CONF-770913--7

PHONON DISPERSION RELATION OF URANIUM NITRATE ABOVE AND BELOW THE NEEL TEMPERATURE

G. Dolling, T. M. Holden, E. C. Evensson, W. J. L. Buyers,
and G. H. Lander

Prepared for

International Conference on
Lattice Dynamics
Paris, France
September 5-10, 1977

UofC-AUA-USDOE

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Operated under Contract W-31-109-Eng-38 for the
U. S. DEPARTMENT OF ENERGY

PHONON DISPERSION RELATION OF URANIUM NITRIDE ABOVE AND BELOW THE NÉEL TEMPERATURE

G. Dolling, T.M. Holden, E.C. Svensson and W.J.L. Buyers

Atomic Energy of Canada Limited, Chalk River, Ontario, Canada, KOJ 1J0

and

G.H. Lander

Argonne National Laboratory, Argonne, Illinois, U.S.A.

Neutron coherent inelastic scattering measurements have been made of the phonon dispersion relation of uranium nitride both above and below the Néel temperature T_N = 50 K. Within the precision of the measurements, about 1% in frequency and 10% in line width and in scattered neutron intensity, no significant changes in these phonon properties were observed as a function of temperature other than those arising from population factor changes and a small stiffening of the lattice as the temperature decreases. At 4.2 K, two acoustic and two optic branches have been determined for each of the [001], [110] and [111] directions. The optic mode measurements revealed (a) a 20% variation in frequency across the Brillouin zone and (b) an interesting disposition of the LO and TO modes, such that $\nu_{LO} > \nu_{TO}$ along [001] and [110], while the reverse is true along the [111] directions. Within the experimental resolution, the LO and TO modes are degenerate near $q = 0$. We have been unable to obtain any satisfactory description of these results on the basis of conventional theoretical treatments (e.g. rigid-ion or shell models). Other possible interpretations of the results are discussed.

To be published in the Proceedings of the International Conference on Lattice Dynamics held in Paris, France, 5 - 10 September 1977.

PHONON DISPERSION RELATION OF URANIUM NITRIDE ABOVE AND BELOW THE NÉEL TEMPERATURE

1. INTRODUCTION

The vibrational and magnetic properties of many simple uranium compounds (e.g. UN[1], UC[2], UO_2[3,4], US[1]) have been extensively studied during the past decade, and a wide variety of behaviour has been observed[5]. In the case of uranium nitride, UN, previous experiments have shown (i) a large electronic contribution to the low temperature specific heat[6], (ii) sharp anomalies in the temperature dependence of the elastic constants[7] near the Néel temperature T_N, indicating a correlation between low frequency acoustic phonons and magnetic properties, and (iii) optic phonon modes with frequencies near 12 THz, almost independent of wavevector[1]. Recent experiments at Chalk River[8,9] showed no definite evidence of well-defined spin waves in the low-temperature antiferromagnetic phase; critical fluctuation effects were observed near T_N in the longitudinal susceptibility but not in the transverse. The relationship between the phase transition and the localized 5f and itinerant 6d-7s electrons remains to be clarified[10]. In view of these observations, it seemed worthwhile to carry out a detailed study of the phonon dispersion relation in UN, both above and below T_N (50 K), in an attempt to throw further light upon the phase transition mechanism.

2. EXPERIMENTAL RESULTS

The present neutron scattering measurements were made with two single crystal specimens, 0.8 cm^3 total volume, using the C5 triple-axis spectrometer at the NRU reactor, Chalk River, operating mainly in its constant-$\vec{Q}$ mode, with fixed analyser energies of 28.6 and 22.3 meV (6.92 and 5.40 THz, respectively). The crystals were oriented with $[1\bar{1}0]$ axes vertical, inside a variable temperature cryostat. A rather complete set of phonon frequency measurements were made at 4.2 K for longitudinal (L) and transverse (T) modes propagating along the [001], [110] and [111] directions. Certain selected modes were also studied at 45 K, 57 K, 77 K and 293 K. Examples of two typical optic modes, with reduced wavevector $a\vec{q}/2\pi = (0,0,0.75)$, are shown in Fig. 1, and the complete results are given in Table 1. Within the precision of our

measurements, about 1% in frequency and 10% in line width and in scattered neutron intensity, no significant changes in these phonon properties were observed as a function of temperature other than those arising from population factor changes and a small stiffening of the lattice (i.e. increase in average phonon frequency) as the temperature decreases. Thus the results at 4.2 K, as shown in Fig. 2, are qualitatively the same at all temperatures up to 293 K; in particular, during the experiments with the [1$\bar{1}$0] crystal orientation, no definite evidence was found for any influence of the magnetic structure and dynamics on the vibrational properties. In addition to these specific phonon studies, a number of constant-$\vec{Q}$ and constant energy (E) scans were made at 4.2 K and 293 K, over wide ranges of $\vec{Q}$ and E (E up to 83 meV, or 20 THz) in efforts to observe magnetic excitations. No neutron scattering was observed other than that which could be attributed to phonons. However, during a subsequent series of experiments (still in progress at the time of writing) with a single UN crystal at 4.8 K oriented with a [100] axis vertical, some interesting results have been found for the intensity of a particular TO mode ($\vec{aq}/2\pi$ = (0,0,0.5)) as a function of $\vec{Q}$. For $a|\vec{Q}|/2\pi > 4$, the intensity varies approximately as expected for a one-phonon scattering process. For lower $\vec{Q}$ values, however, the intensity is higher than expected on this basis, which may indicate the existence of a magnetic contribution. Further experiments on different modes and in different zones are required to obtain conclusive results on this point.

The most striking features of the results (Fig. 2) are (a) a 20% variation in frequency of the optic modes across the Brillouin zone and (b) an interesting disposition of the LO and TO modes, such that $\nu_{LO} > \nu_{TO}$ along [001] and [110], while the reverse is true along the [111] direction. As will be seen in §3, these features make it very difficult to obtain a satisfactory theoretical description of the data in terms of conventional rigid-ion or shell models[11].

3. THEORETICAL DISCUSSION

At high temperatures, UN has the cubic NaCl structure, and the tetragonal distortion which exists below T_N in the Type I antiferromagnetic phase is very small[12] (c/a = 0.99935). Although some uranium compounds, for example UO_2, display ionic character[3], UN has metallic conductivity.

Thus the splitting between the LO and TO modes near $\vec{q} = 0$, which is typical of alkali halides and arises from macroscopic electric field effects, is zero, within experimental error, in the case of UN. If we consider only the modes propagating along [001], the manner in which the LO branch rises sharply above the TO with increasing $\vec{q}$ is very reminiscent of the screening effects characteristic of degenerate semiconductors[13]. However, along [110] the LO branch is almost $\vec{q}$-independent for the first half of the zone, and along [111] it decreases in frequency away from $\vec{q} = 0$. These effects suggest that the types of force model previously used for alkali halides and degenerate semiconductors are not likely to be satisfactory in the case of UN, and that an approach based on the pseudopotential theories for metals may be more suitable. It is clear, in any event, that the picture[1] of UN as a set of Einstein oscillators (the N ions) moving independently within the fcc lattice of U ions is quite inappropriate. In this connection it is of interest to note the published values for the radii of such ions as N^{3-} (1.71 Å[14] or 1.48 Å[15]) and U^{3+} (1.03 Å[16]), as compared with the U–N distance of 2.442 Å. Although the valence state of N is not known, it seems unlikely that the nitrogen ion could be significantly smaller than uranium.

In order to confirm or deny these conjectures, we have fitted the results of Fig. 1, together with the measured elastic constants[7], on the basis of several versions of the well-known rigid-ion and shell models[11]. The most general rigid-ion model included axially-symmetric short-range forces between nearest-neighbour U and N ions and between second-nearest-neighbour ions (U – U and N – N), as well as the ionic charge Z, for a total of 7 adjustable parameters. From a mathematical viewpoint, the least-squares fitting was satisfactory, but the best value for the quality of fit parameter χ was only 5.6, indicating rather poor correspondence between theory and experiment ($\chi \sim 1$ indicates a satisfactory fit). The results of the best 7-parameter fit are shown as solid (transverse) and dashed (longitudinal) curves in Fig. 2. The N – N force constants were very small, less than 5% of the U – N or U – U force constants, and could be set to zero with little change in the quality of fit. This is most probably due to the inherent difficulty in achieving the observed ordering of the LO and TO branches mentioned in §2; the actual N – N forces may well be quite large. The "ionic charge" parameter Z was found to be rather

small (+0.30|e| on the uranium); χ increased only to 5.7 if Z was set equal to zero.

Broadly speaking, one can say that the acoustic branches are reasonably well fitted by the rigid-ion model, but the calculated optic branches are far too flat and too close to each other, displaying at most an 8% variation in frequency and failing to provide the observed ordering of the LO and TO branches in each direction. The situation became noticeably worse when the polarizabilities of either or both of the U and N ions were allowed to vary during the fitting process: in no case were we able to obtain a mathematically satisfactory minimum of χ, and the lowest value obtained during extensive searches of shell model parameter space was about 5.0 - still quite a poor fit, having similar characteristics (too flat optic branches, incorrect ordering of LO and TO modes) to the rigid-ion models. Although it is possible that a suitable shell model fit may eventually be found, this does not seem very likely in view of the difficulties we have encountered up to this point. Alternative theoretical approaches, for example the pseudopotential model, or the recently developed charge fluctuation model[17,18], are clearly required in order to describe the measured dispersion curves. Whatever theoretical approach is attempted, the possibility should be kept in mind that there may indeed be a magnetic response, perhaps extending over a wide energy range (much larger than $k_B T_N$), which may be coupled to and may cause distortions of the phonon response.

REFERENCES

1. WEDGWOOD, F.A., J. Phys. C: Solid State Phys. 7, 3203 (1974).
2. SMITH, H.G. and GLÄSER, W., Proc. Int. Conf. on Phonons, Rennes (Paris: Flammarion Sciences), 1971, pg. 145.
3. DOLLING, G., WOODS, A.D.B. and COWLEY, R.A., Can. J. Phys. 43, 1397 (1965).
4. COWLEY, R.A. and DOLLING, G., Phys. Rev. 167, 464 (1968).
5. Recent reviews of actinide studies can be found in "The Actinides: Electronic Structure and Related Properties", Vol. I, edited by A.J. Freeman and J.B. Darby (New York: Academic Press), esp. chs. 3 and 6.
6. SCARBROUGH, J.O., DAVIS, H.L., FULKERSON, W. and BETTERTON, J.O., Phys. Rev. 176, 666 (1968).
7. DU PLESSIS, P. de V., and VAN DOORN, C.F., Physica 86-88B, 993 (1977).
8. BUYERS, W.J.L., HOLDEN, T.M., DOLLING, G., SVENSSON, E.C. and LANDER, G.H., Proc. 2nd Int. Conf. on the Electronic Structure of the Actinides, Wroclaw, Poland, 13-16 Sept., 1976, pg. 395.
9. BUYERS, W.J.L., HOLDEN, T.M., SVENSSON, E.C. and LANDER, G.H., to appear in Proc. Int. Symp. on Neutron Inelastic Scattering, I.A.E.A., Vienna, October 1977.
10. ROBINSON, J.M. and ERDÖS, P., Phys. Rev. B8, 4333 (1973), and B9, 2187 (1974).
11. COWLEY, R.A., COCHRAN, W., BROCKHOUSE, B.N. and WOODS, A.D.B., Phys. Rev. 131, 1030 (1963).
12. MARPLES, J.A.C., SAMPSON, C.F., WEDGWOOD, F.A. and KUZNIETZ, M., J. Phys. C: Solid State Phys. 8, 708 (1975).
13. COWLEY, R.A. and DOLLING, G., Phys. Rev. Lett. 14, 549 (1965).
14. PAULING, L., "Nature of the Chemical Bond", Cornell University Press, Ithaca, 1945, pg. 346.
15. ZHDANOV, G.S., "Fizika Tverdogo" (Tela M.G.U. Edit., Moscow, 1961) [English transl: "Crystal Physics" (Oliver and Boyd, London, 1965)].
16. ZACHARIASEN, W.H., unpublished, quoted by C. Kittel in "Introduction to Solid State Physics", John Wiley and Sons, New York, 2nd ed., 1956, pg. 81.
17. ALLEN, P.B., to be published.
18. WAKABAYASHI, N., to be published.

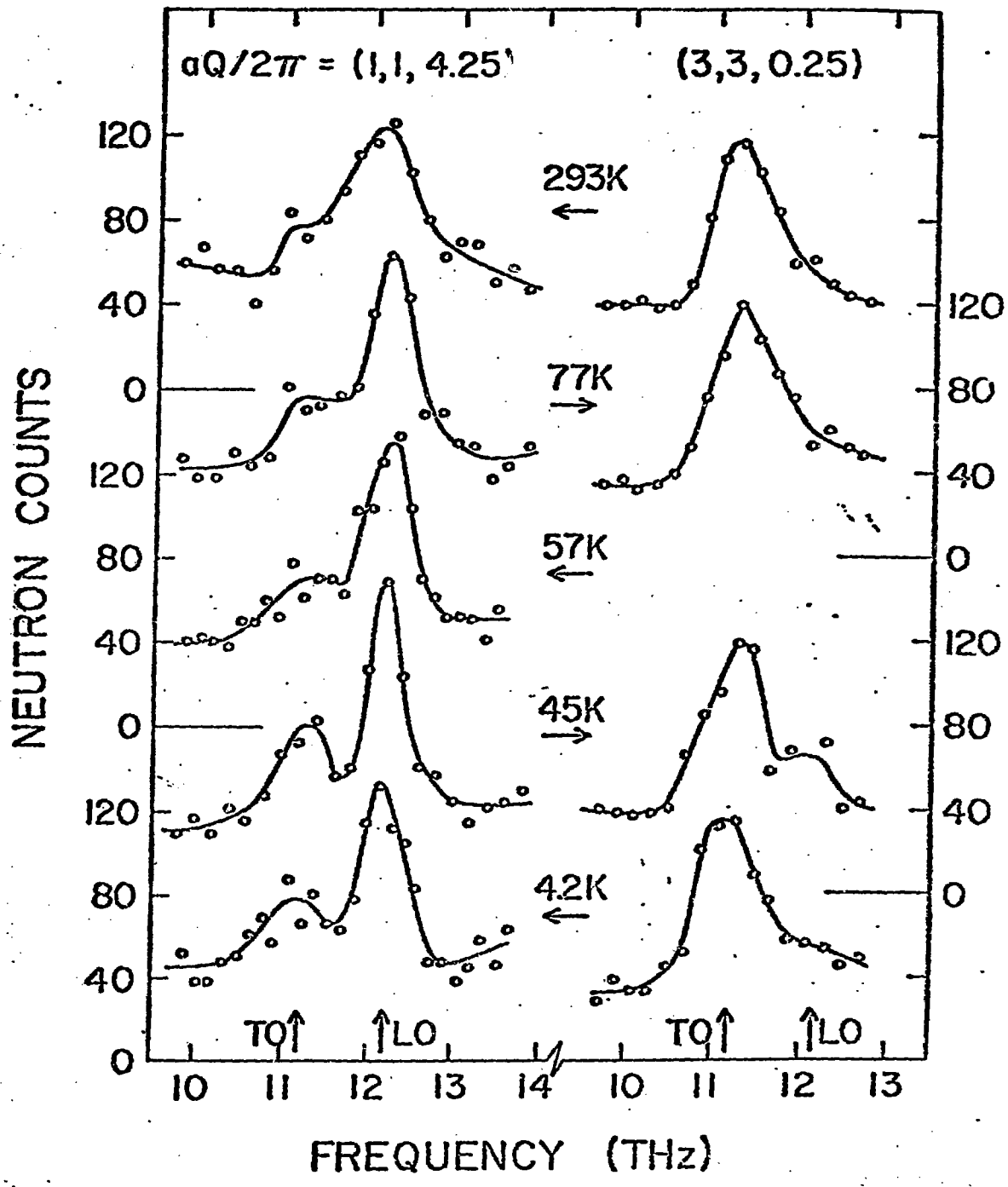
TABLE 1. TEMPERATURE DEPENDENCE OF SELECTED NORMAL MODES IN URANIUM NITRIDE

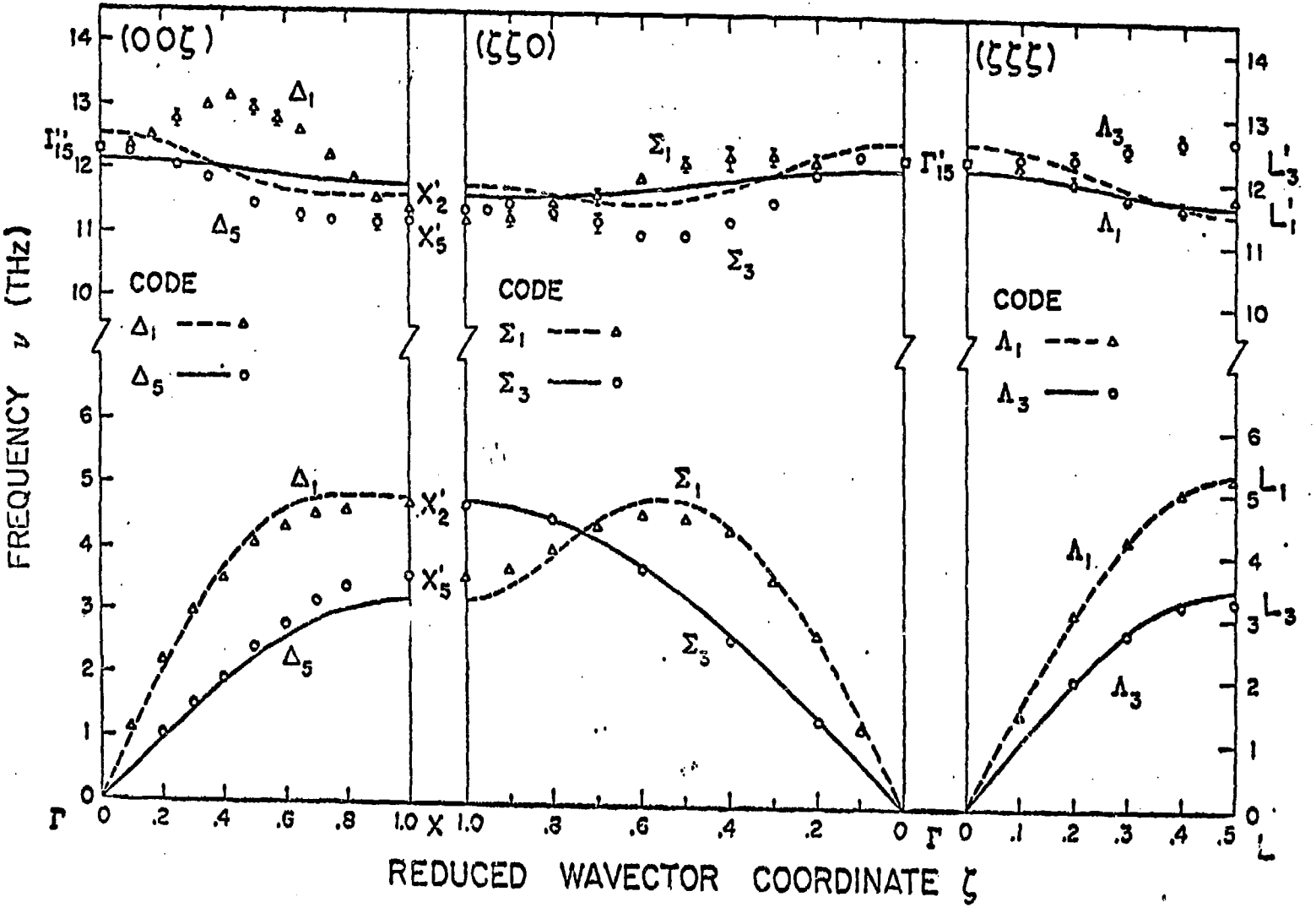
Mode label, wavevector		Normal Mode Frequency (THz) T = 4.2 K	45 K	57 K	77 K	293 K
LO, Δ_1	(0,0,0.0)	12.28 ± .05	12.44 ± .10	–	12.34 ± .06	12.16 ± .05
	(0,0,0.5)	12.95 ± .10	13.00 ± .15	12.94 ± .10	12.99 ± .10	12.90 ± .03
	(0,0,0.65)	12.60 ± .05	12.61 ± .07	12.62 ± .06	12.61 ± .10	12.48 ± .10
	(0,0,0.75)	12.20 ± .05	12.20 ± .06	12.20 ± .06	12.20 ± .08	12.03 ± .10
	(0,0,1.0)	11.40 ± .05	11.37 ± .07	–	11.41 ± .08	11.35 ± .10
TO, Δ_5	(0,0,0.25)	12.05 ± .07	12.05 ± .10	–	12.08 ± .08	11.92 ± .10
	(0,0,0.75)	11.20 ± .08	11.25 ± .10	–	11.25 ± .09	11.23 ± .10
LA, Δ_1	(0,0,0.3)	2.98 ± .05	2.91 ± .07	–	2.92 ± .08	2.90 ± .08
	(0,0,0.6)	4.31 ± .05	4.30 ± .05	–	4.30 ± .04	4.28 ± .05
	(0,0,1.0)	4.68 ± .04	4.63 ± .06	–	–	4.58 ± .07
TA, Δ_5	(0,0,0.2)	1.03 ± .02	1.01 ± .02	1.02 ± .02	1.01 ± .02	0.99 ± .02
	(0,0,0.4)	1.92 ± .02	1.94 ± .03	1.93 ± .02	1.90 ± .02	1.90 ± .03
	(0,0,0.6)	2.78 ± .03	2.77 ± .03	2.77 ± .03	2.74 ± .02	2.73 ± .04
	(0,0,0.8)	3.38 ± .03	3.34 ± .04	3.34 ± .03	3.31 ± .03	3.30 ± .05
	(0,0,1.0)	3.55 ± .05	3.51 ± .04	3.47 ± .05	3.51 ± .05	3.48 ± .05
LA, Λ_1	(0.4,0.4,0.4)	4.99 ± .04	4.94 ± .08	4.78 ± .06	–	–
	(0.5,0.5,0.5)	5.21 ± .05	5.17 ± .06	5.17 ± .06	5.10 ± .10	5.09 ± .10
TA, Λ_3	(0.3,0.3,0.3)	2.74 ± .02	2.71 ± .03	2.71 ± .03	–	–
	(0.4,0.4,0.4)	3.22 ± .03	3.19 ± .03	3.15 ± .05	–	–
	(0.5,0.5,0.5)	3.27 ± .04	3.23 ± .04	3.24 ± .04	3.27 ± .04	3.26 ± .05

Figure Captions

Fig. 1. Scattered neutron energy distributions observed at two different neutron momentum transfers in UN corresponding to the same reduced wave vector $a\vec{q}/2\pi = (0,0,0.75)$. The arrow beneath each temperature value indicates the appropriate intensity scale for each pair of groups.

Fig. 2. Dispersion relation for normal modes in UN at 4.2 K. The solid and dashed curves represent the best rigid-ion model fit to the results.


aQ/2π = (1,1, 4.25)
(3,3, 0.25)
293K
77K
57K
45K
4.2K
TO
LO
TO
LO
NEUTRON COUNTS
FREQUENCY (THz)
0
40
80
120
10
11
12
13
14


(00ζ)
(ζζ0)
(ζζζ)
FREQUENCY ν (THz)
REDUCED WAVECTOR COORDINATE ζ
CODE
Δ1
Δ5
Σ1
Σ3
Λ1
Λ3
Γ'15
X'2
X'5
L'3
L'1
L1
L3
Γ
X
L