to expectations based on considerations of Dienes and Nabarro, and consequently, it makes measurements of elastic constants less useful as a tool for distinguishing between interstitials and vacancies than had previously been expected. The ratio of the relative bulk modulus to the volume change is $-1.8$, which is much smaller than some corresponding values previously reported for copper. A comparison of the experimental results with various available theories shows that a nonlinear elastic sphere-in-hole calculation disagrees the least, the expectations from Zener's considerations come next, and the rest of the theoretical estimates differ in order of magnitude and even in sign from the experimental results.

## I. INTRODUCTION

THE measurements described here were stimulated by an unresolved question in the field of radiation damage. In 1952, Dienes[1–3] gave a theoretical estimate of the effect of radiation on the elastic constants of simple metals. For copper he predicted that interstitials would increase and vacancies would decrease the elastic constants by amounts of the order of 10 and 1% per at.% of interstitials and vacancies, respectively. He thus concluded that the effects should be easily observable in copper or similar metals provided thermal annealing is prevented, and that changes in elastic constants may serve as a useful tool for distinguishing between interstitial atoms and lattice vacancies.

Because of the important need of a measurement which distinguishes between vacancies and interstitials in the interpretation of radiation damage, this prediction was followed by a number of attempts to measure the elastic constants of irradiated materials. Although these calculations stimulated much work in radiation damage, the hopes held for such a measurement have by and large not been realized. The measurements have proved to be very difficult ones. It was early found that dislocation effects often overshadowed the bulk effects of point defects, and extensive studies of dislocation effects in irradiated materials have since been made.

In those cases where the dislocation effects have been isolated, there remains an enormous disagreement (two to three order of magnitude) between different investigators making measurements of the bulk effect on the same materials. At liquid-helium temperature in copper irradiated with $\alpha$ particles, König *et al.*[4] found a Young's modulus change of $\Delta E/E=-130\%$ per at. % of Frenkel defects, while Thompson *et al.*[5] found that the change, if any, for reactor irradiated copper at liquid-helium temperature was less than 1% per at. % of Frenkel defects. In earlier work at $-195°$C, Dieckamp and Sosin[6] reported a change of $\Delta E/E=-(7\pm3)\%$ per at. % of defects. This figure has since been revised[4] to $-140\%$ per at. % of defects since het number of defects formed by irradiation was assumed to be too high in the original work. In the König *et al.* and the Dieckamp and Sosin measurements, the Young's modulus of a polycrystalline copper foil fixed at one end to perform transverse oscillations was measured, whereas the Young's modulus of a single crystalline copper rod oscillating longitudinally was measured by Thompson *et al.* A review of the results of other measurements at different temperatures and in different materials is given by König *et al.* In no case have all the elastic constants been measured.

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