PHYSICAL REVIEW B VOLUME 40, NUMBER 1 1 JULY 1989

Ammonium-ion ordering in a scheelite lattice: NH_4ReO_4

D. R. Taylor
Department of Physics, Queen's University, Kingston, Ontario, Canada K7L 3N6

(Received 26 September 1988)

The anomalous heat capacity and thermal expansion of NH_4ReO_4 near 200 K are attributed to cooperative ordering of ammonium ions, similar to that which occurs in ammonium halides. No phase transition takes place because the ammonium site symmetry in this lattice favors one of the two ammonium orientations. A model of Ising pseudospins in a longitudinal field provides a satisfactory description of the observed lattice strains, heat capacity, and nuclear-quadrupole-resonance and Raman spectra. There is strong coupling between ammonium ions and lattice strain in NH_4ReO_4, so that mean-field theory should be an excellent approximation.

I. INTRODUCTION

The ammonium ion (NH_4^+) forms many compounds which are isostructural to alkali-metal compounds at high temperatures. The rotational degrees of freedom of the ammonium ion, and its preference for tetrahedral symmetry, give rise to some novel and widely studied[1] phenomena at lower temperatures which are absent in the analogous alkali-metal compounds. Ammonium chloride, NH_4Cl, is an archetype, and it will be useful to discuss some of its properties first, in particular its phase transition at 243 K.

Above 243 K, NH_4Cl has bcc (CsCl) structure, with each ammonium ion surrounded by eight Cl ions. In this lattice the ammonium tetrahedron adopts cubic symmetry by reorienting between two equivalent configurations, in each of which the four H atoms are close to four Cl atoms (Fig. 7.21 of Ref. 1). As the temperature is reduced, the free energy of the crystal can be lowered by a cooperative ordering of the NH_4 tetrahedra which minimizes their interaction energy.[1] In NH_4Cl the coupling between ions favors parallel alignment, and results in an order-disorder transition at 243 K which has been investigated in detail. Yamada, Mori, and Noda[2] have interpreted such a transition by associating an Ising spin variable σ^z with the two tetrahedral orientations, and introducing a linear spin-phonon (or rotation-translation) coupling. An effective Ising interaction between ammonium ions results, giving a phase transition below which the order parameter $\langle \sigma^z \rangle$, representing the population difference between the two sets of sites, or the distortion from the cubic phase, develops progressively as the temperature is lowered. In this phase the ammonium site symmetry is tetrahedral, and the ion thus "freezes" into tetrahedral coordination at low temperatures, although quantum-mechanical tunneling always provides some population in the other set of sites. A variety of experimental evidence[1] supports this interpretation, especially heat-capacity measurements which show that the entropy lost at the transition is just $R \ln 2$.

Related phenomena have been studied in other ammonium compounds,[1] with similarities and differences strongly dependent upon the ammonium site symmetry. The principal subject of this paper is ammonium-ion ordering in the scheelite structure compound, ammonium perrhenate NH_4ReO_4, whose properties have been investigated for some time.[3-12] Features observed near 200 K in early experiments suggested a phase transition. More careful investigations have ruled out a phase transition, but a satisfactory interpretation of the anomalous data near 200 K has been lacking.

Heat-capacity measurements[9,12] show a prominent maximum near 200 K but with no sharp feature indicative of a conventional phase transition. X-ray and neutron diffraction experiments[8,11] show that the scheelite structure, C_{4h}, is preserved through this temperature range, but that the unit-cell dimensions change by several percent, in such a manner that the cell volume is almost unaffected. Spectroscopic measurements[6,10] reveal rapid and unusual shifts in nuclear-quadrupole-resonance (NQR) and Raman frequencies near 200 K but again no discontinuous behavior.

The absence of a structural transition in NH_4ReO_4 having been established, an explanation of the heat-capacity peak was sought in terms of the rotational-librational heat capacity of a hindered ammonium rotor.[9] Model calculations[13] do yield a heat capacity maximum in this temperature range, but not of the observed sharpness and magnitude.[9] Subsequently it was suggested[12] that heat capacity contributed by the anomalous thermal expansion could account for much of the observed peak. This contribution is added to the calculated heat capacity (constant-strain) to allow comparison with the measured heat capacity (constant-stress).[12]

In this paper an interpretation of the thermodynamic properties of NH_4ReO_4 (and the related compound NH_4IO_4, as well as their deuterated isomorphs) is proposed on the basis of cooperative ordering of the ammonium tetrahedra (approximate tetrahedra, really), similar to that which occurs in NH_4Cl. No phase transition occurs, however, because the ammonium site symmetry, S_4, is low enough to favor one orientation of the tetrahedra relative to the other, and an excess population in the lower-energy sites exists at all temperatures. This is described in the Ising pseudospin model by the addition of a small constant longitudinal field. The parameters of the model, when fitted to experimental data, imply a strong coupling between ions and the lattice strain. The model gives a satisfactory explanation of known properties near 200 K, and predicts other effects which can be tested experimentally.[14]

II. THE ISING MODEL FOR COOPERATIVE AMMONIUM-ION ORDERING

Some general arguments which suggest cooperative ordering of ammonium tetrahedra as the source of the anomalous properties near 200 K will be presented first. X-ray data at room temperature[15] show that the ammonium site is at the center of a stretched tetrahedron of oxygen ions ("axial") at 2.90 Å and a squashed tetrahedron of oxygen ions ("equatorial") at 3.01 Å. Thus the ammonium ions are at the center of a rough cube of eight oxygen ions, and there should exist two ammonium-ion orientations of similar energies, in close analogy with the NH_4Cl situation. At low temperatures the ammonium H ions are known[15,8] to be located near the axial oxygen ions, but at room temperature their positions could not be determined; this is consistent with considerable disorder above 200 K with comparable occupation of both sets of sites.

In addition, the heat-capacity maximum, although too broad for a conventional phase transition, cannot be fitted to any model based on the freezing out of the rotational and librational motion of independent rotors. Cooperative ordering is the most plausible mechanism for sharpening the heat-capacity peak. More persuasive evidence comes from the absence of a significant temperature shift of the peak on deuteration of the compound.[16] The peak occurs at 195±5 K in both NH_4ReO_4 and ND_4ReO_4. The corresponding peak temperatures in NH_4Cl and ND_4Cl are 243 K and 250 K, respectively.[1] This insensitivity to ionic mass strongly implies a mechanism of electronic origin as opposed to one associated with vibrational or rotational motion.

The introduction of an Ising pseudospin variable to denote the two configurations of an atomic group, and the description of structural phase transitions in terms of an effective coupling between pseudospins, has become a standard approach in a number of cases, especially ferroelectrics[17] and Jahn-Teller systems.[18] For ammonium compounds, the pioneering work of Yamada, Mori, and Noda[2] applies to cubic NH_4Cl, NH_4Br, and NH_4I. For systems requiring additional degrees of freedom, such as the cyanides, a more general analysis has been developed and applied.[19]

The extension of the theory developed for the cubic ammonium halides[2] to NH_4ReO_4 is reasonably straightforward. The Ising variable denotes equatorial and axial orientations of the ammonium ion, where the H atoms are close to the corresponding oxygen atoms. These two states have different energies, and are well-defined quantum mechanically if overlap, and hence tunneling, between them is small. In each state the ammonium complex is invariant under all the symmetry operations of the point symmetry, S_4, and hence both states belong to the totally symmetric representation, A. Only distortions transforming as A of S_4 have matrix elements within these states, and the effective spin Hamiltonian for the ith ion can therefore be written as[18,20]

$$\mathcal{H}(i) = -\Delta_0\sigma^z(i) + \sum_j Q_{jA}\zeta_{jz}\sigma^z(i) , \tag{1}$$

where $2\Delta_0$ is the initial energy splitting of the two configurations, j labels distinct distortions of A symmetry, and ζ_{jz} gives the strength of the coupling between the distortion Q_{jA} and the operator σ^Z. Equation (1) can also include similar terms involving the σ^x operator, but these will be omitted in this case where tunneling between the configurations is assumed negligible. Equation (1), and the development to follow, closely resemble the analysis of cooperative Jahn-Teller effects,[18,20] especially for the case of cerium ethylsulfate[21,22] where the term in Δ_0 also appears.

The summation over all ammonium sites can be simplified by noting that there are two sites per primitive cell, related by inversion. For long-wavelength distortions only the even-parity combination

$$\sigma^z(n) = [\sigma^z(n,1) + \sigma^z(n,2)]/2$$

is of interest.[18] Equation (1) can thus be read as a unit-cell Hamiltonian in terms of these composite operators, provided that Q_{jA} is now a distortion of A_g symmetry in the lattice C_{4h} group.

Three contributions to the local distortions must be considered: from acoustic phonons, from optical phonons, and from bulk strains.[2,18,20] The latter is obviously important in NH_4ReO_4, in view of the observed changes in unit-cell dimensions of several percent near 200 K. For this tetragonal crystal, there are two strains of A_g symmetry, generally written as ϵ_{zz} and $\epsilon_{xx}+\epsilon_{yy}$. However it is often more convenient to work with linear combinations which transform as spherical harmonics.[21] Thus

$$\epsilon_{00} = \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}$$

identifies the change in unit-cell volume, while

$$\epsilon_{20} = (\sqrt{3}/6)(2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy})$$

represents an axial strain with no change in volume. This allows an important simplification since the observed change in cell volume up to room temperature is small,[11] while a large displacement occurs in the ϵ_{20} mode; this implies negligible coupling to the ϵ_{00} strain mode in comparison with the ϵ_{20} mode coupling. If the coupling to the latter strain alone is considered, the system Hamiltonian can be written

$$\mathcal{H} = -\sum_n (\Delta_0 + V_s\epsilon)\sigma^z(n) + \tfrac{1}{2}N\Omega c_0\epsilon^2 , \tag{2}$$

where V_s is the coupling strength and c_0 is the elastic constant for the strain $\epsilon = \epsilon_{20}$, Ω is the unit-cell volume, and N is the number of unit cells. Minimization of the free energy with respect to strain gives $\epsilon = 2V_s\langle\sigma^z\rangle/\Omega c_0$, and Eq. (2) becomes

$$\mathcal{H}=-\sum_{n}\Delta_0\sigma^z(n)-\frac{\mu}{2N}\sum_{n,m}\sigma^z(n)\sigma^z(m)\ , \tag{3}$$

where $\mu=V_s^2/\Omega c_0$ gives the strength of an effective Ising interaction between sites of infinite range. An effective ion-ion interaction of Ising form also arises from the coupling to acoustic and optic phonons,[18] and from direct electrostatic interactions between ammonium multipole moments.[2] These additional contributions are difficult to estimate, and are conveniently collected together as an interaction parameter $J(n-m)$, so that the total pseudospin Hamiltonian becomes

$$\mathcal{H}=-\sum_{n}\Delta_0\sigma^z(n)-\tfrac{1}{2}\sum_{n,m}[J(n-m)+\mu/N]\sigma^z(n)\sigma^z(m)\ . \tag{4}$$

This model differs from that of Yamada *et al.* only in the explicit appearance of strain coupling in Eq. (4), and in the term in Δ_0 which denotes the energy difference between the two ammonium-ion orientations. The effect of this "longitudinal field" is to induce ordering, that is, preferential population in one orientation at all temperatures, and thus to prevent a phase transition.

Mean-field theory should be an excellent approximation in strain-coupled systems where the interactions are very long range, and is widely used in obtaining solutions.[18] A straightforward analysis shows that $\langle\sigma^z\rangle$ is determined self-consistently by $\langle\sigma^z\rangle=\tanh(\beta W)$, where $\beta=1/kT$, $W=\Delta_0+J'\langle\sigma^z\rangle$ represents the ordering field, and $J'=\mu+\sum_{nm}J(n-m)$ is the total effective Ising interaction parameter. $\langle\sigma^z\rangle$ defines the amount of order in analogy to the usual order parameter, but here $\langle\sigma^z\rangle$ is nonzero at all temperatures. Figure 1 illustrates the dependence of $\langle\sigma^z\rangle$ on temperature for a range of values of Δ_0/J'. As expected, this spans the range from that for a well-defined phase transition to a rather featureless variation over accessible temperatures.

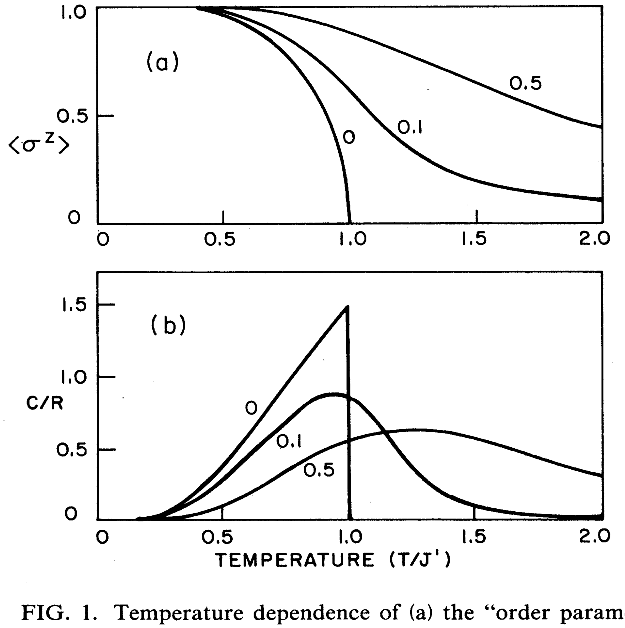

FIG. 1. Temperature dependence of (a) the "order parameter" $\langle\sigma^z\rangle$, and (b) the heat capacity of the Ising model, for indicated values of Δ_0/J', the relative longitudinal field strength.

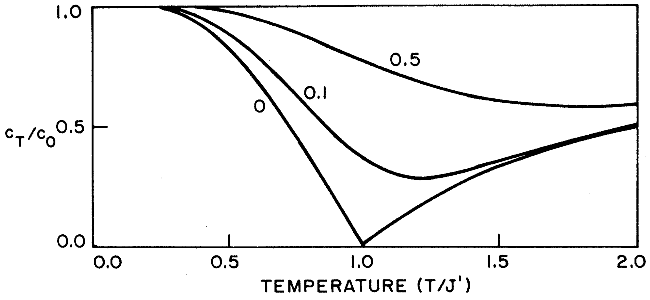

FIG. 2. Calculated isothermal elastic constant vs temperature for indicated values of Δ_0/J', the relative longitudinal field strength.

The heat capacity is readily calculated at all temperatures in the mean-field approximation.[21,23] As already suggested, the distinction between constant-strain and constant-stress heat capacity is important. The latter is the relevant condition both for experiments and for cooperative ordering to occur. Indeed at constant strain ϵ, the energy level splitting W is fixed and a Schottky heat capacity results. The heat capacity at constant (zero) stress was calculated by Fletcher and Sheard[21] for cerium ethylsulfate. Their result is identical to the mean-field heat capacity for the Ising model in a field:[23]

$$\frac{C}{R}=\frac{(\beta W)^2\mathrm{sech}^2(\beta W)}{1-\beta J'\mathrm{sech}^2(\beta W)}\ . \tag{5}$$

The behavior of C/R as the parameter Δ_0/J' is varied from 0 to 0.5 is illustrated in Fig. 1. The limit for J' vanishingly small is not shown, but it is clear that as the denominator of Eq. (5) becomes independent of temperature, C/R approaches a Schottky anomaly for splitting Δ_0.

Another important thermodynamic quantity is the elastic constant corresponding to the ϵ_{20} strain, which is expected to soften in accompaniment with the cooperative ordering. Gehring and Gehring[18] describe the calculation of the coupled elastic constants under appropriate thermodynamic conditions. The isothermal elastic constant for our system is readily found to be

$$\frac{c_T}{c_0}=\frac{1-\beta J'\mathrm{sech}^2(\beta W)}{1-\beta(J'-\mu)\mathrm{sech}^2(\beta W)}\ . \tag{6}$$

Figure 2 shows its temperature dependence with the assumption that $J'=\mu$, i.e., only coupling to the strain is important. As expected, the elastic constant softens considerably, but not to zero if Δ_0 is nonzero.

III. COMPARISON WITH EXPERIMENTS

In this section the experimental information on NH_4ReO_4 will be reviewed and interpreted in terms of cooperative ammonium-ion ordering. The parameters of the model will be fitted to the most appropriate data, and calculations based on the model will be compared with other results. In general the accuracy of both the fits and the comparisons is limited by the presence of other temperature-dependent contributions in the vicinity of 200 K.

A. Lattice strain

Figure 3 shows the strain $\epsilon_{20}=\epsilon$, calculated from x-ray data,[4,11] as a function of temperature. These results were found to be the most suitable for fitting the parameters of the model, since other contributions to ϵ_{20} are expected to be no greater than the observed ϵ_{00} (volume expansion, also shown in Fig. 3), which is an order of magnitude smaller. The resemblance to Fig. 1 is consistent with $\epsilon \propto \langle \sigma^z \rangle$, and hence J' and Δ_0 are determined by, respectively, the location and sharpness of the anomaly. In the fit to the model, the data near and above 300 K were given little weight because of the likelihood that other contributions are increasing above room temperature. Excellent fits at other temperatures could be obtained for some range (±10%) of values of (J',Δ_0). The values $J'/k=210$ K, $\Delta_0/k=9.0$ K were chosen because they also locate the heat-capacity peak (to be discussed) at the observed temperature. From the fit to the magnitude of the strain the coupling constant μ can be determined if the "high-temperature" elastic constant c_0 is known. c_0 can readily be expressed in terms of conventional elastic constants:[24]

$$c_0=\tfrac{2}{3}(c_{11}+c_{12}+2c_{33}-4c_{13}) \ ,$$

but these have not been measured. If a representative value $c_0=3\times10^{10}$ Pa is chosen,[12] μ/k is estimated to be $\sim$400 K, implying that J' is dominated by strain coupling. Since strain coupling is a long-range interaction, mean-field calculations are expected to be excellent approximations.

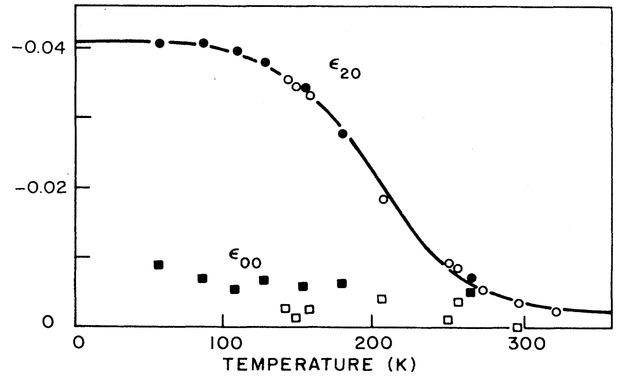

FIG. 3. Temperature dependence of lattice strains ϵ_{00} and ϵ_{20} (see text) in NH_4ReO_4. Circles and squares, data from Ref. 4; solid symbols, data from Ref. 11.

B. Heat capacity

The heat capacity, as given in Eq. (5), also depends on J' and Δ_0. However, there are other substantial contributions to the total heat capacity near 200 K, as discussed in detail by Weir and Staveley[9] and Brown *et al.*[12] These include contributions from acoustic and optic phonons, and from librational modes of both the perrhenate (ReO_4) and ammonium complexes. From the measured heat capacity, these authors were able to extract the heat capacity arising from ammonium-ion degrees of freedom. To the latter they identified major heat-capacity contributions: (i) due to the librational-rotational heat capacity of *independent* ammonium rotors, (ii) due to positional or orientational ordering of ammonium ions, and (iii) arising from thermal expansion in the case of constant-*stress* heat capacity. Weir and Staveley[9] ruled out (ii) because no phase transition occurs. They estimated (iii) by using the *volume* thermal expansion, and found a rather small effect. Brown *et al.*[12] reformulated effect (iii) taking account of crystalline anisotropy, and suggested that an important contribution could arise since the *a*- and *c*-axis strains were large although the volume expansion was small. The point of view of the present model allows comments to be made on these heat-capacity contributions, especially (ii) and (iii).

It appears to be satisfactory to treat the rotational-librational contribution (i) as independent of the ordering contribution (ii). The analysis of heat-capacity data in the ammonium halides shows that (i) appears unaffected by (ii).[25] Various estimates of (i) for NH_4ReO_4 are discussed by Weir and Staveley.[9] Smith's calculation[13] for a tetrahedral rotor in a tetrahedral field probably provides the best available estimate, and this is shown in Fig. 4 for a barrier height of 1280 K along with the residual

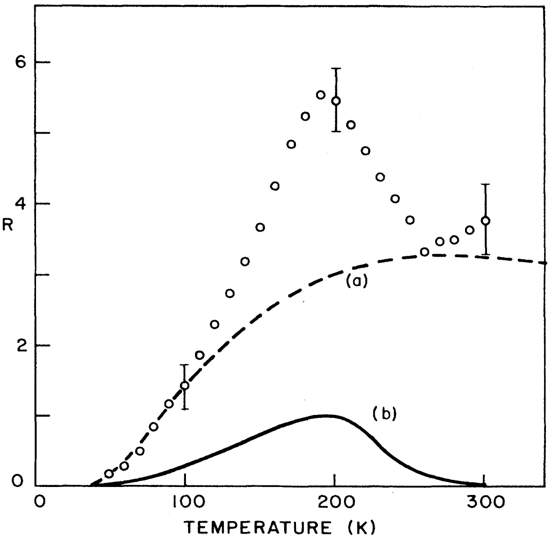

FIG. 4. Ammonium-related heat capacity for NH_4ReO_4. Data points from Ref. 12. Dashed line (a): calculated rotational heat capacity from Ref. 13. Solid line (b): calculated ordering heat capacity (this work).

(ammonium-related) heat capacity derived from experiment.[9,12]

In the case of contribution (ii), the present model shows that ordering of the ammonium ions does contribute to heat capacity in the absence of a phase transition. The entropy of ordering is $R\ \ln 2$ as in NH_4Cl, but it is removed gradually over a much broader temperature range. The calculated contribution (ii) based on the values of J' and Δ_0 previously given is also shown in Fig. 4.

The thermal expansion contribution (iii) for an anisotropic crystal discussed by Brown *et al.*[12] was given by

$$C_\sigma - C_\epsilon = VT \sum c_{ijkl}\alpha_{ij}\alpha_{kl} \ , \tag{7}$$

where C_σ and C_ϵ are heat capacities at constant stress (as measured) and at constant strain (as commonly calculated). c_{ijkl} and α_{ij} are components of the elastic constant and thermal expansion tensors, respectively. If the thermal expansion components are expressed in terms of temperature derivatives ϵ_{00}' and ϵ_{20}' of the strains ϵ_{00} and ϵ_{20} previously defined, Eq. (7) becomes

$$C_\sigma - C_\epsilon = VT(c_V \epsilon_{00}'^2 + c\epsilon_{20}'^2 + c_c \epsilon_{00}'\epsilon_{20}') \ , \tag{8}$$

where the c's are elastic constants. The term in c_V (the bulk modulus) is the contribution considered by Weir and Staveley. It is small since the volume expansion ϵ_{00} is relatively small and also featureless with temperature. Terms in ϵ_{20}', as Brown *et al.* noted, appear to be important. However, terms in ϵ_{20} should not appear in Eq. (8) for the present model because the strain ϵ_{20} was taken as a thermodynamic variable. Hence, no contribution of this nature is expected, but there could be other effects. In their analysis of a coupled pseudospin-lattice system, Fletcher and Sheard[21] found that the constant-stress heat capacity could be separated into a pseudospin part and a lattice part. The pseudospin contribution is just that calculated in (ii), viz., Eq. (5), while the lattice part differs from the "bare" lattice heat capacity because phonon frequencies are altered by the strain. Estimates are not straightforward, but a major effect on the lattice contribution is unlikely considering that in NH_4ReO_4 some frequencies will increase and others will decrease as ϵ_{20} develops.

To summarize, the heat capacity in NH_4ReO_4 is more difficult to interpret than in the ammonium halides where the ordering contribution occurs over a narrow temperature range, and can be readily distinguished from the background. According to Fig. 4, the estimated contributions (i) and (ii) are inadequate to explain the observed peak. However, there are major uncertainties both in the data points, which are differences between large numbers (the error bars are inferred from the analysis of the $KReO_4$ heat capacity[12] and may be underestimates), and in the possibility of a contribution to (iii). Another possibility is that a two-level model, which includes only the lowest energy level in each potential well, is not a good enough approximation.

C. NQR and Raman frequencies

Anomalous temperature dependences in the frequencies of Raman transitions[10] and a number of nuclear quadrupole transitions[6] were observed in NH_4ReO_4. These spectroscopic frequencies are expected to be sensitive to atomic displacements, especially of the nearest neighbors (oxygens in this case). The latter, and hence the frequencies, should be linear functions of the strain ϵ_{20}. This dependence will, as usual, add to the temperature dependence arising from normal mechanisms, i.e., from other than ammonium-ion ordering. Thus, the change in frequency relative to that at a reference temperature may be written, to a first approximation, as

$$\nu(T) - \nu(T_0) = [\nu(T) - \nu(T_0)]_n + \left[\frac{\partial \nu}{\partial \epsilon_{20}}\right][\epsilon_{20}(T) - \epsilon_{20}(T_0)] \ . \tag{9}$$

If the first term (the "normal" dependence) is small, or can be estimated accurately, comparison of the data with the model involves only one adjustable parameter. Unfortunately this condition is not met in the cases considered here; thus, in spite of the precision of NQR and Raman spectroscopy, the fitting of the data is not straightforward.

NQR measurements have been made for a variety of nuclei in NH_4ReO_4, but those for $^{187}Re(\frac{5}{2} \leftrightarrow \frac{3}{2})$ (see Fig. 5)

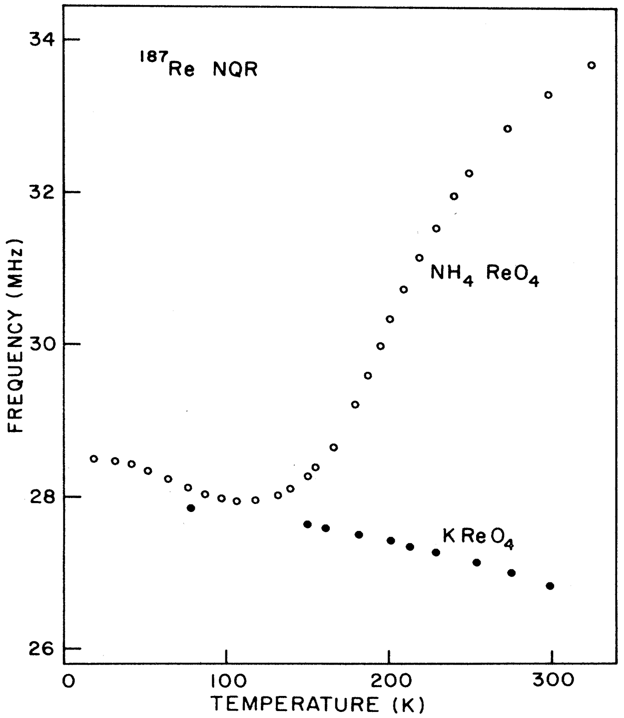

FIG. 5. Measured NQR frequencies for ^{187}Re in NH_4ReO_4 ($\frac{5}{2} \leftrightarrow \frac{3}{2}$, Ref. 6), and in $KReO_4$ ($\frac{3}{2} \leftrightarrow \frac{1}{2}$, Ref. 26).

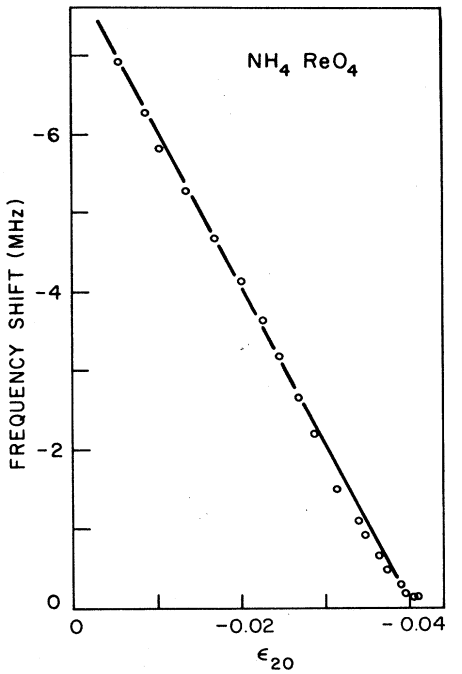

FIG. 6. NQR frequency shift (see text) vs calculated strain ϵ_{20}.

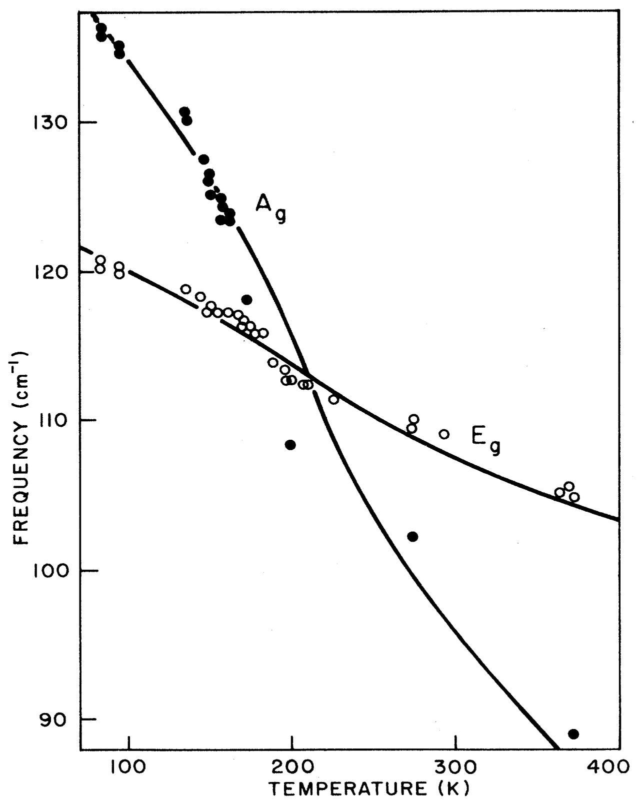

FIG. 7. Temperature dependence of NH$_4$ReO$_4$ librational modes (Raman data from Ref. 10). Lines are best fits to Eq. (9).

are perhaps the most accurate over a wide temperature range. The frequency of this transition increases by about 5 MHz from low temperatures to room temperature[6] in contrast to the decrease by about 1 MHz of an NQR signal of similar frequency in KReO$_4$.[26] In terms of Eq. (9), this anomalous increase is attributed to ϵ_{20}, which in general could give a frequency shift of either sign. At low temperatures where ϵ_{20} is small, the normal effect dominates, giving an initial decrease (Fig. 5). A crude estimate of the normal effect in NH$_4$ReO$_4$ for temperatures up to 300 K can be made by scaling the data for KReO$_4$ by the necessary factor (3.0) to give a good fit to this initial downturn. Then a plot of the remaining frequency shift $\nu(T)-\nu(T)_n$ versus ϵ_{20} (calculated from parameters determined earlier) should be a straight line. As shown by Fig. 6, a good linear relationship indeed obtains. Brown and Segel[6] also suggested, and demonstrated, a roughly linear correlation of NQR frequency and lattice parameter, but they did not correct for the normal temperature variation.

Other NQR frequencies in NH$_4$ReO$_4$ have temperature dependences which suggest a similar ϵ_{20} contribution, but fits have not been attempted for these measurements. In addition, the pressure dependence of some NQR frequencies has been investigated.[6] This also changes dramatically near 200 K, but its interpretation appears to require knowledge of individual elastic constants.

Data[10] for two of the Raman-active librational modes in NH$_4$ReO$_4$ are shown in Fig. 7. They show a characteristic variation near 200 K which again is consistent with a ϵ_{20} strain contribution. In this case the "normal" variation is quite linear with temperature, as data on KReO$_4$ demonstrate.[10] A least-squares fit of the data for the A_gReO$_4$ librational mode, which shows a dramatic anomaly, to linear temperature and ϵ_{20} dependences gave the fit indicated by the solid line in Fig. 7. Again, a convincing explanation in terms of the present model is achieved.

D. Nuclear magnetic relaxation

In contrast to the above results, measurements of nuclear relaxation rates, such as T_1^{-1} for the ammonium protons,[5,7] show no unusual features near 200 K. As in other ammonium compounds, the dominant relaxation mechanism is ammonium rotational-librational motion, with an activation energy near 1100 K. This can be understood because, as discussed earlier, the rotational-librational motion is relatively unaffected by the cooperative ordering of the ammonium ions. Likewise, the Ising model with a longitudinal field has no dynamics which would give a relaxation contribution. In principle, there could be indirect effects of the ϵ_{20} strain on nuclear relaxation, for example by modifying the librational potentials, but these would not be conspicuous.

While this analysis does not exhaust the available data, it is clear from these examples that the pseudospin model presented here gives a satisfactory interpretation of a variety of experimental observations.

IV. CONCLUSIONS

The pseudospin model for ammonium-ion ordering in NH_4ReO_4 is supported by good agreement between model calculations and many experimental results, and by the analogies to the ammonium halides where a similar model is well established. It represents a simple physical situation where the ammonium ions order cooperatively in the lower of two potential wells, with corresponding changes in unit-cell dimensions but no reduction in symmetry. The anomalous properties of NH_4ReO_4 have been discussed in terms of such a mechanism in some earlier papers,[3,7] but not quantitatively. For further confirmation of the model it would be desirable to have direct evidence for the existence of a double potential well, and for the energy difference between minima. Calculations of energies based on atom-atom potentials are consistent with a double potential well[27] but are not quantitatively reliable.

As pointed out, the model does not fit the heat-capacity anomaly adequately although there are large uncertainties in estimating the other contributions. The measured peak remains significantly larger than expected, with an ordering entropy close to $R \ln 2.5$ according to Weir and Staveley.[9] This extra entropy, if real, suggests that the populations of the excited librational levels assist in driving the ordering. If this were so, the model would have to be extended beyond the Ising model, perhaps along the lines of models applied to cyanide ion ordering.[19] The simplicity of the two-level pseudospin description is such, however, that it should not be discarded without clear necessity.

Ammonium-ion ordering in NH_4ReO_4 differs from that in the ammonium halides not only in the absence of a phase transition, but also in the dominance of ion-strain coupling over other coupling mechanisms. This long-range coupling leads to ferrodistortive, mean-field-type ordering in contrast to the effects of competing short-range interactions evident in the halides.

ACKNOWLEDGMENTS

This research was stimulated by R. J. C. Brown, to whom I am indebted for a number of valuable discussions, especially on heat capacity. Research support was provided by the Natural Sciences and Engineering Research Council of Canada.

---

[1] N. G. Parsonage and L. A. K. Staveley, *Disorder in Crystals* (Clarendon, Oxford, 1978).

[2] Y. Yamada, M. Mori, and Y. Noda, J. Phys. Soc. Jpn. **32**, 1565 (1972).

[3] R. A. Johnson and M. T. Rogers, J. Magn. Reson. **15**, 584 (1974).

[4] R. J. C. Brown, J. G. Smeltzer, and R. D. Heyding, J. Magn. Reson. **24**, 269 (1976).

[5] R. L. Armstrong, J. A. J. Lowrens, and K. R. Jeffrey, J. Magn. Reson. **23**, 115 (1976).

[6] R. J. C. Brown and S. L. Segel, J. Chem. Phys. **67**, 3163 (1977).

[7] I. Svare, A. M. Raaen, and K. Otnes, Phys. Scr. **22**, 519 (1980).

[8] R. J. C. Brown, S. L. Segel, and G. Dolling, Acta Crystallogr. Sect. B **36**, 2195 (1980).

[9] R. D. Weir and L. A. K. Staveley, J. Chem. Phys. **73**, 1386 (1980).

[10] J. Korppi-Tommola, R. J. C. Brown, and H. F. Shurvell, J. Raman Spectrosc. **11**, 363 (1981).

[11] S. L. Segel, H. Karlson, T. Gustavson, and K. Edstrom, J. Chem. Phys. **82**, 1611 (1985).

[12] R. J. C. Brown, J. E. Callanan, R. D. Weir, and E. F. Westrum, Jr., J. Chem. Phys. **85**, 5963 (1986).

[13] D. Smith, J. Chem. Phys. **58**, 3833 (1973).

[14] A brief account has been given by D. R. Taylor, J. Chem. Phys. **87**, 773 (1987).

[15] G. J. Kruger and E. C. Reynhardt, Acta Crystallogr. Sect. B **34**, 259 (1978).

[16] S. L. Segel and R. J. C. Brown, J. Chem. Phys. **70**, 3840 (1979).

[17] R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1974).

[18] G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. **38**, 1 (1975).

[19] K. H. Michel, in *Condensed Matter Research Using Neutrons*, Vol. 112 of *NATO Advanced Study Institute, Series B: Physics*, edited by S. W. Lovesey and R. Scherm (Plenum, New York, 1984), p. 195.

[20] R. J. Elliott, R. T. Harley, W. Hayes, and S. R. P. Smith, Proc. R. Soc. London Ser. A **328**, 217 (1972).

[21] J. R. Fletcher and F. W. Sheard, Solid State Commun. **9**, 1403 (1971).

[22] D. R. Taylor, D. B. McColl, J. P. Harrison, R. J. Elliott, and L. L. Goncalves, J. Phys. C **10**, L407 (1977).

[23] R. B. Stinchcombe, J. Phys. C **6**, 2507 (1973).

[24] J. F. Nye, in *Physical Properties of Crystals* (Clarendon, Oxford, 1957).

[25] C. C. Stephenson and A. M. Karo, J. Chem. Phys. **48**, 104 (1968).

[26] M. T. Rogers and K. V. S. R. Rao, J. Chem. Phys. **49**, 1229 (1968).

[27] R. J. C. Brown and R. Russell (private communication).