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Rotary modes in the antifluorite crystal $(ND_4)_2SnCl_6$

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A selection of normal modes of vibration and libration in a single crystal of $(ND_4)_2SnCl_6$ is studied at several temperatures by means of thermal neutron inelastic scattering techniques. In particular, the behavior of the longitudinal rotary mode of the $SnCl_6$ octahedra is investigated and compared with the "soft-mode" behavior of this libration in other antifluorite crystals. We also observe the lowest-lying librational mode of the $ND_4{}^+$ ions, and find it to be dispersionless. Values are obtained for the elastic constants of $(ND_4)_2SnCl_6$ from the slopes of the low-frequency acoustic-mode dispersion curves.

INTRODUCTION

Many crystals with the chemical composition R_2MX_6, where R is an alkali metal, M a heavy transition or polyvalent metal, and X a halogen, have the antifluorite structure (space group $Fm3m$) at room temperature. As the temperature is lowered many of the crystals undergo at least one structural phase transition to a lower-symmetry structure. The properties of these crystals have been extensively reviewed.[1,2] In some cases the transitions are correlated with the temperature and wave-vector dependence of the longitudinal rotary mode (we define a longitudinal rotary mode to be one whose rotation axis is parallel to the propagation vector) of the MX_6 octahedra and the softening of this mode may lead to various ferro-rotative and antiferro-rotative phase transitions. In other cases the transition appears to lead to a pure lattice distortion with no coupling to the octahedral rotations. Investigations of the low-temperature structures have been made for K_2ReCl_6,[3] K_2SnCl_6,[4] K_2OsCl_6,[5] and Rb_2PtI_6,[6] and interpretation of the structural phase transitions in terms of a softening of the longitudinal rotary mode has been suggested for K_2ReCl,[3,7] K_2OsCl_6,[8,9] and K_2SnCl_6.[10]

The substitution of the ammonium ion $NH_4{}^+$ (or the deuterated analog $ND_4{}^+$) in place of the alkali metal introduces additional librational degrees of freedom into the structure. The structural transition in $(NH_4)_2SiF_6$ (Ref. 11) has been investigated by single-crystal neutron diffraction, while transitions in $(NH_4)_2PtBr_6$ (Ref. 6), $(NH_4)_2PtI_6$ (Ref. 6), and $(NH_4)SnBr_6$ (Ref. 12) have been investigated using neutron powder profile analysis. In all these compounds the root-mean-square librational amplitudes of the ammonium ions are found to be very large (20°–25°). However, despite these large amplitude librations, the structural transitions in ammonium antifluorites do not appear to be simply correlated with the ammonium librational modes. Coupling between the librations of the ammonium and octahedral ions may, however, be important in determining the detailed nature of the transitions. The contrast between the temperature dependence of the structures of K_2SnCl_6 and $(NH_4)_2SnCl_6$ illustrates this point. Whereas K_2SnCl_6 has a first-order transition to a tetragonal structure at 261 K followed by a transition to a monoclinic structure at 255 K, the ammonium analog has no phase transition down to the lowest temperatures. The rotational potential of the ammonium ion in the cubic phase has been determined previously from neutron elastic scattering measurements.[13]

Neutron inelastic scattering experiments[14] carried out on powder samples of $(NH_4)_2SnCl_6$ have determined the excitation energy for rotational jump diffusion, the excited librational states, and the rotational tunneling states. The temperature dependence of the latter has been investigated and, in general, the tunneling states decrease in energy and simultaneously broaden with increasing temperature. The role played by the external (lattice) modes in this temperature dependence is not understood. In particular, it is not clear whether the lattice modes constitute a general heat bath for the rotational states or whether coupling to particular lattice modes is the important feature.[15] At 6 K, an intense broad peak was observed[14] at ≈ 3.2 THz and was interpreted as the NH_4 librational excitation. The reason for the large linewidth of this excitation is also not clear. It has been suggested this may be due to lifetime effects, to a finite splitting of the line, or to dispersion of the mode.

Measurement with a deuterated single crystal avoids the intense incoherent scattering from hydrogen and allows an investigation of the wave-vector dependence of the various modes. In the present paper, we describe coherent inelastic neutron scattering measurements of low-frequency modes of vibration and libration in a single crystal of $(ND_4)_2SnCl_6$.[16] Particular emphasis was placed on the librational excitations of both the $SnCl_6{}^{-2}$ and $ND_4{}^+$ ions, and in addition, at 5 K an outline of the overall dispersion curves up to ≈ 4 THz was obtained. The temperature dependence of selected modes was measured up to 300 K and values of the elastic constants determined at 5 K.

EXPERIMENTAL DETAILS

The single crystal of $(ND_4)_2SnCl_6$ (grown by S. Haussühl) had a volume of ≈ 0.5 cm^3 and was mounted in a variable-temperature cryostat. The neutron scattering measurements were made on the $C5$ triple-axis crystal spectrometer at the NRU reactor, Chalk River. The

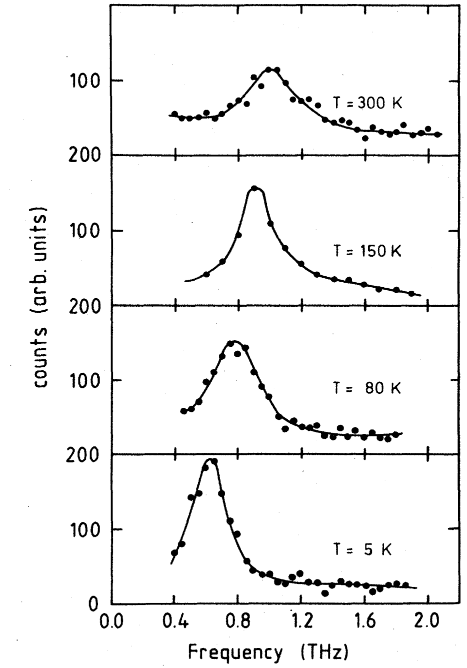

FIG. 1. Typical neutron groups corresponding to the librational mode of the $SnCl_6$ ion with zero reduced wave vector ($\zeta=0$), measured at the reciprocal-lattice point (353). The measurements were made with various monitor settings, but all have been normalized to the same integrated incident neutron flux for ease of comparison.

monochromator and analyzer were Si(111) and pyrolitic graphite (0002), respectively, and the incident and scattered beam collimations were 0.42° and 0.63°. A sapphire filter was placed in the incident beam to reduce the background. Analyzing energies of 3.51 and 3.00 THz was used for the majority of measurements and the corresponding energy resolutions [full-width at half-maximum (FWHM) of the incoherent scattering from vanadium] were 0.19 and 0.15 THz, respectively. Two specimen orientations were used for the measurements. It has been shown[7,8] that the inelastic structure factors for the longitudinal rotary mode of the MX_6 octahedra are particularly large in the (351) and (353) Brillouin zones. To observe the mode in these zones the $(5\bar{3}0)$ plane was oriented in the horizontal scattering plane of the spectrometer. Typical constant-**Q** scans made at the (353) reciprocal-lattice point (Γ point) are shown in Fig. 1. This specimen orientation has few reciprocal-lattice points favorable for the measurement of other phonon modes. Consequently the remaining phonon frequencies were determined with the specimen in the more conventional $[1\bar{1}0]$ orientation. Nine wave vectors, $\mathbf{Q}(\equiv Q_x,Q_x,Q_z)$, in this plane were used for a detailed study of the temperature dependence of the phonon modes in the frequency range 0.3 to 4.0 THz. The wave-vector components (Q_x,Q_z) were (4.6,0), (3.8,1.0), (5.0,0), (4.0,1.0), (4.0,4.0), (1.0,4.0), (3.0,3.0), (3.5,2.5), and (0.0,8.0) and measurements were made at temperatures of 5, 14, 22, 40, 60, and 80 K. Typical results for three of these wave-vector transfers are shown in Figs. 2(a), 2(b), and 2(c). The dispersion curves for the three high-symmetry directions at 5 K are shown in Fig. 3.

DISCUSSION

The phonon groups shown in Fig. 1 have all been normalized to the same integrated incident neutron flux. The mode clearly softens as the temperature is reduced. Its frequency decreases from 1.2±0.04 THz at 300 K, to 0.63±0.03 THz at 5 K, but does not decrease to zero. A plot of ν^2 against T (Fig. 4) is consistent with the linear behavior characteristic of "soft-mode" transitions,[17,18] but in the present case no phase transition actually occurs at finite temperature. The linear dependence was also assumed in the analysis of the corresponding data for K_2OsCl_6,[5] where a ferro-rotative transition does occur. The temperature dependence of the complete dispersion curve of the longitudinal rotary mode is shown in Fig. 5. At 300 K the curve shows very little frequency variation along [001], in agreement with the corresponding measurements in K_2OsCl_6 (Refs. 5 and 9) and K_2ReCl_6 (Ref. 7). Along [350], however, the frequency of the mode with the same librational displacement about [001] rises steeply from the Γ point (see Fig. 3). At $\zeta=0.1$, its frequency at 300 K has increased to 1.55±0.05 THz and is only weakly temperature dependent. The strong anisotropy of the mode frequency as a function of propagation direction is a signature of the two-dimensional nature of the correlated displacements of the MX_6 octahedra; the coupling is strong within [001] layers but weak between the layers. However, in contrast to the behavior of K_2OsCl_6 and K_2ReCl_6, as the temperature is lowered in $(ND_4)_2SnCl_6$ the frequency of the Γ-point mode shows a large decrease, while that of the X point shows little change. The two-dimensional character of the correlations weakens and the octahedra develop an incipient ferro-rotation. Analysis of the transition showed that in K_2OsCl_6 (Ref. 9) it results from a temperature-dependent change in the closely balanced forces on the octahedra. In terms of the simple model used to describe K_2OsCl_6 these forces arise from two different Cl-Cl interactions and a K-Cl interaction. In the present case, the greater dispersion shown at low temperatures by the longitudinal rotary-mode dispersion curve indicates that (in the notation of Ref. 9) the force constant B_1 must be larger than in K_2OsCl_6. However, at the Γ point, this dispersion term has no effect. If we assume that apart from the value of B_1 (which is very small in K_2OsCl_6), the remaining Cl-Cl force constants are similar for the two antifluorites, the different behavior of the two crystals as a function of temperature is caused by differences in the values of the force constants A_6 and B_6 (the notation of Ref. 9) of the R-Cl interaction. In K_2OsCl_6, where $R\equiv K$, this is a K-Cl force constant, while in $(ND_4)_2SnCl_6$ it is an effective (ND_4)-Cl force constant. Since the rotary mode remains of nonzero frequency in $(ND_4)_2SnCl_6$ this suggests that A_6 and B_6 are larger for the (ND_4)-Cl interaction than for the K-Cl interaction.

The spectra shown in Fig. 2 show a series of multiple peaks of varying intensities and the complexity of these

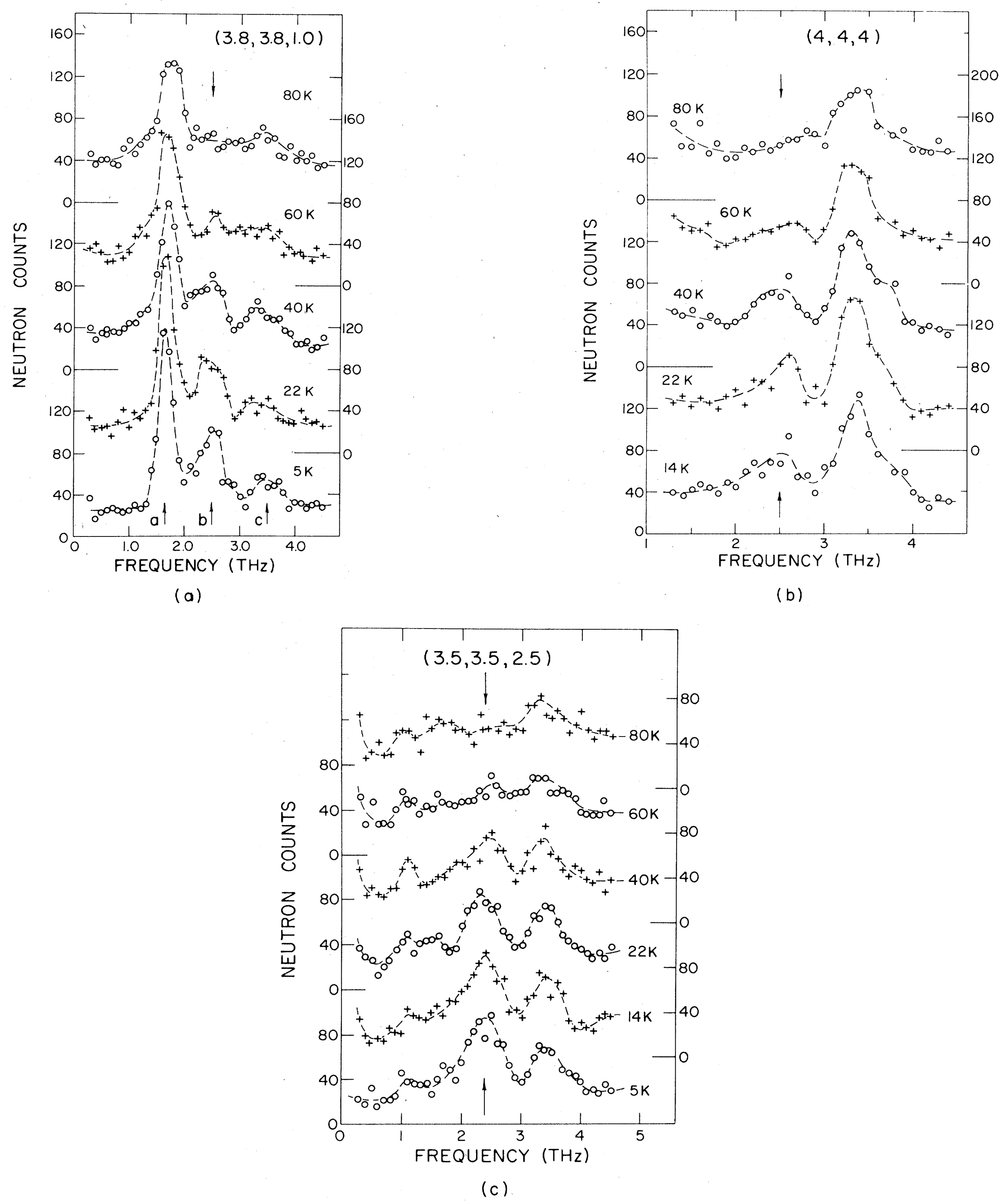

FIG. 2. (a) Constant-**Q** scans at (3.8,3.8,1.0). The ordinates are shifted by 80 counts for each temperature. Peaks *a* and *c* do vary with temperature, but much less dramatically than peak *b*, near 2.5 THz. The latter has virtually disappeared at $T=80$ K. (b) Constant-**Q** scans at (4,4,4). As in (a), the peak near 2.5 THz broadens and decreases markedly in intensity as T rises to 80 K; the peak near 3.4 THz is much less temperature dependent. (c) Constant-**Q** scans at (3.5,3.5,2.5). Same comments as for (b).

spectra is reflected in the complexity of the dispersion curves shown in Fig. 3. Since there are 18 external translational and librational modes of the molecular ions (assumed to be rigid units) and 33 internal modes of vibration, we cannot give a detailed interpretation of these spectra (and hence the dispersion curves) without a detailed lattice-dynamical model. However, there is a distinctive feature common to the three spectra shown in Fig. 2 and to others not shown here. Most of the observed peaks show a weak temperature dependence with some broadening and frequency shifts as the temperature increases from 5 K to 80 K. The peak near 2.5 THz shows

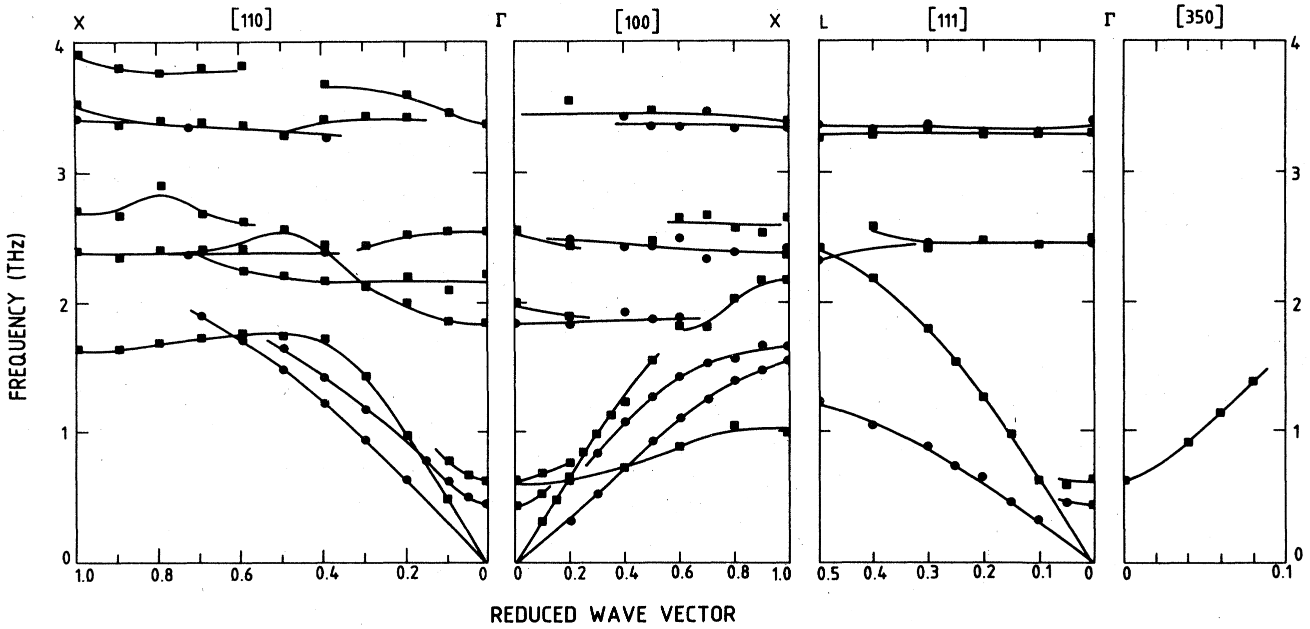

FIG. 3. Experimental phonon dispersion curves of $(ND_4)_2SnCl_6$ at 5 K. The solid circles and squares indicate measurements made in transverse and longitudinal configurations, respectively. The lines are hand drawn to show the assumed connectivity of the points.

little frequency change as a function of temperature, but its intensity diminishes virtually to zero as the temperature increases to 80 K. We believe the peak arises from transitions from the librational ground state to the first excited state of the ND_4^+ ion.

The frequency of this excitation is observed to be essentially independent of reduced wave vector for all high-symmetry directions in which measurements were made (see Fig. 3). Its ratio compared to the frequency (3.24 THz) of the librational excitation observed in $(NH_4)_2SnCl_6$ powder[14] is 0.77. Since the librational potential is strongly anharmonic this is in fair agreement with the value $1/\sqrt{2}$ expected for the deuterated analog in a harmonic potential. A temperature of 80 K is a large fraction of the temperature of this excited librational state (2.5 THz $\equiv 120$ K). Thus the large decrease in the observed intensity of the peak as the temperature increases to 80 K is probably due to increasing population of the first excited librational state. However, we have also suggested above that the interaction between the MX_6 octahedra and the ammonium ion is stronger than that between MX_6 and an alkali ion. Consequently, the displacements of these two molecular ions behave, to some extent,

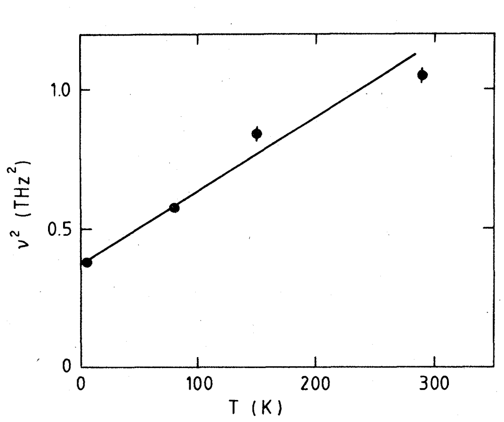

FIG. 4. Variation of squared frequency of the $q=0$ librational mode of the $SnCl_6$ ion with temperature, showing a characteristic Cochran-Anderson "soft-mode" behavior (Refs. 17 and 18).

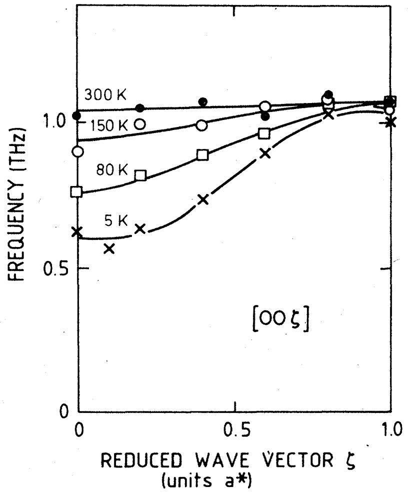

FIG. 5. Temperature dependence of the $SnCl_6$ librational mode propagating along the [001] direction: the solid circles, open circles, squares, and crosses correspond, respectively, to 300, 150, 80, and 5 K. The solid lines are guides for the eye.

as a coupled pair of librations allowing transfer of intensity between the two librational "modes." The present interpretation suggests that the linewidth observed for the corresponding mode in $(NH_4)_2SnCl_6$ is not caused by dispersion of the mode.

In addition to the excitation at 2.5 THz discussed above, it can be seen from the dispersion curves of Fig. 3 that there are several other optical branches that are essentially independent of wave vector. Branches at ≈ 3.4 THz and ≈ 1.9 THz are particularly prominent. However, these modes do not seem to show the strong temperature dependence of the modes at ≈ 2.5 THz. It is evident that all these "optical" branches are actually frequency bands consisting of several distinct branches. It is tempting to assume that the two closely spaced branches at ≈ 3.4 THz along both [100] and [111] directions, are in reality, the same branch observed in different experimental configurations. However, the number of branches in the dispersion relation for even an antifluorite crystal containing an alkali rather than an ammonium ion is so large (see, for example, Refs. 1 and 9) that this simplifying assumption cannot be made without confirmation by means of a detailed lattice-dynamical model. Similarly, until such a model is developed, a detailed interpretation of the scattered neutron groups cannot be made and the lines shown in Fig. 3 indicating different branches of the dispersion relation are based only on simple continuity arguments. The dispersionless character of many of these optical branches is rather unexpected, since the optic branches calculated for K_2ReCl_6 (Ref. 3) and K_2OsCl_6 (Ref. 9) show significant dispersion. The modes with frequency ≈ 3.4 THz are particularly interesting for it is near this frequency that a strong peak is observed in $(NH_4)_2SnCl_6$.[14] This peak was interpreted[14] as the transition from the librational ground state to the first excited state of the NH_4^+ ion. Since the peak in the hydrogenous compound is broad and observed predominantly through the intense incoherent hydrogen cross section, it may also have components from other modes which cannot be resolved. If these are independent of the motion of the ammonium ion their frequencies would be unaffected by deuteration of this ion. Some of the modes with frequency ≈ 3.4 THz in $(ND_4)_2SnCl_6$ may be of this character and so would be optical modes or librations of the $SnCl_6$ ion.

The acoustic branches were measured along the three high-symmetry directions (see Fig. 3) and the elastic constants have been derived from the slopes of these branches at small wave vectors. Their values at 5 K are (in units of 10^{10} $\mathrm{N\,m^{-2}}$) $C_{11}=2.90\pm0.25$, $C_{12}=1.48\pm0.30$, $C_{44}=1.12\pm0.18$. The relatively large errors arise because the experimental configuration was not optimized for measurements at the low frequencies and small wave vectors necessary to determine accurate values of the elastic constants. From these elastic constants the value calculated[19] for the Debye temperature Θ_D is 259 K.

SUMMARY

We have observed the longitudinal rotary mode of the $SnCl_6$ octahedra in $(ND_4)_2SnCl_6$ and studied its temperature dependence. Several dispersion curves along the high-symmetry directions have been outlined at 5 K. Also observed is a mode interpreted as the excitation of the ammonium ion to the first excited librational state, an interpretation based in part upon the temperature dependence of its observed intensity. Qualitative explanations for the observed behavior of these two modes are proposed, but a more detailed understanding of these and the other observed modes awaits a more complete description of the interactions in these antifluorite crystals. Such a description may also lead to an understanding of the fundamentally different temperature dependence of the crystal structures of the isomorphous antifluorites $(NH_4)_2SnCl_6$ and $(NH_4)_2SnBr_6$.[12]

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