

INVESTIGATION OF REORIENTATION OF THE GUANIDINIUM ION IN THE FERRO-ELECTRIC $C(NH_2)_3 \cdot Al(SO_4)_2 \cdot 6H_2O$ BY THE NUCLEAR MAGNETIC RESONANCE METHOD

A. G. LUNDIN, G. M. MIKHAĬLOV, and S. P. HABUDA

Physics Institute, Siberian Division Academy of Sciences; The Siberian Technological Institute

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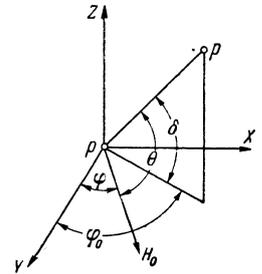
Reorientation of the $[C(NH_2)_3]^+$ ion has been detected in the ferroelectric $C(NH_2)_3 \cdot Al(SO_4)_2 \cdot 6H_2O$ at temperatures above $130^\circ K$ by means of nuclear magnetic resonance. The temperature dependence of the second moment of the absorption line of a polycrystalline sample has been examined between 90 and $400^\circ K$. The height of the potential barrier for the reorientation of the $C(NH_2)_3$ group has been estimated and some conclusions are drawn regarding the reorientation mechanism.

It has been remarked in the literature^{1,2} that the properties of the ferroelectric guanidine aluminum sulfate hexahydrate (GASH) are determined to a marked degree by the peculiarities of the guanidinium ion $[C(NH_2)_3]^+$. On the basis of the structural investigation of Geller and Booth³ it has been noted that in the GASH structure this ion is but weakly bound to its surroundings and that this could lead to its mobility.

In the present paper the question of the mobility of the guanidinium ion is investigated by means of the nuclear magnetic resonance (NMR) of its protons. The apparatus used for these studies has been described earlier.⁴ Temperature measurements were carried out in a special dewar similar to that described by Gutowsky et al.⁵ For the experiments a monocrystal of GASH was used, cut into the shape of a cube oriented along the principal axes, with dimensions $8 \times 8 \times 8$ mm (the $\bar{3}$ axis of the GASH crystal was taken as the z axis, and the y axis was taken perpendicular to the prism face). For studying polycrystalline samples a powdered GASH was compressed under a pressure of 100 kg/cm^2 into a cylindrical tablet of diameter 10 mm and height 12 mm.

The spectra were recorded in a magnetic field $H_0 = 3000$ oe with a time constant of 1–2 sec and field scanning rates of 0.08 and 0.04 oe/sec. Field modulation amplitude was 0.8 oe. In order to avoid saturation in the monocrystal at low temperatures the rf oscillator was adjusted to the lowest possible power level at which stability could be maintained. With polycrystalline samples saturation was observed in the same temperature range at significantly higher power levels.

FIG. 1. Definition of angles for different orientations of the vector pp in the magnetic field.



It is well known that systems containing relatively isolated pairs of nuclei, for example pairs of protons in molecules of water of crystallization, give an NMR spectrum in the form of a doublet with a component separation equal to⁶

$$\begin{aligned} \Delta H &= 3\mu r^{-3} (3 \cos^2 \theta - 1) \\ &= 3\mu r^{-3} [3 \cos^2 (\varphi - \varphi_0) \cos^2 \delta - 1]. \end{aligned} \quad (1)$$

Here μ is the magnetic moment of the nucleus (proton), r is the distance between the protons, θ is the angle between the direction of the proton-proton (pp) vector and the direction of the external magnetic field H_0 , φ is the angle between H_0 and one of the crystal axes that lie in the plane of rotation of the crystal (or the magnetic field relative to the crystal⁴), φ_0 is the angle between this axis and the projection of the vector pp on the plane of rotation, and δ is the angle between the vector pp and the plane of rotation (Fig. 1). By measuring H_0 for different values of φ , one can determine r , φ_0 , and δ .

In the elementary cell of GASH there are three formula units $C(NH_2)_3 \cdot Al(SO_4)_2 \cdot 6H_2O$,³ i.e., 18 molecules of H_2O ; however, in conformity with the symmetry of the crystal, these pertain to three coplanar, but not collinear, pp vectors.^{7,8}

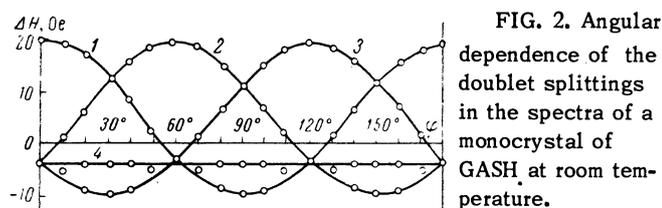


FIG. 2. Angular dependence of the doublet splittings in the spectra of a monocrystal of GASH at room temperature.

Thus the proton resonance spectrum of GASH should be composed of a sum of the spectra of the water protons and the protons of the $C(NH_2)_3$ group.

In Fig. 2 is shown the room temperature dependence of the doublet splitting of the proton resonance spectra of a GASH monocrystal on the orientation of the magnetic field rotating about the z axis, which is perpendicular to the basal plane. Curves 1, 2, 3 pertain to the values $r = 1.63 \pm 0.015 \text{ \AA}$, $\delta = 0$, and φ_0 equal respectively to 0, 60, and 120°. (The angles are measured from the y axis of the GASH monocrystal.) This gives three pp vectors lying in the basal plane at an angle of 60° with one another. Curve 4 corresponds to a pp vector that is situated perpendicular to the plane of the base with $r = 2.18 \pm 0.015 \text{ \AA}$, $\varphi_0 = 0$, and $\delta = 90^\circ$. Just the same orientational dependence for the fourth vector is obtained if it is located in the basal plane and rotates in this plane at a sufficiently high rate, since⁹ in this case one also obtains a doublet with a splitting between components:

$$\Delta H = \frac{3\mu}{2r^3} [3 \cos^2(\varphi - \varphi_0) \cos^2 \delta - 1]. \quad (2)$$

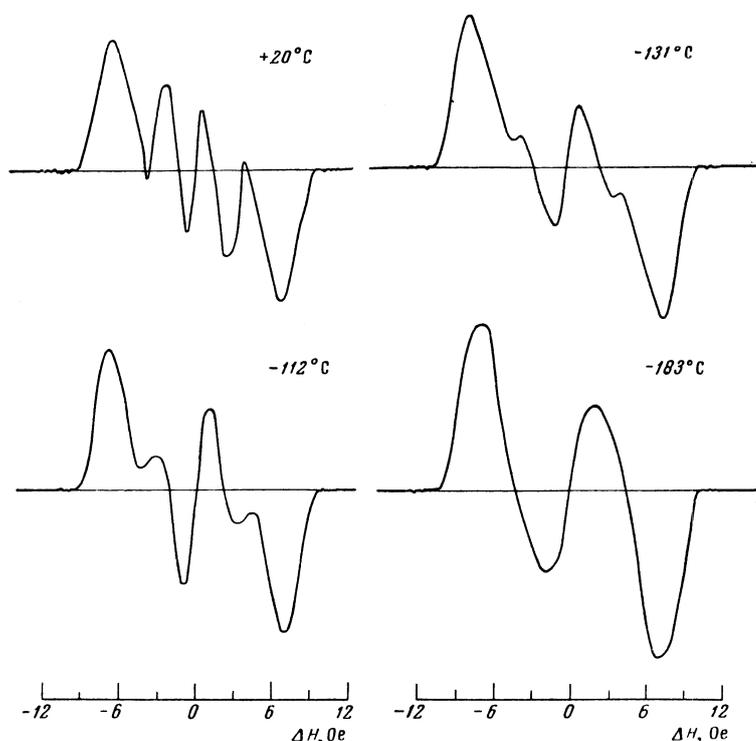


FIG. 3. Derivative proton resonance spectra of a monocrystal of GASH at different temperatures.

Here the symbols mean the same as in Eq. (1), but now the angles φ_0 and δ describe not the direction of the vector pp , but the direction of the axis of its reorientation. In this case curve 4 corresponds to $r = 1.73 \pm 0.02 \text{ \AA}$, $\varphi_0 = 0$, and $\delta = 90^\circ$.

The intensities of the spectral components were determined by the areas under the resonance peaks. It turned out that the intensity of the peak corresponding to curve 4 of Fig. 2 amounted to $\frac{1}{3}$ of the total intensity of the spectrum. Considering that the z axis, perpendicular to the basal plane, is a threefold axis and that the number of water protons amounts to $\frac{2}{3}$ of the total number of protons in the GASH crystal, we come to the conclusion that curves 1, 2, and 3, which account for $\frac{2}{3}$ of the intensity of the spectrum, correspond to different vectors pp of the waters of crystallization, and curve 4 corresponds to the $C(NH_2)_3$ group. Thus the investigation of the angular dependence of the spectra at room temperature leads to the conclusion that the vectors pp of the waters of crystallization lie in the basal plane at angles of 60° with one another and have a proton separation of $r = 1.63 \pm 0.015 \text{ \AA}$, and the vectors pp of the group $C(NH_2)_3$ are distributed perpendicular to the basal plane with $r = 2.18 \pm 0.015 \text{ \AA}$, or rotate in the basal plane, in which case $r = 1.73 \pm 0.02 \text{ \AA}$. Analogous conclusions have been obtained also by Spence and Muller.⁷

In reference 8, indirect evidence was presented that rendered unlikely the supposition that the vec-

tors pp of the guanidinium group were perpendicular to the basal plane. On the other hand, preliminary low-temperature investigations of polycrystalline GASH by NMR were reported by McCall.¹⁰ A broadening of the spectrum was observed, which could indicate a cessation of any kind of internal motion leading at room temperature to a decrease in the line width. It was assumed that this motion was associated with the guanidinium ion. However, direct demonstration of the presence of mobility of the guanidinium ion at room temperature was not given. We obtained a direct demonstration of the presence of reorientation of this ion in the basal plane by a study of the temperature dependence of the proton resonance spectrum of GASH.

The temperature dependence of the form of the spectrum was first studied in monocrystalline samples of GASH. An orientation of $\varphi = 30^\circ$ was chosen (see Fig. 2), for which the spectrum consists of two doublets: An outer one, which in reality is an unresolved dual doublet belonging to H_2O , and an inner one belonging to the guanidinium ion. The derivative NMR spectrum for this orientation at room temperature is shown in Fig. 3.

The form of the spectrum does not change when the temperature is reduced to $-100^\circ C$. Below this temperature the intensity of the outer doublet begins to increase at the expense of the inner one, and by $-145^\circ C$ the inner doublet has completely disappeared. Moreover, the spectrum hardly changes as the temperature is lowered down to $-183^\circ C$.

An investigation of the angular dependence of the spectra of a monocrystal of GASH at $-183^\circ C$ showed that at this temperature the doublet corresponding to curve 4 in Fig. 2 is absent, whereas the intensity of the doublets corresponding to the curves 1, 2, and 3 in Fig. 2 has increased by $\frac{1}{3}$, in comparison with the intensity of the same doublets at room temperature.

This means that at temperatures below $-145^\circ C$ the vectors pp of the NH_2 group of the guanidinium ion are situated at angles of 60° with one another and this "triangle" of the vectors pp is oriented in just the same way as the triangle of the vectors pp of the waters of crystallization. No splitting of the lines caused by an inequality of the proton separation in H_2O and NH_2 was ever observed.

Thus, at temperatures above $-145^\circ C$, the guanidinium ion $[C(NH_2)_3]^+$, existing as a planar group in agreement with the structure investigations of Geller and Booth,³ reorients itself around the z axis, which is perpendicular to the basal plane of GASH, and this leads to a change in the shape and width of the NMR spectrum.

One can describe the effect of the reorientation on the NMR line width in terms of the "correlation time" of the motion τ_C introduced by Bloembergen, Purcell, and Pound,¹¹ which is a measure of the time interval during which a molecule (or a group of atoms within a molecule that contains the nuclei under study) completes a transition from one state of motion to another (for rotational motion τ_C is equal to the time necessary to rotate about an angle of one radian).

Such transitions can be transitions between vibrational states in the same potential well, transitions between vibrational states from one well to another by means of the quantum mechanical tunnel effect, or transitions to levels lying above a potential barrier. In this case the molecule rotates (reorients itself) in conformity with classical theory as long as it does not return to some vibrational level of one of the wells.

Since the amplitude of the vibrational motions is not large, they give only a small contribution to the change in line width.¹² Hence they can be left out of consideration. Nor shall we consider the possibility of reorientation by means of the tunnel effect, since from the calculations of Das¹³ it follows that this can be neglected in comparison to the classical reorientation for rotating groups containing nuclei that are heavier than protons.

The probability of rotation of a molecule through an angle $2\pi/N$, where N is the multiplicity of the periodic potential barrier V_0 , according to Das,¹³ in the classical rotation case is*

$$W = (N/2\pi) (2V_0/J)^{1/2} \exp(-V_0/kT). \quad (3)$$

Here J is the moment of inertia of the reorienting group, k is the Boltzmann constant, and T is the absolute temperature. From this it is easy to calculate the time necessary for rotation through an angle $2\pi/N$, which is inversely proportional to W , and the correlation time τ_C necessary to make a rotation through one radian.

Instead of τ_C it is more convenient to use an expression for the correlation frequency of reorientation ν_C , related to the correlation time by the equation $2\pi\nu_C\tau_C = 1$. For this we find

$$\nu_C = (1/2\pi) (2V_0/J)^{1/2} \exp(-V_0/kT). \quad (4)$$

The correlation frequency of reorientation, on the other hand, can be determined from experimental data by the dependence of the second moment of the NMR line of a polycrystalline sample on the basis of an expression assumed by Gutowsky and Pake.¹⁴

*In Das¹³ this expression is erroneously written in a form that differs from Eq. (3) by the factor $\frac{1}{2}$.

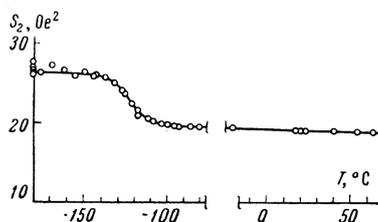


FIG. 4. Temperature dependence of the second moment of the NMR line of polycrystalline GASH.

$$\ln \nu_c = \ln \frac{\gamma S_2^{1/2}}{2\pi} - \ln \tan\left(\frac{\pi}{2} \frac{S_2 - V_2}{U_2 - V_2}\right), \quad (5)$$

where S_2 is the second moment of the absorption line⁹ at a given temperature, V_2 and U_2 are the second moments at higher and lower temperatures, and γ is the gyromagnetic ratio. A comparison of (5) and (4) makes it possible to determine the height of the potential barrier V_0 for classical reorientation.

Equation (5) is derived for the case in which the second moment is completely caused by groups reorienting themselves above a certain temperature. It is not possible to use it for a calculation of the correlation frequency from experimental data on the dependence of the second moment of the NMR line of polycrystalline GASH since the second moment in this case consists of two parts:

$$S_2 = \frac{2}{3} S_2(\text{H}_2\text{O}) + \frac{1}{3} S_2(\text{NH}_2), \quad (6)$$

where $S_2(\text{H}_2\text{O})$ is the second moment arising from protons of "motionless" molecules of H_2O , and $S_2(\text{NH}_2)$ is the second moment caused by protons of the $[\text{C}(\text{NH}_2)_3]^+$ ions. The coefficients in the right member of Eq. (6) are proportional to the relative numbers of protons occurring in water molecules and guanidinium ions in a crystal of GASH.

In order to make use of Eq. (5), it is necessary to eliminate from S_2 the constant component $S_2(\text{H}_2\text{O})$ belonging to water molecules. From Eq. (6) we obtain

$$S_2(\text{NH}_2) = 3S_2 - 2S_2(\text{H}_2\text{O}), \quad (6')$$

and substituting into (5),

$$\ln \nu_c = \ln \frac{\gamma (3S_2 - 2S_2(\text{H}_2\text{O}))^{1/2}}{2\pi} - \ln \tan\left(\frac{\pi}{2} \frac{S_2 - V_2}{U_2 - V_2}\right). \quad (5')$$

Figure 4 shows the experimental temperature dependence of the second moment for powdered GASH. The value of $S_2(\text{H}_2\text{O})$ can be calculated using the data presented above on the inter-proton distance in the water molecules and the data on the distribution of the other protons in GASH⁸ with the aid of the formula of Van Vleck.¹⁵

Calculation of $S_2(\text{H}_2\text{O})$ gives for GASH the value 21.5 oe^2 , of which the intra-molecular part, aris-

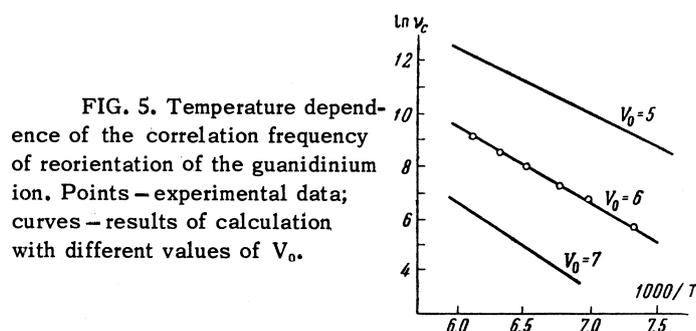


FIG. 5. Temperature dependence of the correlation frequency of reorientation of the guanidinium ion. Points—experimental data; curves—results of calculation with different values of V_0 .

ing from the interaction between the pair of protons in H_2O amounts to 19.5 oe^2 , and the intermolecular part, caused by the interaction with protons from other water molecules and $\text{C}(\text{NH}_2)_3$ groups, amounts to 2 oe^2 . The same magnitude for the intermolecular part is also obtained from the experimental data on the width of the resolved peaks.

It should be noted that if we also calculate $S_2(\text{NH}_2)$ in the same manner (using Van Vleck's formula and knowing the structure of the guanidinium ion), then the theoretical value of the second moment of a polycrystalline sample of GASH, calculated from Eq. (6), turns out to be lower than the experimentally observed magnitude of the second moment of GASH by approximately 10% both before and after the rotational transition. However, this discrepancy, the source of which is not clear, practically makes no difference in the magnitude of the height of the potential barrier as calculated below.

In Fig. 5 are presented the experimental values of the correlation frequency at various temperatures, based on Eq. (5'). Also indicated is the theoretical temperature dependence calculated from Eq. (4) for $V_0 = 5, 6, \text{ and } 7 \text{ kcal/mole}$. The moment of inertia of the guanidinium ion was calculated on the basis of the known structure of this ion³ and the data of the present paper on the inter-proton distance in the NH_2 groups and is $J = 167.88 \times 10^{-40} \text{ g-cm}^2$.

The excellent agreement between the experimental data and the values calculated from Eq. (4) with $V_0 = 6 \text{ kcal/mole}$ attests to the correctness of the model assuming classical reorientation of the guanidinium ion in the GASH structure.

The existence of reorientation of the guanidinium ion at temperatures above -145°C is important for the explanation of the ferroelectrical properties of GASH. In particular, it is possible that the strong increase in polarization time of GASH at low temperatures¹⁶ is associated with the decrease in mobility of the $\text{C}(\text{NH}_2)_3$ group.

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219