

Nuclear Magnetic Resonance in $(\text{NH}_4)_2(\text{BeF}_4)_x(\text{SO}_4)_{1-x}$ and Other Ferroelectric Systems

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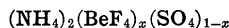
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The temperature dependence of fluorine and proton nuclear magnetic resonance (NMR) in polycrystalline samples of the solid solution $(\text{NH}_4)_2(\text{BeF}_4)_x(\text{SO}_4)_{1-x}$ has been measured for several x . This solid solution is ferroelectric for high and low x and is paraelectric in between. A sharp transition in the second moment of the F^{19} resonance was observed but found to be independent of x , while the ferroelectric properties are dependent on x . The proton NMR showed the nonequivalence of the NH_4 groups, but again the temperature dependence could not be correlated with the ferroelectric properties. Thus, the ferroelectric

behavior of this system cannot be associated with the appealing hypothesis of the freezing in of the vibrating NH_4 or BeF_4 groups. The temperature dependence of the proton NMR was also observed in the ferroelectric compounds $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ and NH_4HSO_4 . Similar conclusions can be drawn from these measurements as those given above. In some of the alums, the crystallographic phase transition is again not accompanied by any change in the proton resonance line. However, in $\text{N}_2\text{H}_5\text{Al}$ alum and NH_3OHAl alum, there is a very abrupt change in the NMR line at the temperature of the phase transition.

INTRODUCTION

ONE of the methods of investigating compounds that have phase transitions, in particular, ferroelectric compounds, is the nuclear magnetic resonance (NMR) technique. This method is particularly suited to the study of the rotational and vibrational properties of ionic groups that contain nuclei with spin $\frac{1}{2}$ (i.e., H^1 and F^{19}). The NMR technique has already been applied to several ferroelectric or closely related compounds.¹ In this paper, a number of ferroelectric compounds and one solid solution are studied by the NMR technique. In particular, ionic groups of high symmetry are studied (NH_4 , etc.). In the ferroelectric $(\text{NH}_4)_2\text{BeF}_4$, both the positive and negative ions are studied. The object of this work is to understand better the connection between the rotational properties of the ions and ferroelectricity.



Ferroelectricity has been discovered by Matthias and Remeika² in $(\text{NH}_4)_2\text{SO}_4$ and by Pepinsky and Jona³ in $(\text{NH}_4)_2\text{BeF}_4$. Although these compounds are not isomorphous,⁴ they are completely soluble in one another and the ferroelectric phase diagram has been investigated.⁵ The results for this mixed system, $(\text{NH}_4)_2(\text{BeF}_4)_x(\text{SO}_4)_{1-x}$, show that as x decreases from 1.0 to ≈ 0.8 the solid solution is ferroelectric and the Curie temperature T_c decreases from -96° to $\sim -130^\circ\text{C}$. For $0.8 > x > 0.2$, it is not ferroelectric. For $0.2 > x$, the solid solution is again ferroelectric. The space group in the three regions of x is different.^{4,5}

¹ R. Newman, *J. Chem. Phys.* **18**, 669 (1950); D. W. McCall, *ibid.* **26**, 706 (1957); R. D. Spence and J. Muller, *ibid.* **26**, 706 (1957); J. W. Emsley and J. A. S. Smith, *Arch. sci. (Geneva)* **12**, 122 (1959); R. Blinc, *J. Chem. Phys.* **31**, 849 (1959); R. Blinc and A. Prelesnik, *ibid.* **32**, 387 (1960); R. Blinc and I. Levstek, *J. Phys. Chem. Solids* **12**, 295 (1960); F. Holuj and H. E. Petch, *Can. J. Phys.* **38**, 515 (1960).

² B. T. Matthias and J. P. Remeika, *Phys. Rev.* **103**, 262 (1956).

³ R. Pepinsky and F. Jona, *Phys. Rev.* **105**, 344 (1957).

⁴ Y. Okaya, K. Vedam and R. Pepinsky, *Acta Cryst.* **11**, 307 (1958).

⁵ S. Hoshino, K. Vedam, Y. Okaya, and R. Pepinsky, *Phys. Rev.* **112**, 405 (1958).

Both the positive and negative ions have high symmetry and often partake in free or hindered rotation in the solid. By analysis of the temperature dependence of the NMR line shape, one can tell when the motion of the ions freezes in.⁶ Thus, an NMR study of the line shapes of the F^{19} and H^1 nuclei might be expected to help one to understand or to eliminate some of the possible causes of the ferroelectric phenomenon.

Blinc and Levstek⁷ have already reported on the temperature dependence of the proton resonance for $x=0$ and 1.0. For $x=0$, $(\text{NH}_4)_2\text{SO}_4$, they note some anomalous behavior in the proton line but it is not directly associated with the ferroelectric transition.

Using a slightly modified Pound, Knight, Watkins spectrometer, capable of operating at low rf levels, the temperature dependence of the line shape of the proton and fluorine NMR in polycrystalline samples was measured at 15.800 Mc/sec. The fluorine NMR lines were all simple absorption lines showing no structure. The second moment of the fluorine line vs temperature is plotted in Fig. 1.⁸ As can be seen, there is a sharp break in each curve. Since the proton resonances are independent of temperature in this region, the break in the F^{19} second-moment curve at -62°C can only be associated with the freezing in of the vibrating BeF_4 groups. This temperature is independent of the concentration and occurs for solid solutions that show no ferroelectric behavior as well as solid solutions that are ferroelectric for large and small x . There does ap-

⁶ The NMR line begins to broaden when the vibrational or tunneling frequency becomes less than the line width (~ 30 kc/sec). For general references to the field of NMR, see E. R. Andrew, *Nuclear Magnetic Resonance* (Cambridge University Press, New York, 1955); or G. E. Pake, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2.

⁷ R. Blinc and I. Levstek, *J. Phys. Chem. Solids* **12**, 295 (1960).

⁸ The author is indebted to S. Phillips and E. Morgan for determining x of the compounds used. Briefly, the following was done. They added HCl and boiled off HF . The Be was precipitated out as $\text{Be}(\text{OH})_2$. Then a standard SO_4^{2-} test was applied to the solution. The SO_4^{2-} and Be weights compared very well.

TABLE I. Proton nuclear magnetic resonance results for the alums studied.

Compound	Temperature of phase transition	Proton NMR results
$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$		A broad absorption from 24° to -196°C is obtained. The second moment is 26 gauss ² (~ 16 gauss peak to peak).
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	-202°C^{14}	A narrow line (~ 4 gauss pp) superimposed on a broad one similar to the above is observed between $+24^\circ$ and -196°C .
$\text{NH}_4\text{Ga}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	-163°C^a	The same results are obtained here as in the NH_4Al alum case.
$\text{NH}_3\text{CH}_3\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	-96°C^{14}	The high-temperature results are the same as in the above two compounds. However, somewhere between -162°C and liquid nitrogen temperature, the NMR broadens. Since this temperature is so far from the phase transition temperature, it was not pursued further.
$\text{N}_2\text{H}_5\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	-118°C^{14}	At high temperatures, the results are similar to the above three compounds. However, the narrow line is not seen at -113°C , while at -110°C the spectrum is the same as at room temperature. The difference in transition temperatures between the NMR and phase transition is probably fortuitous.
$\text{NH}_3\text{OHAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	-12°C^{14}	The results for this compound are the same as for $\text{N}_2\text{H}_5\text{Al}(\text{SO}_4)_2$, except that the narrow line disappears between -9° and -12°C .

^a T. G. Dunne (private communication).

pear to be a slight shift in the freezing in temperature for the deuterated compound.⁹

The proton resonance line shape for $x=0$ and 1.0 is in agreement with Blink and Levetek's⁷ work except that for $x=0$, the wide absorption they discuss (see their Fig. 1) occurs about 40°C lower than they reported. The reason for this difference is not known. It seems natural to associate the observed wide absorption with one-half the NH_4 groups freezing in and the rest still performing hindered rotations with a frequency >30 kc/sec, thus causing the narrow absorption. This interpretation gives a second moment consistent with the one observed, for example, in NH_4Cl .¹⁰ As x increases, the distinct wide absorption for $x=0$ decreases in size with respect to the narrow one, but is visible in the nonferroelectric phase and continues into the phase that is ferroelectric at large x . However, for $x=1.0$, it cannot be seen—at least not down to liquid nitrogen temperature.

Thus, the behavior of this system can be summarized as follows. At room temperature the NH_4 group is undergoing hindered rotations⁷ and this continues through the ferroelectric Curie temperature for all x . The wide absorption line of the proton resonance, although dependent on x , shows no correlation with the structural changes. Therefore, it appears not to be directly associated with the ferroelectric properties. However, in $(\text{NH}_4)_2\text{SO}_4$ the proton data shown the nonequivalence of the NH_4 groups since half of them freeze in above liquid nitrogen temperatures while the other half do not. The BeF_4 group ceases its hindered rotation at -62°C . Again, there is no correlation with the fact that T_c varies with x and compounds for certain

x are not ferroelectric at all. Since the compounds contain only two basic units and these measured rotational properties of both appear to have little correlation with the ferroelectric properties, one must look elsewhere for the cause of ferroelectricity.

$(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ AND NH_4HSO_4

The temperature dependence of the proton resonance in $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ and NH_4HSO_4 has also been measured. $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ is ferroelectric with $T_c = -182^\circ\text{C}$.¹¹ NH_4HSO_4 is ferroelectric between -3°

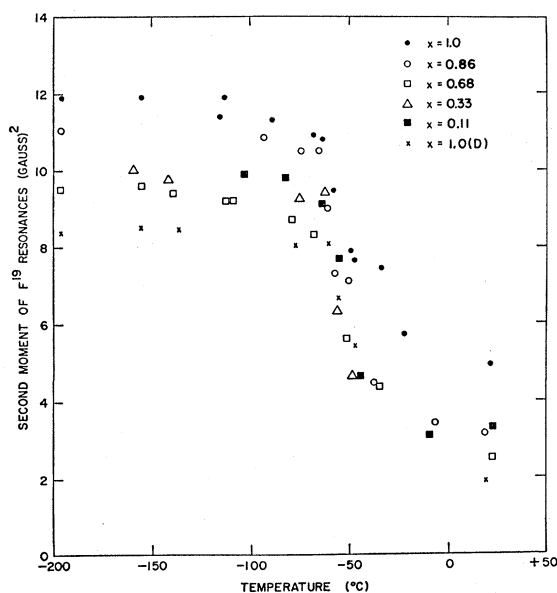


FIG. 1. The temperature dependence of the second moment of the F^{19} resonance in the mixed system $(\text{NH}_4)_2(\text{BeF}_4)_x(\text{SO}_4)_{1-x}$ for several x . The crosses are the results from $(\text{ND}_4)_2\text{BeF}_4$.

⁹ By careful intensity measurements of the proton resonances with respect to the F^{19} resonances in the deuterated and undeuterated $x=1.0$ compound, the deuterated compound was found to be 80% deuterated.

¹⁰ H. S. Gutowsky and G. E. Pake, J. Chem. Phys. **16**, 1164 (1948).

¹¹ F. Jona and R. Pepinsky, Phys. Rev. **103**, 1126 (1956).

and -119°C .¹² The former compound has a proton line width of 3 gauss between points of maximum slope. This does not change from room temperature to liquid nitrogen temperature. Thus, there is no freezing in of the NH_4 group at T_c . Also, no change in the line shape is found in NH_4HSO_4 through the two phase transitions to liquid nitrogen temperature. The second moment of the proton line is 7 gauss.² Again, the small second moment indicates a vibration frequency of the protons, 30 kc/sec above liquid nitrogen temperatures.

ALUMS

The situation in the alums is somewhat different.¹³ A large number of crystals in this group of compounds are ferroelectric.¹⁴ The general formula for the sulphate alums considered here is $M^{+1}A^{+3}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The crystals that were studied are listed in Table I along with the crystallographic transition temperature and the results. Several alums have already been studied by electron spin resonance¹⁵ and nuclear quadrupole¹⁶ techniques.

As can be seen from the general formula, there are always 12 water molecules to consider when measuring the proton NMR. However, in the KAl alum case (see Table I) the H_2O molecules are rigid at room temperature giving rise to a broad absorption line that should not, and does not, change with temperature. In NH_4Al alum, for example, at room temperature, the same broad absorption is observed and in addition, a narrow line is seen. Thus, it can be inferred that the narrow line is due to the vibrating NH_4 group and the broad absorption to the 12 H_2O molecules.¹⁷ The same pattern is observed at -196°C . Similar results are observed in the NH_4Ga alum to -196°C . In this alum, a nonferroelectric phase transition is observed at -163°C . Thus, it appears that the vibrational properties of the NH_4 group do not play an important role in the phase transitions in the NH_4 alums. A similar conclusion can be drawn in the case of the $\text{NH}_3\text{CH}_3\text{Al}$ alum as can be

seen in Table I. This alum has a ferroelectric phase transition at -96°C .

The opposite is observed in the $\text{N}_2\text{H}_5\text{Al}$ and NH_3OHAl alums. Again, at room temperature an absorption was observed that had a broad and narrow component. In both of these cases, there was a sharp transition between this spectrum and the one observed at low temperatures. In both of these cases, the change from the broad to the narrow spectrum occurred very suddenly within a three degree interval at a temperature corresponding to, or very close to, the previously reported phase transition.¹⁴ Thus, in the low-temperature phase the NH_3OH and N_2H_5 groups are rigid.

DISCUSSION AND SUMMARY

In some crystals, the fact that nothing happened to the NMR pattern at the Curie point was somewhat surprising. For example, neither the positive nor the negative ionic groups in $(\text{NH}_4)_2\text{BeF}_4$ freeze in at -96°C . Since there are only two ionic groups, the ferroelectric properties are probably associated with bending or stretching of the bonds. Again, in the mixed system $(\text{NH}_4)_2(\text{BeF}_4)_x(\text{SO}_4)_{1-x}$, three phases exist in different regions of x , and within the two ferroelectric phases the Curie point depends on x , but again freezing in of the NH_4 and BeF_4 groups could not be related to the phase transitions. However, in $(\text{NH}_4)_2\text{SO}_4$ the NMR does show the nonequivalence of the NH_4 group since half of them appear to freeze in above liquid nitrogen temperatures. This is consistent with x-ray data, which indicate that one NH_4 group has much shorter hydrogen-bond lengths than the other.¹⁸ The ferroelectric compound NH_4HSO_4 has three phases above liquid nitrogen temperature, but again the proton NMR does not show any change in going from one phase to another.

In the alums no cessation of motion occurred for the plus one ions in the NH_4 or ferroelectric NH_3CH_3 alums at or near the temperatures for which the phase transition occurred. However, in the NH_3OH and $\text{N}_2\text{H}_5\text{Al}$ alums, the proton NMR broadens at the same temperature as the phase transition. Thus, in the low-temperature phase, the plus one ion is rigid in the lattice. In both of these alums, the phase transition causes the crystals to shatter.¹⁴ Thus, it is difficult to tell if they are ferroelectric.

ACKNOWLEDGMENTS

The author is grateful to Professor R. Pepinsky for the mixed-system crystals used in this investigation, to Dr. S. Triebwasser for many stimulating discussions, and to Bernard Jenkins for technical assistance.

¹⁸ Y. Okaya (private communication).

¹² R. Pepinsky, K. Vedam, S. Hoshino, and Y. Okaya, *Phys. Rev.* **111**, 1508 (1958).

¹³ For a review of some alum properties, see J. Eisenstein, *Revs. Modern Phys.* **24**, 74 (1952).

¹⁴ R. Pepinsky, F. Jona, and G. Shirane, *Phys. Rev.* **102**, 1181 (1956); R. Pepinsky, K. Vedam, and F. Jona (to be published); and R. Pepinsky (private communication).

¹⁵ See K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The physical Society, London, 1955), Vol. 18, p. 305, for the references to the published work. Also, G. Burns, *Bull. Am. Phys. Soc.* **5**, 253 (1960).

¹⁶ G. Burns, *J. Chem. Phys.* **32**, 1585 (1960).

¹⁷ The broad absorption cannot be due to the NH_4 ion since the second moment of a frozen-in NH_4 ion is about 50 gauss² (see reference 10) and the second moment of the broad lines in the alums are all about equal to that found in the KAl alum.