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MAGNETIC RESONANCE OF F^{19} *NUCLEI IN THE FERROELECTRIC SUBSTANCE* $(NH_4)_2BeF_4$

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A polycrystalline sample of ammonium fluoroberyllate was investigated from −183° C up to room temperature and a single crystal of $(NH_4)_2BeF_4$ was investigated at room temperature by means of magnetic resonance of F^{19} nuclei. Reorientation of $(BeF_4)^{2-}$ ions has been established above the ferroelectric Curie point at −97° C. Reorientation of $(BeF_4)^{2-}$ ions is shown to occur about an axis fixed with respect to the crystal structure and coincident with the c axis of the crystal. The height of the potential barrier for the reorientation of the BeF_4 group is 9.5 ± 0.4 kcal/mole.

THE method of nuclear magnetic resonance (n.m.r.) is a comparatively simple and convenient method for studying the position and the degree of mobility of nuclei in crystals. We have used the n.m.r. method to study a number of ferroelectrics [1-3] and in some cases we have established the existence of a correlation between the ferroelectric properties and the change in the degree of mobility of certain groups occurring in the structure of these ferroelectric substances.

In the present work we have used the method of magnetic resonance of F^{19} nuclei to investigate samples of ammonium fluoroberyllate $(NH_4)_2BeF_4$, the ferroelectric properties of which below −97° C have been discovered by Pepinsky and Yona.[4] We have studied the temperature dependence of the second moment of the n.m.r. absorption line in the temperature range from −183° C up to room temperature. This dependence is shown in Fig. 1. The second moment of the n.m.r. absorption line is determined by the crystal structure and can be calculated by means of Van Vleck's formula.[5] In the case of ammonium fluoroberyllate the second moment can be written in the form of the following sum:

$$S_2 = S_2^{F-F} + S_2^{F-F'} + S_2^{F-Be} + S_2^{F-H}. \tag{1}$$

Here the first term on the right represents the contribution to the second moment of the dipole-dipole interaction between the F^{19} nuclei in a BeF_4 group, the second term represents the contribution due to the interaction between the F nuclei of neighboring BeF_4 groups, the third term represents the contribution of the Be^9 nuclei, and the fourth term represents the contribution of the protons of the NH_4 groups.

In the case of a polycrystalline sample these terms depend on the distances between the nuclei and their direct calculation by means of Van Vleck's formula gives for a fixed position of the nuclei

$$S_2^{F-F} = 316{,}3\cdot 10^{-48}\sum_i r_i^{-6}, \tag{2}$$

$$S_2^{F-Be} = 15.6\cdot 10^{-48}\sum_j r_j^{-6}, \tag{3}$$

$$S_2^{F-H} = 155.0\cdot 10^{-48}\sum_k r_k^{-6}, \tag{4}$$

where the subscripts i, j, k refer respectively to the distances from a given F nucleus to other fluorine nuclei belonging to the same BeF_4 group and to neighboring groups, from a given F nucleus to the beryllium nuclei, and from the F nucleus to the protons.

For the numerical evaluation of the second moment it was assumed that the BeF_4 group can be represented by a regular tetrahedron with the Be atom at the center, and that the F—F and the F—Be distance (cf. reference [6]) are respectively equal to 2.63 and 1.61 A. Since the complete structure of ammonium fluoroberyllate is as yet unknown, the calculation of the second and of the fourth terms in the sum S_2 presents certain difficulties. However, it is known that in general terms the structure of $(NH_4)_2BeF_4$ is close to the structure of the $(NH_4)_2SO_4$ crystal. Until very recently these structures were even considered to be isomorphic, but Pepinsky et al.[7] have shown

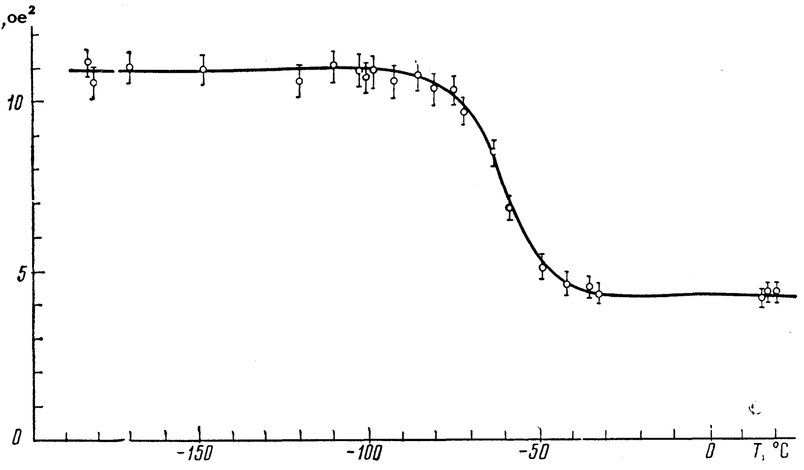

FIG. 1. Temperature dependence of the second moment of the magnetic resonance absorption line due to F^{19} nuclei in $(NH_4)_2BeF_4$.

that small differences between these structures exist even at room temperature. In carrying out the calculation it was assumed that the BeF_4 and NH_4 groups in ammonium fluoroberyllate are situated similarly to the SO_4 and NH_4 groups in the structure of $(NH_4)_2SO_4$. For this reason the calculation can be regarded only as a first approximation, particularly at low temperatures.

With respect to the NH_4 groups it was assumed that they undergo spherically isotropic reorientation within the whole range of temperatures studied. This follows from the experimental data of Blinc and Levstek[8] who drew this conclusion on the basis of studying $(NH_4)_2BeF_4$ by proton n.m.r. We have also observed proton resonance in $(NH_4)_2BeF_4$ at room temperature: the results obtained confirm the conclusion with respect to the isotropic reorientation of the NH_4 groups.

The results of the calculation are shown in the table. The calculations have been carried out for two cases. In the first case it was assumed that the BeF_4 groups are stationary—"rigidly" fixed in the structure, in the second case it was assumed that they undergo reorientation about axes fixed in the structure and coincident with the third order axes of the BeF_4 groups themselves. As can be seen from the table, the results of the calculation in the first case agree with the experimental values of the second moment in the range from −183° C to −100° C, and in the second case agree with the value of S_2 measured in the range from −20° C to +20° C. Therefore, the variation in the second moment within the range from −100° C to −20° C is a consequence of the usual rotational transition associated with a reorientation of the BeF_4 groups about fixed axes.

In order to answer the question as to the direction in the elementary crystal cell about which the BeF_4 groups undergo reorientation additional experiments were carried out on a single crystal sample of ammonium fluoroberyllate at room temperature. The sample was a crystal of 10 × 6 × 1.5 mm with well defined faces; the crystal axes were denoted by a, b, c, and their directions coincided with the directions of the axes of the elementary cell whose parameters are equal to a = 5.89 A, b = 10.39 A and c = 7.49 A.

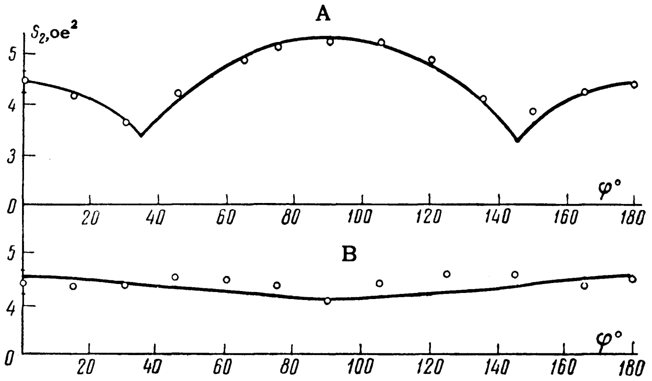

FIG. 2. Dependence of the second moment on the orientation of the single crystal of $(NH_4)_2BeF_4$ at t = 20°C: A – for a rotation about the a axis; B – for a rotation about the c axis. The angle φ is measured from the b direction.

BeF_4 groups	S_2^{F-F}	S_2^{F-Be}	$S_2^{F-F'}$	S_2^{F-H}	S_2	Experimental values of S_2	T, ° C
Stationary	2,835	0,90	0,10	6.25	10.1	11.0±0.5	to —183 from —100
Undergoing reorientation	0,71	0,25	0,03	3.10	4.1	4.2±0.2	to —20 from +20

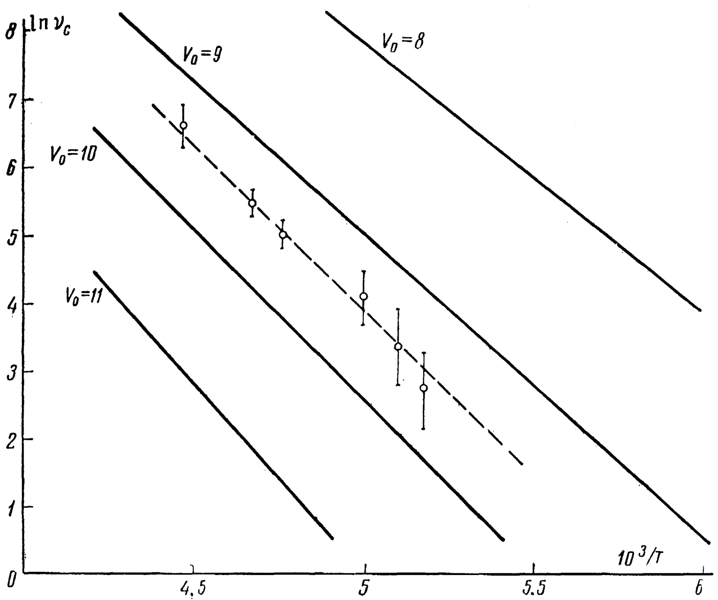

FIG. 3. Temperature dependence of the correlation frequency for the reorientation of the BeF_4 group in ammonium fluoreberyllate (the value of V_0 is given in kcal/mole).

We have studied the dependence of the second moment of the n.m.r. absorption line on the orientation of the crystal in a magnetic field as the crystal was rotated about the a and c axes. The results of this experiment are shown in Fig. 2. The solid lines on the same diagram represent the results of a numerical calculation of the angular dependence of the second moment on the assumption that all the BeF_4 undergo reorientation about the c axis. In this calculation we have used Van Vleck's formula for a single crystal; in order to take into account the reorientation of the BeF_4 groups we have averaged over all the motions occurring. The method of evaluating such an average in the general case is given by Andrew and Eades.[9]

The absence of any appreciable angular dependence of the second moment as the crystal is rotated about the c axis is explained by the fact that the BeF_4 groups themselves undergo reorientation about this axis. The small angular dependence which appears in the calculated curve is explained by the contribution to the second moment of the neighboring BeF_4 and NH_4 groups.

Thus, the experimental results shown above give evidence for the existence of reorientation ("hindered rotation") of the BeF_4 groups in the $(NH_4)_2BeF_4$ crystal about the c axis at temperatures above −100° C. The temperature dependence of the second moment enables us to determine the height of the potential barrier hindering the rotation of these groups. As Gutowsky and Pake[10] have shown, the temperature dependence of the second moment is given by the expression

$$S_2(T) = S_2^{\text{rig}} + (S_2^{\text{rot}} - S_2^{\text{rig}}) \cdot \tfrac{1}{2}\pi \tan^{-1} (\gamma \sqrt{S_2(T)}/2\pi\nu_c), \quad (5)$$

where S_2^{rig}, S_2^{rot} and $S_2(T)$ are respectively the second moments at low temperatures (when there is no reorientation), at high temperatures (above the rotational transition) and at the given temperature; ν_c is the correlation frequency for reorientation, which can be represented in the form[11,3]

$$\nu_c = \frac{1}{2\pi}\left(\frac{2V_0}{J}\right)^{1/2} \exp\left(-\frac{V_0}{kT}\right), \quad (6)$$

where k is the Boltzmann constant, T is the absolute temperature, V_0 is the height of the potential barrier for reorientation, J is the moment of inertia equal to 219.1×10^{-40} $g\text{-}cm^2$ for the rotation of the regular BeF_4 tetrahedron about its threefold axis. This formula is valid for the case of the so-called classical reorientation when the tunnel effect can be neglected. As Das[11] has shown, the tunnel effect can always be neglected when the nuclei undergoing reorientation are heavier than protons. Thus, the use of formula (6) in our case is completely justified.

Figure 3 shows the dependence of the correlation frequency on the temperature for different values of V_0; it also shows the experimental values of ν_c calculated by means of formula (5). The experimental values agree well with the calculated ones for $V_0 = 9.5 \pm 0.4$ kcal/mole, and this once again confirms the classical mechanism for the reorientation of the BeF_4 groups.

The correlation between the beginning of the decrease in S_2 at a temperature of −100° C and the Curie point of ammonium fluoroberyllate is noteworthy. At the present time it is difficult to say whether this correlation indicates some deeper relation between the decrease in the mobility of the BeF_4 groups at temperatures below −100° C and the existence of spontaneous electric polarization in $(NH_4)_2BeF_4$ at these temperatures. It is also possible to assume that the appearance of spontaneous polarization is accompanied by a change in the relative position of the structural elements of the lattice, and also by deformations of the structure elements themselves. The latter possibility, apparently, agrees with the deformation of the electronic shells of the $[NH_4]^+$ and $[BeF_4]^{2-}$ ions found by Blinc[8] in the course of his investigation of the infrared spectra of ammonium fluoroberyllate below the Curie point. The appearance of spontaneous polarization in this crystal can, thus, be related to the combined effect of these factors. As regards the mechanism responsible for the appearance of polarization as a result of the ordering of the rotational transitions of the NH_4 groups proposed by Matthias and Remeika,[12] in the light of the proton magnetic resonance data[8] we can be dealing only with the ordering of the positions or of the polarization of the ammonium ions themselves, since the nature of the reorientation of these ions does not change as a result of passage through the Curie point.

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