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NMR study of ammonium magnesium langbeinite

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Recent studies have shown that ammonium langbeinites have low-temperature phase transitions uncharacteristic of the rest of the langbeinite family. In this study, proton NMR spin-lattice relaxation times T_1 and spin-spin relaxation times T_2 for powder samples of $(NH_4)_2Mg_2(SO_4)_3$ are reported in the temperature range from 77 to 373 K. The ammonium ions occupy two different kinds of sites in the crystal. The measured barrier to thermally activated ammonium reorientations is found to be 2.0 and 3.3 kcal/mol for the two sites, respectively. Additionally, there is no observable discontinuity in T_1 at the reported phase transition at 161 K, in agreement with heat-capacity studies, suggesting that the transition mechanism may be different from those of most langbeinites.

I. INTRODUCTION

Langbeinites have the general chemical formula $A_2^+B_2^{2+}(SO_4)_3$ and take their name from the naturally occurring mineral, $K_2Mg_2(SO_4)_3$. More than 26 langbeinites have been synthesized, and all those which have been characterized exhibit a high-temperature cubic structure (space group $P2_13$).[1] From group theoretical arguments of the Landau theory, Dvorák[2] predicted that structural phase transitions from the cubic phase could result in either a monoclinic phase (space group $P2_1$) or an orthorhombic phase (space group $P2_12_12_1$). Most langbeinites have been shown experimentally to exhibit these two types of behavior.[3] $Tl_2Cd_2(SO_4)_3$ is considered an example of the first type,[4] while many of the potassium langbeinites ($A^+ = K$) appear to exhibit the second type.[5]

Ammonium langbeinites ($A^+ = NH_4^+$) have not been as well characterized as the potassium langbeinites. However, recent heat capacity studies of $(NH_4)_2Cd_2(SO_4)_3$ (ACdS),[6] $(NH_4)_2Mn_2(SO_4)_3$ (AMnS),[7] and $(NH_4)_2Mg_2(SO_4)_3$ (AMgS),[7] suggest that transitions other than those predicted by Dvorák's mechanisms may be present. Artman[7] has suggested that the phase behavior in AMgS and AMnS may arise from phenomena associated with motional dynamics of the ammonium ion rather than from the langbeinite-type transition pathways. Additional support for a different mechanism is provided by the anomalous behavior of the temperature dependence of the transition temperatures in the ammonium langbeinites when compared to that observed for the potassium series.[7]

We have undertaken an NMR study of AMgS in order to probe the motional behavior of the ammonium ions near the reported[7] phase transition at $T_c = 161$ K, and hence to examine their possible role in the transition. We also make comparisons to previous NMR data[8,9] for ACdS, for which a "langbeinite-type" transition mechanism has been well-established.

II. SAMPLES

Two different powdered samples of AMgS were used in this study. Both powdered samples were taken from the same batch which was used by Artman[7] in her heat capacity studies. The material was prepared by dissolving stoichiometric ratios of the salts $(NH_4)_2SO_4$ and $MgSO_4$ in hot distilled H_2O, mixing together the two solutions, and then evaporating off the aqueous solvent through a capillary tube at 120 °C. It was subsequently stored under an environment of dry N_2. Because AMgS is very hydroscopic, care had to be taken to ensure that water did not affect our NMR measurements. Sample 1 was kept in a pyrex test tube sealed with a polyethylene cap. This sample was later found by thermogravimetric differential-temperature analysis (TG/DTA) to contain 3% water (by weight). Sample 2 was baked in a pyrex test tube under a 1-m torr vacuum at 40 °C for 12 h. We found that this process reduced the water content in a sample to less than 0.3% by weight. This sample was then kept under a dry N_2 atmosphere, reevacuated to 10^{-6} torr, and sealed with a torch in a pyrex glass capsule under vacuum.

III. EXPERIMENT

Using pulsed NMR techniques, we measured the spin-lattice relaxation time T_1 and the spin-spin relaxation time T_2 of ^1H nuclei in samples of AMgS at various temperatures between 77 K and 373 K. The measurements were made at two different frequencies, 42.16 and 10.95 MHz. The 42.16-MHz data were obtained using sample 1, and the 10.95-MHz data were obtained using sample 2. We also took several measurements at 42.16 MHz using sample 2 and concluded that the higher water content of sample 1 did not appreciably affect the T_1 and T_2 measurements. Our T_1 measurements are plotted in Fig. 1.

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IV. DISCUSSION

A. Relaxation data

Reorientational motion of NH_4^+ ions in a solid provides a mechanism for the relaxation of nuclear magnetization. The standard expression[10] for the relaxation rate is given by

$$\frac{1}{T_1} = A\Big(\frac{\tau}{1+\omega^2\tau^2} + \frac{4\tau}{1+4\omega^2\tau^2}\Big), \tag{1}$$

where ω is the NMR frequency, and τ is the correlation time of the reorientations. The coefficient A is a measure of the strength of the intramolecular spin-spin interaction in an NH_4^+ ion. For many ammonium compounds, the value of A is approximately 1.9×10^{10} s^{-2}. (For example, see the data in Ref. 11.)

For thermally activated reorientations, we have the Arrhenius relation

$$\tau = \tau_0 \exp(E_a/kT), \tag{2}$$

where E_a is the activation energy (the height of the energy barrier to reorientation), and τ_0 is approximately the inverse of the NH_4^+ libration frequency. For many ammonium compounds,[11] the value of τ_0 is found to be approximately 4×10^{-14} s.

The curve described by Eq. (1) has a minimum with respect to τ. The minimum occurs at $\omega\tau \approx 0.616$, and the value of T_1 at the minimum is approximately $(0.70)\omega/A$. Using $A = 1.9\times10^{10}$ s^{-2}, we evaluate this expression for the two NMR frequencies in our study and find that the value of T_1 at the minimum should be 10 ms for 42.16 MHz and 2.5 ms for 10.95 MHz.

Our data are shown in Fig. 1. Instead of one T_1 minimum, we observe two minima at each frequency. At 42.16 MHz, the minima are 20 ms, and at 10.95 MHz, the minima are about 6 ms. These minima are only about half as deep as predicted. Our data suggest that the NH_4^+ ions are equally divided among two different kinds of sites in the crystal. The motion of the NH_4^+ ions in one kind of site satisfies $\omega\tau = 0.616$ at a different temperature than the motion of the ions in the other kind of site, leading to two distinct T_1 minima, as observed. Intermolecular spin-spin interactions are sufficiently strong to maintain a common spin temperature among all of the ^1H nuclear spins at both kinds of sites. The relaxation due to reorientations of NH_4^+ ions at one kind of site is shared by all of the spins and is consequently only half as effective, resulting in T_1 minima which are only half as deep, as observed.

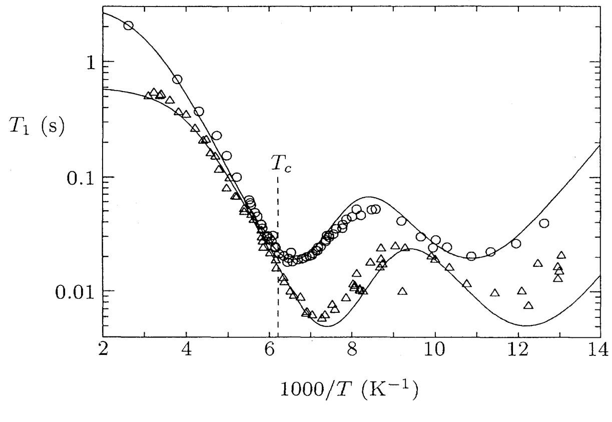

FIG. 1. Spin-lattice relaxation rates ($1/T_1$) for ^1H nuclei in AMgS: ○ = 42.16 MHz and △ = 10.95 MHz. The solid lines are theoretical fits to the data.

There are, in fact, two different kinds of NH_4^+ sites in the cubic $P2_13$ structure of the ammonium langbeinites.[7] Each unit cell contains eight NH_4^+ ions, equally divided among two Wyckoff 4a positions. These two sites differ in distances to nearest-neighbor atoms and therefore differ in the energy profile for reorientations and the resulting activation energy. In the unknown phase below T_c, more than two different kinds of sites could be present, but it is apparent from our data that further splitting of the sites into more than two kinds is probably negligible.

Let us label the sites with the larger activation energy site 1, and the sites with the lower activation energy site 2. We fit our data to the expressions

$$\frac{1}{T_1} = \tfrac{1}{2}A\Big(\frac{\tau_1}{1+\omega^2\tau_1^2} + \frac{4\tau_1}{1+4\omega^2\tau_1^2}\Big) + \tfrac{1}{2}A\Big(\frac{\tau_2}{1+\omega^2\tau_2^2} + \frac{4\tau_2}{1+4\omega^2\tau_2^2}\Big) + \frac{1}{T_{1,\mathrm{back}}} \tag{3}$$

and

$$\tau_i = \tau_0 \exp(E_{a,i}/kT), \tag{4}$$

where the index i refers to NH_4^+ ions at site i. We have added to Eq. (3) a term $1/T_{1,\mathrm{back}}$ which is the background relaxation rate, probably caused by paramagnetic impurities in the sample. This background relaxation is only important at the high-temperature end of the data where the relaxation due to reorientations becomes very weak. As seen in Fig. 1, this background relaxation is frequency dependent. We assume $1/T_{1,\mathrm{back}}$ to be temperature independent in the fits to our data.

The best fit of Eqs. (3) and (4) to the data is shown by the solid lines in Fig. 1. There are four adjustable parameters, the value of $1/T_{1,\mathrm{back}}$ at each frequency and the values of the two activation energies, $E_{a,1}$ and $E_{a,2}$. (We use $A = 1.9\times10^{10}$ s^{-2} and $\tau_0 = 4\times10^{-14}$ s.) The values of $1/T_{1,\mathrm{back}}$ only affect the fit at the high-temperature end of the data. Each value of $E_{a,i}$ determines the position of one of the T_1 minima at each frequency as well as the slope of the curve on each side of the minimum. The fit is quite satisfactory except for the 10.95-MHz data at low temperatures. The good fit to the data with so few adjustable parameters is strong evidence that the correct model has been used. We obtain from our fit $E_{a,1} = 3.3$ kcal/mol and $E_{a,2} = 2.0$ kcal/mol.

Incidently, McDowell *et al.*[8] conducted an NMR study of ACdS similar to our study. They observed a T_1 minimum equal to 14 ms at 30.8 MHz. If all of the NH_4^+ ions were contributing to this minimum, it should have been 7 ms. The value of 14 ms indicates that only half of the NH_4^+ ions contribute. The other half are in another site and contribute to a second minimum at lower temperature, as in our data. Indeed, they did observe the beginning of a second T_1 minimum at lower temperature, but were uncertain about an interpretation. They also miscalculated the activation energy. From their Fig. 3, we obtain 2.1 kcal/mol for the T_1 minimum at higher temperature.

If we subtract from the relaxation data the contribution from reorientations at site 2 and the contribution from the background, we can solve for τ_1 as a function of temperature. Similarly, if we subtract from the relaxation data the contribution from reorientations at site 1 and the contribution from the background, we can solve for τ_2. The results of these calculations are shown in Fig. 2. (The low-temperature 10.95-MHz data are omitted due to their large scatter.) The solid lines in this figure are plots of Eq. (4) using our values of $E_{a,i}$ from the fit. As Figs. 1 and 2 suggest, we do not detect, within the accuracy of our data, any change in $E_{a,1}$ across the phase transition at $T_c = 161$ K. The distortions in the crystal accompanying the phase transition to lower symmetry below T_c apparently do not significantly alter the energy barrier to NH_4^+ reorientations at site 1.

We measured T_2 from the free induction decay (FID) and found it to be between 40 and 50 μs over the entire temperature range of our experiment. We obtained NMR line shapes from the Fourier transform of the FID's. We found the second moment M_2 of the line shape at 77 K to be 1.6 G^2.

We also calculated the second moment in the cubic phase. (We used atomic positions[7] in ACdS scaled by the known lattice parameter of AMgS at room temperature.) We found the rigid-lattice value to be $M_{2,\mathrm{RL}} = 48$ G^2, most of the contribution being from the intramolecular interactions between ^1H nuclei. If the NH_4^+ ions are rapidly reorienting, then the intramolecular interactions are averaged to zero and only the contribution from the intermolecular interactions remains, resulting in $M_2 = 1.0$ G^2. This value is in fair agreement with our experimental measurement, and we conclude that the intramolecular interactions are motionally averaged out, even at 77 K. This requires that $\tau_i \ll 1/\sqrt{\gamma^2 M_{2,\mathrm{RL}}} = 5\times10^{-6}$ s. As seen in Fig. 2, this requirement is *not* satisfied for the NH_4^+ ions in site 1 at the lowest temperatures. Perhaps NH_4^+ reorientational tunneling is responsible for the averaging out of the intramolecular interactions at low temperatures.

Above about 220 K, the FID develops a long tail, a small second component with $T_2 \approx 500$ μs. We do not understand the origin of this long tail. It is reproducible with temperature cycling, and it appears the same in both the "wet" and "dry" samples (samples 1 and 2, respectively).

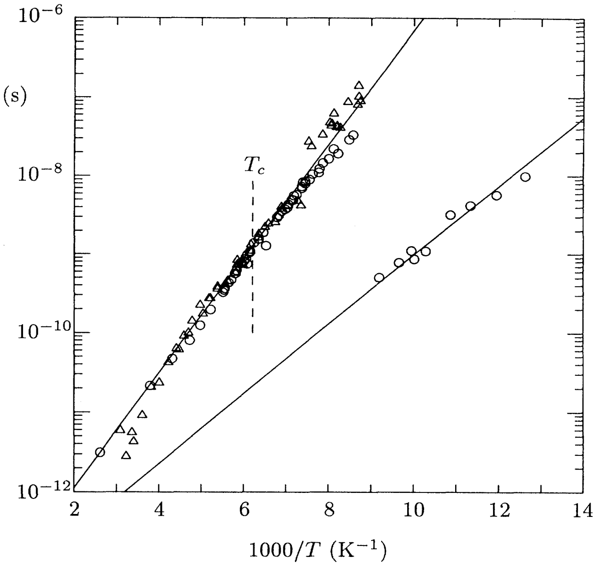

FIG. 2. Ammonium reorientation correlation times τ in AMgS computed from T_1 data: ○ = 42.16 MHz and △ = 10.95 MHz. The solid lines are the best linear fits to the data.

B. Nature of the phase transition

Heat capacity measurements[6] for AMgS reveal a phase transition at $T_c = 161$ K with a very small excess enthalpy and entropy. As can be seen from Figs. 1 and 2, there is no observable discontinuity at this temperature. Also, the theoretical fits to the data do not suggest any significant change in E_a across the transition. This behavior is in contrast to that observed for ACdS where there is a large latent heat[6] and a sharp discontinuity in T_1 (Refs. 8 and 9) at the transition temperature. Both the small excess heat, which appears under a broad hump in the heat capacity curve, and the continuity of T_1 near 161 K suggest that the AMgS phase transition is second order, as opposed to the strongly first-order behavior observed in ACdS and other langbeinites.

Landau theory does not allow *any* phase transition from $P2_13$ to be second order.[12] If the space-group symmetry of AMgS just above 161 K is in fact $P2_13$, then the transition must be first order. From the experimental data, we would conclude that the first-order nature of the transition is rather weak. On the other hand, it is possible that the space-group symmetry just above 161 K is not $P2_13$, potentially allowing a second-order transition. While Artman's x-ray diffraction studies[7] of powder samples of AMgS indicated a $P2_13$ structure at 273 K, the structure near 161 K has not yet been determined. In any case, it is apparent that the transition in AMgS is not like the one in ACdS.

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