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# Proton dynamics in hydrated gallium sulfate\*

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The proton relaxation times in the laboratory,  $T_1$ , and rotating frame,  $T_{1\rho}$ , and the dipolar relaxation time  $T_{1D}$  have been measured in hydrated gallium sulfate. A proton to gallium cross-relaxation mechanism has been observed. By employing spin thermometry the previous cw work has been reanalyzed and the existence of the  $\text{OH}_3^+$  group confirmed.

## INTRODUCTION

The oxonium ion in solids has been studied by inelastic neutron scattering<sup>1</sup> and nuclear magnetic resonance.<sup>2-7</sup>

The study of hydrated gallium sulfate is of more than intrinsic interest because it has bearing on a problem, basic in geochemistry, that the water of hydration in alunite and isomorphous minerals is uncommonly variable. The structure of hydrated gallium sulfate is so closely related to that of alunite that the same considerations as to the state of the water of hydration are likely to apply.

NMR techniques were used to study hydrated gallium sulfate,<sup>4</sup> and the results indicated the existence of  $\text{OH}_3^+$ . In the present work spin thermometry and various pulse techniques have been employed to obtain a better understanding of the proton dynamics in this system. With the understanding obtained the previous cw work has been reanalyzed and the existence of  $\text{OH}_3^+$  confirmed.

## STRUCTURE

It has been found from x-ray diffraction studies of gallium sulfate<sup>8</sup> and from the NMR study<sup>4</sup> that the water of hydration may exist as  $\text{OH}_3^+$  and  $\text{OH}^-$  in which case the formula should be written as  $(\text{H}_3\text{O})\text{Ga}_3(\text{OH})_6(\text{SO}_4)_2$ . Projections of the heavy atoms in the structure along  $[010]$  and  $[001]$  are shown in schematic form in Fig. 1; atoms are labeled according to Johansson's nomenclature.<sup>8</sup> The  $\text{OH}_3^+$  is thought to be centered on the  $\text{O}_4$  and probably is a triangular configuration forming hydrogen bonds with three  $\text{O}_3$  which are in a plane, with the  $\text{O}_4$ - $\text{O}_3$  distance equal to 2.82 Å. The  $\text{OH}_3^+$  group could also form hydrogen bonds with the  $\text{O}_2$ , and the  $\text{O}_4$ - $\text{O}_2$  distance is equal to 2.92 Å. The  $\text{O}_3$  are associated with one hydrogen each to form hydroxyl groups. This hydrogen forms a hydrogen bond to  $\text{O}_1$  where the  $\text{O}_3$ - $\text{O}_1$  distance is 2.88 Å.

## EXPERIMENTAL

To investigate the dynamics and structure further the relaxation rates in the laboratory ( $T_1^{-1}$ ) and the rotating frame ( $T_{1\rho}^{-1}$ ) and the dipolar relaxation rate ( $T_{1D}^{-1}$ ) have been measured.

The sample was prepared as previously reported.<sup>4</sup> The  $T_{1D}$  measurements were made using a  $90^\circ$ - $45^\circ$ - $45^\circ$  pulse sequence on a Bruker BK R321s spectrometer.

Using standard pulse techniques,  $T_1$  and  $T_{1\rho}$  were measured by a Spin Lock CP-2 spectrometer at 17.13 MHz.

## RESULTS AND DISCUSSION

The  $T_{1\rho}$  and  $T_{1D}$  results suggest at least one new mechanism which was not indicated by the previous<sup>4</sup>  $T_1$  data. This new mechanism is predominant in the  $T_{1\rho}$  and  $T_{1D}$  relaxation below the inverse temperature  $\beta = (1000/T)^\circ\text{K}^{-1}$ ,  $\beta = 4$ . As can be seen from Fig. 2 the  $T_{1\rho}^{-1}$  and  $T_{1D}^{-1}$  are only mildly temperature dependent in this region. This type of dependence can be explained by a proton cross relaxation to the gallium spin and will be discussed later in the paper.

The  $T_1^{-1}$  data indicate that three mechanisms affect the relaxation rate in the temperature range studied. At low temperatures one process has an apparent activation energy of  $0.5 \pm 0.2$  kcal/mole. This activation energy is typical for an intrabond motion<sup>10</sup> and is likely due to the  $\text{OH}^-$  group. The second process has an apparent activation energy of  $1.8 \pm 0.2$  kcal/mole. This can be shown to be caused by the reorientation of the  $\text{OH}_3^+$  ion.

Using a BPP perturbation theory formula and a H-H distance of 1.72 Å for the  $\text{OH}_3^+$  group the calculated rate at the minimum for a  $\text{C}_3$  rotation is 132 msec<sup>-1</sup> at 17.13 MHz. Since there are six  $\text{OH}^-$  groups for every  $\text{OH}_3^+$  the rate can be written

$$R = \frac{1}{3}R(\text{OH}_3^+) + \frac{2}{3}R(\text{OH}^-). \quad (1)$$

The  $R(\text{OH}^-)$  contribution is likely a factor of 10 smaller than  $R(\text{OH}_3^+)$  therefore  $R \sim \frac{1}{3}R(\text{OH}_3^+)$ . Within experimental accuracy (10%) at the minimum the agreement is good for 17.13 MHz. These two relaxation rates if extrapolated for  $T_{1\rho}^{-1}$  become dominant in the region below  $\beta \approx 13$ ; therefore they are not evident in the present  $T_{1\rho}^{-1}$  data which are above  $\beta \approx 13$ .

At higher temperatures another process is apparent. From the  $T_{1\rho}$  data an activation energy of  $2.2 \pm 0.3$  kcal/mole was derived. This can be attributed to a general tumbling of the  $\text{OH}_3^+$ .

To interpret the low temperature  $T_{1\rho}$  and  $T_{1D}$  data,  $H_1$  dependencies of  $T_{1\rho}$  were taken and the data analyzed using spin thermometry.<sup>11</sup>

At exact resonance and for fields ( $H_1$ ) of the order of the local field

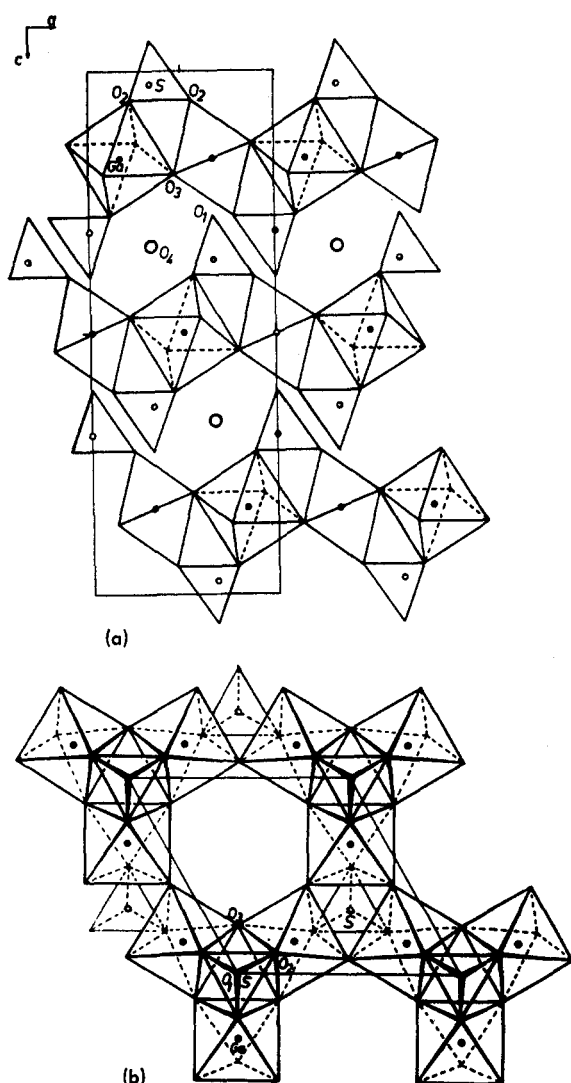


FIG. 1. Crystal structure of hydrated gallium sulfate.  $\circ$ , sulfur;  $\bigcirc$ , oxygen;  $\bullet$ , gallium.

$$T_{1\rho}^{-1} = T_{1x}^{-1} \left( \frac{H_1^2}{H_L^2 + H_1^2} \right) + T_{1D}^{-1} \left( \frac{H_L^2}{H_L^2 + H_1^2} \right) \quad (2)$$

where  $T_{1x}^{-1}$  and  $T_{1D}^{-1}$  can contain many terms to account for all possible motions including cross relaxation. Usually a plot of  $T_{1\rho}^{-1}(H_r^2 + 1)$  vs  $H_r^2$ , where  $H_r^2 = H_1^2/H_L^2$ , is made and the intercept gives  $T_{1D}^{-1}$  and from the slope  $T_{1x}^{-1}$  is obtained. If one of the contributing terms in  $T_{1x}^{-1}$  has  $H_1^2$  dependency then this term will alter the intercept on the graph such that  $T_{1\rho}^{-1}(0)$  is not equal to  $T_{1D}^{-1}$  but is equal to  $T_{1D}^{-1} + \text{constant}$ . In the present case the cross relaxation  $T_{1x}^{-1}(\text{CR})$  can be written<sup>11</sup>

$$T_{1x}^{-1}(\text{CR}) = \gamma^2 M_2(\text{Ga-H}) T_1(\text{Ga}) / [1 + \gamma^2 H_1^2 T_1^2(\text{Ga})].$$

Two limiting cases occur when  $\gamma^2 H_1^2 T_1^2 \ll 1$  and  $\gamma^2 H_1^2 T_1^2 \gg 1$ . For case  $\gamma^2 H_1^2 T_1^2 \ll 1$  we may write

$$T_{1\rho}^{-1}(H_r^2 + 1) = [T_{1x}^{-1} + \gamma^2 M_2(\text{Ga-H}) T_1(\text{Ga})] H_r^2 + T_{1D}^{-1} \quad (3)$$

and for case  $\gamma^2 H_1^2 T_1^2 \gg 1$  we have

$$T_{1\rho}^{-1}(H_r^2 + 1) = (T_{1x}^{-1} H_r^2 + [T_{1D}^{-1} + M_2(\text{Ga-H}/H_L^2 T_1(\text{Ga}))]). \quad (4)$$

The cross-relaxation effect also appears in the evaluation of the local field. From cw techniques the local

field is given by<sup>12</sup>

$$H_L'^2 = \frac{1}{3} [M_2(\text{H-H}) + M_2(\text{H-Ga})]. \quad (5)$$

Using pulse techniques<sup>11</sup> the local field can be determined independently of the cw. The gallium dipolar contribution is about  $0.02 \text{ G}^2$  and can be ignored. The difference ( $\Delta$ ) between the cw and pulse methods for the square of the local field, assuming no quadrupolar interactions, is

$$\Delta = \frac{2}{3} M_2(\text{H-Ga}) = H_L'^2(\text{cw}) - H_L'^2(\text{pulse}) \\ = \frac{2}{3} \gamma_{\text{Ga}}^2 S(S+1) \hbar^2 \sum_{jk'} \frac{(1 - 3 \cos^2 \theta_{jk'})^2}{r_{jk'}^6}, \quad (6)$$

where the notation is the same as that of Abragam.<sup>12</sup> Since  $\gamma_{\text{Ga}}^2$  is of the same order as  $\gamma_{\text{H}}^2$  and  $r_{jk'}$  is likely to be of the order  $3 \text{ \AA}$ , this difference could be large ( $> 1 \text{ G}^2$ ). The data, which are summarized in Table I, for two temperatures, are analyzed to determine the extent of cross relaxation.

At  $\beta = 5.9$ , Fig. 3, only one mechanism appears to dominate  $T_{1\rho}$ . Since  $T_{1\rho}^{-1}(0) \sim T_{1D}^{-1}$  this relaxation mechanism is in the white region of its spectral density. From the experiment  $\Delta = 1.8 \text{ G}^2$  therefore the coupling between the gallium and protons is strong and this mechanism could be cross relaxation. If this mechanism is white, then  $T_{1x}^{-1}$  should be equal to  $T_{1D}^{-1}$  at high fields. Within experimental error this is true and the analysis appears self-consistent.

At  $\beta = 13$ , Fig. 4, one would expect that the  $\text{OH}_3^+$  reorientation should become more effective. It would also be in the white region. Since  $T_{1\rho}(0) \sim T_{1D}$  this relaxation mechanism is frequency independent. The coupling between the gallium and protons may be weaker due to changes in the  $T_1(\text{Ga})$  and as a result the cross relaxation becomes

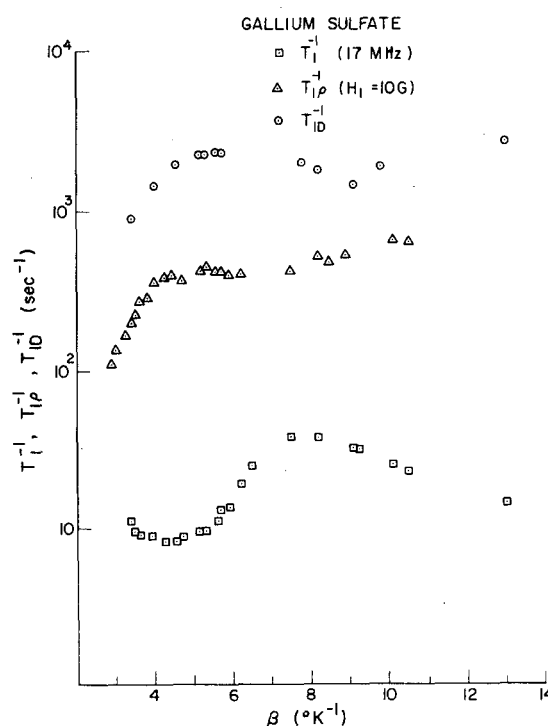


FIG. 2.  $T_1^{-1}$ ,  $T_{1\rho}^{-1}$ ,  $T_{1D}^{-1}$  vs  $\beta$ .

TABLE I. Experimental values at  $\beta = 5.9$  and  $\beta = 13.0$ .

$\beta$ (°K <sup>-1</sup> )	$T_{1\rho}^{-1}(0)$ (msec <sup>-1</sup> )	$T_{1\rho}^{-1}$ (msec <sup>-1</sup> )	$T_{1\rho}^{-1}(H_1 \gg H_r)$ (msec <sup>-1</sup> )	$T_{1x}^{-1}$ (msec <sup>-1</sup> )	$\Delta$ (G <sup>2</sup> )
5.9	2.5 ± 0.3	2.3 ± 0.2	0.44 ± 0.05	0.52 ± 0.05	1.8 ± 0.9
13	3.1 ± 0.3	2.6 ± 0.2	0.85 ± 0.09	0.77 ± 0.08	0.5 ± 0.3

weaker. Again  $T_{1x}^{-1} \sim T_{1\rho}^{-1}$  (high field) this indicates that the cross relaxation is weak as the  $T_{1x}^{-1}$  value is  $T_{1x}^{-1} = \frac{1}{3}T_{1x}^{-1}(\text{OH}_3^+ \text{ reorientation}) + T_{1x}^{-1}(\text{cross relaxation})$  and  $\frac{1}{3}T_{1x}^{-1}(\text{OH}_3^+)$  from theoretical calculations is about equal to the experimental value. This analysis does not prove conclusively that there is cross relaxation but it does make this mechanism appear to be probable. At much lower temperatures the cross relaxation should become frequency dependent and if  $R(\text{OH}_3^+)$  is slow the cross-relaxation term may be seen.

Using the preceding mechanisms it is now possible to reanalyze the cw data previously done. Assuming that the  $M_2(\text{Ga-H})$  is a constant and equal to  $\frac{3}{2}(1.8 + 0.5) \times \frac{1}{2} = 1.8 \text{ G}^2$  we can estimate the second moment,

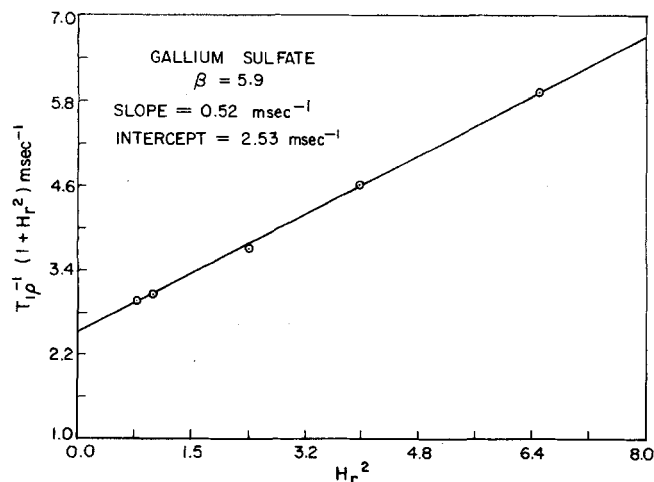
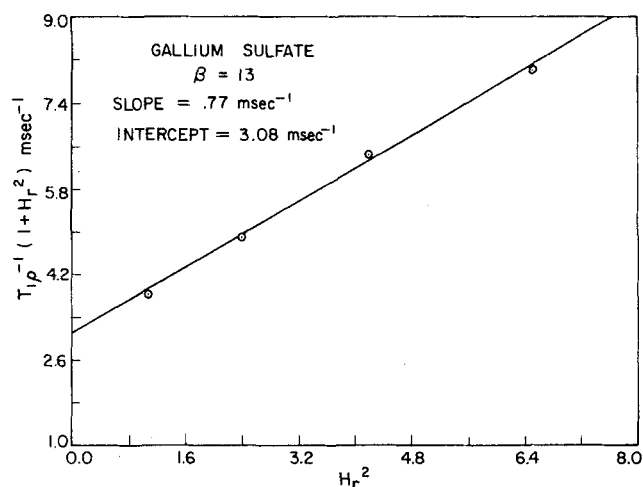
$$\begin{aligned}
 M_{2\text{exp}} &= \frac{1}{3}M_2(\text{OH}_3)_{\text{intra}} + M_2(\text{OH}_3)_{\text{inter}} + M_2(\text{Ga-H}) \\
 &\quad + \frac{2}{3}M_2(\text{OH}) + M_2(\text{OH})_{\text{inter}} \\
 &= \frac{1}{3}(29.6) + 2.3 + 1.8 + 0 + M_2(\text{OH})_{\text{inter}}, \\
 15.3 &= 14 + M_2(\text{OH})_{\text{inter}}.
 \end{aligned}$$

From crystal data  $M_2(\text{OH})_{\text{inter}}$  is not possible to calculate but  $1.3 \text{ G}^2$  is certainly not an unreasonable number. The values for  $M_2(\text{OH}_3)_{\text{intra}}$  and  $M_2(\text{OH}_3)_{\text{inter}}$  were taken from Ref. 6. As the sample is heated the OH groups will be the first to undergo a change and their second moment contribution is probably reduced to a small number. Unfortunately no cw data exist in this region.

When the  $\text{OH}_3^+$  group reorients about a  $C_3$  axis the second moment should become<sup>6</sup>

$$(9.9/4) + 2.3 + 1.8 = 6.6 \text{ G}^2.$$

Experimentally<sup>13</sup>  $6.3 \text{ G}^2$  is measured. The agreement is excellent within experimental accuracy. From the

FIG. 3.  $T_{1\rho}^{-1}(H_r^2 + 1)$  vs  $H_r^2$  for  $\beta = 5.9$ .FIG. 4.  $T_{1\rho}^{-1}(H_r^2 + 1)$  vs  $H_r^2$  for  $\beta = 13.0$ .

correlation time and activation energy from the pulse experiment the motion should affect the second moment around  $35^\circ \text{K}$ . This indeed is the case.

With a further increase in temperature, the  $\text{OH}_3^+$  now begins to tumble and the intra second moment contribution should be reduced even further. From the cw data a change of  $\sim 1 \text{ G}^2$  is seen in the temperature range  $300$ – $350^\circ \text{K}$ . It should be noted that the reduction of  $\sim 1 \text{ G}^2$  could also be attributed to the decrease in the cross-relaxation effect which can contribute up to  $1.8 \text{ G}^2$ .

From the above discussion it can be seen that the existence of the  $\text{OH}_3^+$  ion in gallium sulfate is compatible with both the cw and the pulse data. Using spin thermometry the cross-relaxation term is isolated and the  $M_2(\text{Ga-H})$  is determined.

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