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Nuclear Spin-Lattice Relaxation in Some Ferroelectric Ammonium Salts*

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The temperature dependence of H^1 and F^{19} spin-lattice relaxation times in polycrystalline $(NH_4)_2SO_4$, $(NH_4)_2BeF_4$, NH_4HSO_4, and $(NH_4)_2H_3IO_6$ have been measured in both the ferroelectric and nonferroelectric phases, using a pulse technique at 30 Mc/sec. The spin-lattice relaxation processes were found to be determined by molecular reorientation. Definite changes in the proton relaxation behavior in the neighborhood of the Curie points indicate a change in the state of internal motion at the transition. The same was found to be true for two solid solutions of $(NH_4)_2BeF_4$ in $(NH_4)_2SO_4$. The results suggest that the ferroelectric phase changes in these solids are in general accompanied by a change in lattice structure which alters the potential in which the nuclei move, but do not involve an important change in the degree to which nuclei must cooperate in order to surmount the potential barriers.

INTRODUCTION

It is common knowledge that a good deal of information regarding the structure and internal motion of solids can be obtained by nuclear magnetic resonance techniques. This information is gathered either through the second moment of the resonance line, which is important for calculating internuclear distances and rates of motion in a certain narrow range of frequencies, or through the spin-lattice relaxation time, which provides information about rates of motion over a wider range of frequency. This latter technique has proven valuable in pinning down the processes involved in solid-state phase transitions in a number of compounds. Prominent among the solids studied in this manner have been ammonium salts, where the protons in the NH_4^+ ions act as the resonant nuclei and reflect the ionic motion in their relaxation times. The solids discussed in the following pages are likewise ammonium salts, but in addition they all exhibit ferroelectric or antiferroelectric phases. These compounds are $(NH_4)_2SO_4$, $(NH_4)_2BeF_4$, solid solutions of $(NH_4)_2BeF_4$ in $(NH_4)_2SO_4$, NH_4HSO_4, and $(NH_4)_2H_3IO_6$.

The molecular mechanisms leading to disorder-order type ferroelectric or antiferroelectric transitions are not well understood at the present time, especially in the above-named compounds where it might be suspected that the NH_4^+ ions play some part.

In recent studies of several of these compounds by the second-moment method[1–3] no correlations were found between the proton resonance linewidth transitions and the onset of the ferroelectric phases. From this evidence Burns[1] has implied that the motion of the NH_4^+ ions is not related to the phase changes. However, linewidth measurements are insensitive to any change in molecular motion that does not pass through a rather narrow frequency range (10^3–10^5 cps), and it is not unreasonable to suppose that in the compounds studied in this way the motional frequencies on both sides of the phase change are greater than 10^5 cps. It will be demonstrated presently that this actually is the case.

From relaxation time measurements, it is found that in the neighborhood of the Curie points of these compounds the slope—and sometimes the actual value—of relaxation time plotted as a function of temperature undergoes an abrupt change. From this information it is concluded that a change in NH_4^+ motion accompanies and reflects the phase change in every case. The exact manner in which this motion changes will be considered in the discussion which follows the report of experimental results.

The mathematical model used to analyze the relaxation time T_1 measurements into correlation times τ_c characteristic of the NH_4^+ motion is that introduced by Bloembergen *et al.*,[4] and will henceforth be termed the BPP formula. A more rigorous treatment by Hubbard[5] of the relaxation due to the rotation of a tetrahedron of spins shows the relaxation to be governed by two separate terms exponential in time; but, as is born out experimentally here, the relative weights of the two make the total relaxation indistinguishable from the single exponential form that is described by the BPP formula.

EXPERIMENTAL DETAILS

The nuclear spin-lattice relaxation times (T_1's) were measured at 30 Mc/sec, using a transient method.[6] A regular sequence of $\pi/2$ pulses was used.[7] The recovery function of the z component of spin magnetization was obtained by plotting the free induction amplitude

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‖ Alfred P. Sloan Research Fellow.

[1] G. Burns, Phys. Rev. **123**, 64 (1961).

[2] R. Blinc and I. Levstek, J. Phys. Chem. Solids **12**, 295 (1960).

[3] J. H. Loehlin and J. S. Waugh (unpublished).

[4] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

[5] P. S. Hubbard, Phys. Rev. **109**, 1153 (1958).

[6] T. P. Das and E. L. Hahn, *Nuclear Quadrupole Resonance Spectroscopy* (Academic Press, Inc., New York, 1958), p. 93.

[7] E. L. Hahn, Phys. Rev. **80**, 580 (1950).

against the time between pulses. (This method gives consistent T_1 values only when, as in the case of our solids, $T_2 \ll T_1$.) The cryostat and temperature controls were of a conventional design, that has been previously described.[8] Polycrystalline samples, pressed into cylindrical form, were used. The solid solutions were donated by Professor C. C. Stephenson, and had been analyzed for $SO_4^{=}$ and F.[9] The other samples were from commercial sources except for $(NH_4)_2H_3IO_6$. The last was prepared according to the procedure of Helmholtz[10] and was analyzed for N by the Kjeldahl method. Unless otherwise indicated, all data were obtained in warming runs.

RESULTS

Figure 1 shows the results of the T_1 measurements on $(NH_4)_2SO_4$, 5% and 22% solutions of $(NH_4)_2BeF_4$ in $(NH_4)_2SO_4$, and $(NH_4)_2BeF_4$. The form of the proton T_1 vs inverse temperature curves and the value of minimum T_1 leads us to believe that the relaxation process is effected by NH_4^+ motion and that the BPP relation between T_1 and the characteristic frequency of motion ν_c can be applied. Good agreement between ν_c's calculated from the relaxation time data and those directly measured in the far infrared at room temperature[11] further supports this assumption.

Since all T_1 curves were found to exhibit a minimum, it was possible to determine the constant in the BPP formula. Thence we were able to calculate the parameter $\omega\tau_c$ $[\tau_c = 1/(2\pi\nu_c)]$ as a function of temperature. The straight line plots of $\log\omega\tau_c$ vs $1/T$ give the potential hindering rotation of the NH_4^+ ions.

In all the samples, T_1 decreases with decreasing temperature down to about 150°K, showing that the characteristic frequencies of internal motion in this range are greater than the Larmor frequency (30 Mc). Since this is the temperature range within which all the crystals undergo their phase transitions, it is clear why no changes in the rate of NH_4^+ motion manifest themselves in linewidth transitions.

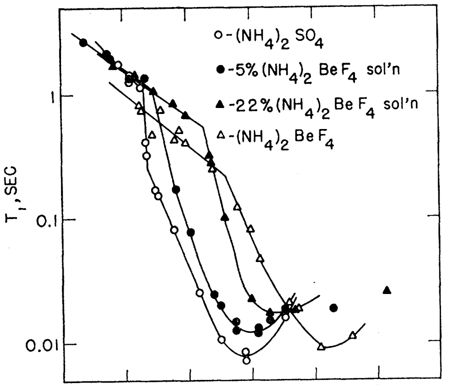
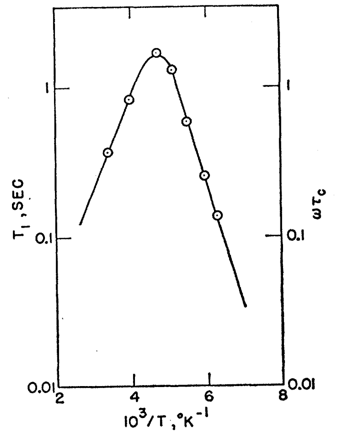


FIG. 1. Proton T_1 in powdered $(NH_4)_2SO_4$, $(NH_4)_2BeF_4$, and solid solutions of these two.

FIG. 2. F^{19} spin-lattice relaxation time in $(NH_4)_2BeF_4$.



$(NH_4)_2SO_4$

A marked discontinuity in T_1 for $(NH_4)_2SO_4$ was found in the vicinity of the ferroelectric phase transition, which is reported to be of the first order.[12,13] T_1 abruptly decreases from 1 sec to 300 msec, indicating a large change in the rate of NH_4^+ motion on going to the ferroelectric phase. The slope of the curve also changes. From the slope of the $\omega\tau_c$ curve we calculate the potential hindering the NH_4^+ reorientation to be 2.3±1.1 kcal/mole in the room-temperature phase of $(NH_4)_2SO_4$ and 6.1±1.2 kcal/mole in the low-temperature phase.

$(NH_4)_2BeF_4$

$(NH_4)_2BeF_4$ is claimed to undergo a ferroelectric transition of second order[13] though this substance shows double hysteresis loops above the transition temperature. This salt exhibits only a change in the slope of the proton T_1 vs $1/T$ curve in the vicinity of the Curie point. The absence of a discontinuity in the relaxation time itself supports the assumption of a less violent nature of the transition, which was reached on the basis of dielectric and thermal data.[13] In the ferroelectric phase, the hindering potential increases from 1.5±0.7 to 5.3±1.2 kcal/mole.

In contrast to the proton spin-lattice relaxation behavior, the fluorine T_1 of $(NH_4)_2BeF_4$ [Fig. 2] steadily increases in the nonferroelectric phase from room temperature down to about −70°C, where it exhibits a maximum and then, in the ferroelectric phase, decreases with decreasing temperature. The slope of

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[8] G. R. Murray, Jr. and J. S. Waugh, J. Chem. Phys. **29**, 207 (1958).

[9] G. E. Grenier, Bachelor's thesis, Massachusetts Institute of Technology, 1953 (unpublished).

[10] L. Helmholtz, J. Am. Chem. Soc. **59**, 2036 (1937).

[11] D. Hadzi (private communication).

[12] B. T. Mathias and J. P. Remeika, Phys. Rev. **103**, 262 (1956).

[13] S. Hoshino, K. Vedam, Y. Okaya, and R. Pepinsky, Phys. Rev. **112**, 405 (1958).

the fluorine T_1 vs $1/T$ curve in the ferroelectric phase ($E'=3.3\pm0.7$ kcal/mole) is distinctly smaller than the corresponding protonic one ($E_{\mathrm{H}}=5.3\pm1.2$ kcal/mole).

Previous study of the F^{19} linewidth transition at $-60°\mathrm{C}$ gave an activation energy E_{F} of about 5.2 ± 0.1 kcal/mole,[3] a value which is consistent with the variation of the fluorine T_1 with temperature above the Curie point [cf. Eq. (4) below]. This suggests that the relaxation process at high temperature is governed by the relatively slow fluctuation of the intra-$\mathrm{BeF_4}^{2-}$ dipolar interactions. This mechanism becomes ineffective in the ferroelectric phase, and is probably supplanted by one which involves the interionic F-H interactions, whose time dependence arises primarily from the reorientation of $\mathrm{NH_4}^+$ ions, i.e., the correlation frequencies $\nu_c^{(\mathrm{H})}$ and $\nu_c^{(\mathrm{HF})}$ are approximately the same.

The effective relaxation time for F^{19} at any temperature is thus given by the sum of two contributions:

$$(1/T_1)_{\mathrm{F}}=(1/T_1)_{\mathrm{FF}}+(1/T_1)_{\mathrm{FH}}. \tag{1}$$

If we neglect correlations between the relative motions of various internuclear vectors, the intra-$\mathrm{BeF_4}^{2-}$ relaxation process is adequately described by the well-known BPP equation. Since the characteristic frequency of motion $\nu_c^{(\mathrm{F})}$ is much lower than the F^{19} Larmor frequency, $(T_1)_{\mathrm{FF}}$ is inversely proportional to $\nu_c^{(\mathrm{F})}$ throughout the temperature range investigated.

Relaxation between unlike nuclei has been extensively discussed by Abragam.[14] $(T_1)_{\mathrm{FH}}$ is given by

$$\begin{aligned}(1/T_1)_{\mathrm{FH}}=\tfrac{3}{4}\gamma_i^2\gamma_k^2\hbar^2 \textstyle\sum_k[\tfrac{1}{12}J_{ik}^{(0)}(\omega_k-\omega_i)\\ +\tfrac{3}{2}J_{ik}^{(1)}(\omega_i)+\tfrac{3}{4}J_{ik}^{(2)}(\omega_k+\omega_i)].\end{aligned} \tag{2}$$

Here $J_{ij}^{(n)}(\omega)$ is the spectral density of the random fluctuations at the frequency ω and ω_k and ω_i are the proton and F^{19} Larmor frequencies, respectively.

The spectral densities may be written

$$J_{ik}^{(n)}(\omega)=|H_{ik}^{(n)}(t)|^2\cdot\frac{2\tau_c}{1+\omega^2\tau^2}, \tag{3}$$

where $H_{ik}^{(n)}(t)$ is the matrix element of the appropriate term in the dipolar Hamiltonian, and τ_c is the correlation time for the nuclear motion producing relaxation. The proton relaxation data show that $[\tau_c(H)]^{-1}$ is larger than ω_{H} or $(\omega_{\mathrm{H}}+\omega_{\mathrm{F}})$ in the temperature range studied, so that $(T_1)_{\mathrm{FH}}$ is proportional to the $\mathrm{NH_4}^+$ reorientation frequency $\nu_c^{(\mathrm{H})}$.

Assuming that the temperature dependence of $\nu_c^{(\mathrm{H})}$ $(\cong\nu_c^{(\mathrm{HF})})$ and $\nu_c^{(\mathrm{F})}$ follow Arrhenius expressions, the slope of the usual T_1-temperature plot is

$$\begin{aligned}E'&\equiv-\frac{d\ln(T_1)_{\mathrm{F}}}{d(1/kT)}\\ &=E_{\mathrm{H}}\left[1-\frac{(T_1)_{\mathrm{FH}}}{(T_1)_{\mathrm{FF}}+(T_1)_{\mathrm{FH}}}\left(1+\frac{E_{\mathrm{F}}}{E_{\mathrm{H}}}\right)\right],\end{aligned} \tag{4}$$

where E_{H} and E_{F} are the activation energies for $\mathrm{NH_4}^+$ and $\mathrm{BeF_4}^{2-}$ reorientations. E_{F} and $(T)_{\mathrm{FF}}$ can be obtained from a combination of linewidth and high temperature F^{19} relaxation data. E_{H} and $(T_1)_{\mathrm{FH}}$ are obtained from the proton and low-temperature F^{19} relaxation data. Now the temperature at which the T_1 maximum occurs may be calculated by setting $E'=0$; the result agrees with experiment and thus supports the proposed model.

The fact that in the ferroelectric phase $(T_1)_{\mathrm{H}}$ is considerably shorter than $(T_1)_{\mathrm{F}}$ and $E'<E_{\mathrm{H}}$ is easily understood from Eqs. (3) and (4) and the fact that the F–H distances are larger than the H–H distances, thus leading to smaller dipolar matrix elements in the former case although the characteristic frequencies of motion are effectively the same.

Solid Solutions

T_1 values in the 5% and 22% solid solutions of $(\mathrm{NH_4})_2\mathrm{BeF_4}$ in $(\mathrm{NH_4})_2\mathrm{SO_4}$ in the high-temperature phase closely approximate those of $(\mathrm{NH_4})_2\mathrm{SO_4}$ itself. Below the transitions, however, variations appear and a shift is seen to occur for the temperature of transitions and T_1 minima, bringing them nearer those for pure $(\mathrm{NH_4})_2\mathrm{BeF_4}$ as the fraction of this compound in the solution is increased. The fact that the slopes change abruptly near the Curie points, demonstrates the close relationships between $\mathrm{NH_4}^+$ reorientation rate and the phase transition. In the 5% solution the hindering potential goes from 1.8 ± 0.9 kcal/mole above the transition temperature to 8.7 ± 1.5 below, while that for the 22% solution goes from 1.8 ± 0.9 to 10.1 ± 1.5 kcal/mole.

Table I gives the transition temperatures for these compounds and solutions measured by three independent methods. The discrepancies between the reported T_c[13] for the solutions of $(\mathrm{NH_4})_2\mathrm{BeF_4}$ in $(\mathrm{NH_4})_2\mathrm{SO_4}$ and the change in slope of the T_1 curve are difficult to explain. Also the question of whether the 22% solution actually does exhibit a ferroelectric phase cannot be resolved with existing evidence. The otherwise helpful phase diagram by Hoshino *et al.*[13] of the $(\mathrm{NH_4})_2\mathrm{BeF_4}$, $(\mathrm{NH_4})_2\mathrm{SO_4}$ system leaves the exact limit of the ferroelectric composition range rather uncertain, since from the data shown one could reasonably place this limit anywhere between 20 and 30% of $(\mathrm{NH_4})_2\mathrm{BeF_4}$.

TABLE I. Transition temperatures for $(\mathrm{NH_4})_2\mathrm{SO_4}$, $(\mathrm{NH_4})_2\mathrm{BeF_4}$, and solid solutions.

Mole percent of $(\mathrm{NH_4})_2\mathrm{BeF_4}$ in solid solution	Transition temperature (°K) found by ϵ[a]	C_p[b]	T_1
0	223	223	230
5	~220	219	225
22	~203	180	189
100	176	···	178

[a] See reference 9. [b] See reference 13.

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[14] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), p. 294.

In any event there is no question of the existence of a phase transition accompanied by an abrupt change in the effective potential hindering NH_4^+ reorientation for both these solutions; and parallel behavior of the T_1 and ϵ[13] transition temperatures as functions of composition make it clear that both phenomena are caused by the same structure transition. Thermal transitions in these solutions[9] also parallel T_1 and ϵ behavior but are not precisely identical.

NH_4HSO_4

The variation of the proton spin-lattice relaxation time with temperature in NH_4HSO_4 presents a particularly interesting problem, since NH_4HSO_4 is one of the few known ferroelectric crystals with two Curie points, −3° and −119°C.[15] It has been shown[15] that a transition of the second order occurs at −3°C on going from a paraelectric to a ferroelectric phase. The high-temperature limit of the apparatus precludes any definite statement about a possible change of slope of the T_1 curve at the upper Curie point but, in any case, since even in the ferroelectric range the activation potential is still quite low (2.0±0.5 kcal/mole), we ought not to expect a very great change in potential at this upper Curie point.

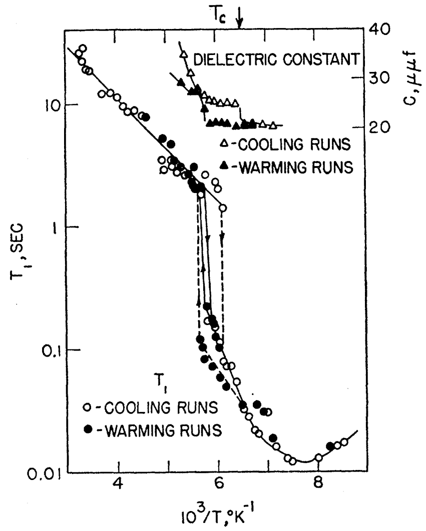

FIG. 3. Proton T_1 and ϵ in powdered NH_4HSO_4. The dashed and solid lines in the T_1 hysteresis curve indicate first and second runs, respectively, on the same sample. First and second runs of ϵ gave identical curves. (ϵ is indicated in terms of the capacitance between two copper plates surrounding the sample. Conductivity of sample caused larger ϵ at higher temperatures.)

The low-temperature transition, however, gives clear evidence of a change in NH_4^+ motion. The hindering potential increases from 2.0 kcal/mole to 2.9±0.4 kcal/mole.

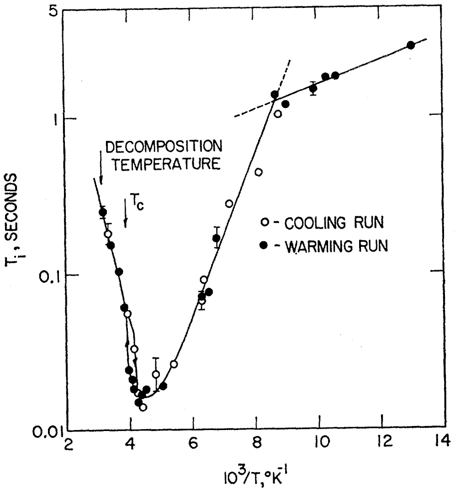

FIG. 4. Proton T_1 in powdered $(NH_4)_2H_3IO_6$.

Because of the discrepancy between the reported Curie point[15] of −119°C and our T_1 transition at −100°C, a second run of T_1 data were gathered from a fresh NH_4HSO_4 sample, and the dielectric constant discontinuity was also sought using the same low-temperature apparatus. Figure 3 shows the results of these measurements. Again T_c indicates the lower Curie point obtained by Pepinsky *et al.* The center of the T_1 hysteresis curve is still some 10°C above the center of the hysteresis of our ϵ curve. However, the large overlap of the two hysteresis curves, together with the fact that the rather broad anomaly in the specific heat curve[15] brackets all these temperatures, leaves little doubt that the transitions in both T_1 and ϵ are direct results of the same structure change.

$(NH_4)_2H_3IO_6$

The case of $(NH_4)_2H_3IO_6$ is in many ways similar to that of NH_4HSO_4. A discontinuity and hysteresis in the T_1 vs $1/T$ curve [Fig. 4] are observed at 250°K, corresponding nicely with the reported dielectric anomaly[16] at 254°K. The chief difference between the two compounds is that the potential hindering NH_4^+ rotation in $(NH_4)_2H_3IO_6$ *decreases* from 3.3±1.0 to 2.4±0.5 kcal/mole on going from the high-temperature to the antiferroelectric phase. (The larger uncertainty in the slope above T_c is due to the narrow accessible range of this phase, since the solid decomposes at about 40°C.)

The change in slope of T_1 in $(NH_4)_2H_3IO_6$ at about 120°K is not believed to have much to do with NH_4^+ motion. Rather it is believed to be due to a second relaxation mechanism's becoming prevalent at these low temperatures. That is, we can think of T_1 as

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[15] R. Pepinsky, K. Vedam, S. Hoshino, and Y. Okaya, Phys. Rev. **111**, 1508 (1958).

[16] G. Busch, W. Känzig, and W. M. Meier, Helv. Phys. Acta **26**, 385 (1953).

always due to two mechanisms and write

$$1/T_1 = (1/T_1)_{\mathrm{NH}_4^+} + (1/T_1)_X,$$

where X may represent paramagnetic impurities or perhaps proton motion in hydrogen bonds. The latter choice seems especially attractive due to the fact that when we measured T_1 in $Ag_2H_3IO_6$ [curve not shown], it was found below 170°K to have the same slope (an effective energy of about 350 cal/mole) and magnitude (2 sec at 150°K) as the low-temperature part of the T_1 curve for $(NH_4)_2H_3IO_6$.

PRE-EXPONENTIAL FACTORS

Of these ammonium compounds, the sulfate, bisulfate, and periodate exhibit discontinuities in T_1 at the phase transitions. Such behavior also gives a discontinuity in the τ_c vs $1/T$ plot. These facts, together with the necessary time-average configurational ordering in the ferroelectric phases of these substances, suggest that the transition may be accompanied by a cooperative increase of motion of the NH_4^+ ions, i.e., by what might be called dynamical order. To check this possibility, the pre-exponential factor τ_c^0, was determined for the high-temperature and low-temperature phases of each compound. τ_c^0 is defined by the expression

$$\tau_c = \tau_c^0 \exp(E_a/RT),$$

where E_a is the activation energy required to surmount the potential barrier as determined by the slope of the τ_c curve. It is expected that when the phase change involves a change from fairly independent motion of the NH_4^+ ions to a state where cooperative reorientation is important, τ_c^0 will increase from a value of 10^{-15}–10^{-12} sec appropriate to torsional oscillation of a NH_4^+ ion in a typical crystalline potential to a value perhaps orders of magnitude larger. That is to say, if cooperation between a number of ions becomes necessary for reorientation, the probability that an individual ion will reorient itself within a certain time will decrease, and τ_c^0 will increase. On the other hand, if the change in τ_c occurs only because the lattice parameters determining E_a are altered without introducing a dynamical coupling between separate NH_4^+ ions, no significant change in τ_c^0 can be expected.

The respective values of τ_c^0 in the high-temperature and low-temperature phases are 9×10^{-15} and 1×10^{-16} sec for $(NH_4)_2SO_4$, 1×10^{-14} and 3×10^{-14} sec for NH_4HSO_4, and 6×10^{-13} and 1×10^{-11} sec for $(NH_4)_2H_3IO_6$. (All values are subject to an order of magnitude uncertainty.) We see that only $(NH_4)_2H_3IO_6$ shows a significant increase in τ_c^0. Reorientation can be described adequately in terms of the motion of independent ions in some sort of effective potential, which changes when the lattice is modified at the ferroelectric transition. It is not necessary to invoke explicitly a many-body treatment or the idea of dynamical order.

DISCUSSION

It has been clearly demonstrated that in the solids studied here an anomalous change in proton spin-lattice relaxation of NH_4^+ ions goes hand in hand with a phase transition as determined by changes in electrical properties. With the possible exception of the high-temperature transition in NH_4HSO_4 and in $(NH_4)_2H_3IO_6$, the barrier to NH_4^+ rotation is higher in the ferroelectric than in the paraelectric phase, and we can say that the change to a ferroelectric phase involves a change in lattice structure[13,15] and hence alters the effective potential against which the motion occurs. Furthermore, the calculation of τ_c^0 has shown that reorientation can be described adequately in terms of the motions of independent ions, and that it is not necessary to invoke explicitly a many-body treatment or the idea of dynamical order.

In NH_4HSO_4 the low value of the potential hindering rotation in the ferroelectric phase suggests that the upper transition is not connected with NH_4^+ ordering, but is more likely due to a change in the equilibrium distribution of protons along the O—H—O bonds. The striking change in NH_4^+ motion at the lower Curie point, on the other hand, indicates the possibility that an ordering of these ions occurs in the low-temperature phase. The absence of a similar low-temperature Curie point in isomorphous $RbHSO_4$,[17] which suffers a second-order ferroelectric transition at −15°C, supports this view. The relatively small effect of the antiferroelectric phase transition on the potential hindering NH_4^+ in $(NH_4)_2H_3IO_6$ suggests a situation similar to the high-temperature transition in NH_4HSO_4, and that the transition is due chiefly to the ordering of protons in O—H—O bonds.[18] The fact that the isomorphous silver salt, $Ag_2H_3IO_6$, undergoes a transition to an antiferroelectric state at 207°K [19] supports this assumption. However, we ought not to overlook the possibility, as indicated by the increase in τ_c^0 and an antiferroelectric superstructure[20] different from that in $Ag_2H_3IO_6$, that some long-range cooperation between NH_4^+ ions may be in effect in the antiferroelectric phase. Indeed, the fact that τ_c^0 is relatively large on both sides of the transition and that some N—N distances are as small as 3.55 Å at room temperature,[10] suggests that cooperative NH_4^+ ion motion is important in both phases.

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[20] W. Känzig, Solid State Phys. **4**, 127, 159 (1957).