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Phase transition structural changes of $(\text{NH}_4)_2\text{SO}_4$ investigated by electron paramagnetic resonance of the Ti^{2+} ion

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Abstract. The electron paramagnetic resonance of the Ti^{2+} centre in the two chemically distinct ammonium sites in $(\text{NH}_4)_2\text{SO}_4$ was investigated in the temperature range 85–227 K. The mirror symmetry of the sites in the paraelectric phase is preserved by the impurity. At T_c the spin-Hamiltonian tensors undergo discontinuous rotations which keep on increasing with decreasing temperature in the ferroelectric phase. The different rotations, in amplitude and direction, for the spin-Hamiltonian tensors associated with the two inequivalent ammonium sites are consistent with the ferrielectric model of $(\text{NH}_4)_2\text{SO}_4$. The coexistence of the two phases is observed at about 4 K below T_c .

1. Introduction

Ammonium sulphate (AS) $(\text{NH}_4)_2\text{SO}_4$ undergoes a first-order structural phase transition at 223 K. The crystal changes from a paraelectric phase, belonging to the $Pnam$ (orthorhombic) space group, to a polar phase, belonging to the $Pna2_1$ (orthorhombic) space group. The unit cell consists of four formula units and contains two types of NH_4^+ radical. Neutron diffraction studies [1] showed that the two types of radical are distorted in both phases and have different bonds to neighbouring oxygen ions; the radical identified as NH_4^+ (I) has a stronger bonding to the lattice than the radical identified as NH_4^+ (II) has.

The anomalous temperature dependence of the low-temperature spontaneous polarization and the small value of the Curie constant led Unruh and co-workers [2, 3] to suggest that the polar phase is ferrielectric, consisting of two oppositely polarized sublattices.

Dielectric constant and electric conductivity [4, 5] measurements showed an anomaly at $T_c - 8$ K, which was interpreted as due to an additional phase transition. The two nearby transitions would then be related to successive distortions of the two inequivalent NH_4^+ radicals.

Aiming to elucidate the existence of this additional phase transition and the mechanism of lattice polarization, we have studied by electron paramagnetic resonance (EPR) the Ti^{2+} ion in $(\text{NH}_4)_2\text{SO}_4$ crystals in the temperature range 85–227 K.

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The Tl^+ ion isomorphously replaces the radical NH_4^- —the ionic size is approximately the same—and can subsequently be converted to Tl^{2+} by x-ray irradiation at liquid-nitrogen temperature. This impurity centre has interesting properties as a paramagnetic probe and has been used to investigate phase transitions in a variety of crystals. The hyperfine interaction is exceptionally large—of the order of 100 GHz—and small changes in its value result in significant changes in the spectra. Therefore, the EPR spectra are very sensitive to local structural changes. The position of the spectral lines in a magnetic field sweep is far from $g = 2$, making it possible to analyse the spectrum easily. Both isotopes ^{203}Tl and ^{205}Tl have almost equal magnetic moments and, therefore, the respective lines are not resolved, resulting in a very simple spectrum.

The EPR spectra of Tl^{2+} may be described by the simple spin Hamiltonian

$$\mathcal{H} = H \cdot g \cdot S + S \cdot A \cdot I$$

where $S = \frac{1}{2}$ and $I = \frac{1}{2}$. On account of the high value of the Tl hyperfine interaction ($A \simeq 100$ GHz), two transitions are observed at microwave frequencies of about 10 GHz: a high-field transition, at approximately 7000 G, corresponding to $(F = 1, m_F = -1) \rightarrow (F = 1, m_F = 0)$ and a low-field line, at approximately 6000 G, corresponding to $(F = 1, m_F = 1) \rightarrow (F = 1, m_F = 0)$, where $F = I + S$. Two other allowed transitions are not observed.

There are two distinct Tl^{2+} defects in AS owing to the existence of two differently bonded NH_4^+ radicals. If one assumes that the Tl^{2+} ion does not break the symmetry of the NH_4^+ site, a hypothesis verified *a posteriori*, it is possible by a simple symmetry analysis to foresee the number of lines of the EPR spectra as follows.

In the paraelectric phase, for a general direction of the magnetic field, there are two magnetically non-equivalent defects for each NH_4^+ site (I or II) and, as each defect yields a pair of lines, we should observe four pairs denoted A and A' for one site, and B and B' for the other site. The projections of the spin-Hamiltonian tensors for A and A' (as well as for B and B') on the ac and bc planes will coincide and, therefore, only two pairs of lines are observed for the magnetic field on these planes.

In the ferroelectric phase, because of the polarization of the lattice, eight pairs of lines should be observed for a general orientation of the magnetic field. This number should be reduced to four, on symmetry grounds, for the magnetic field on the ab , bc and ac planes.

2. Experimental results

$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Tl}^+$ crystals were grown by slow evaporation of a solution containing approximately 2 mol% Tl_2SO_4 . Different crystal habits resulted from different growth conditions. Crystals in the form of needles along the c axis, which are usually reported in the literature, were chosen for this study. The largest surface under visual inspection is identified as (010), perpendicular to the b axis; a perpendicular surface, which is an easy plane for cleavage, is identified as (100), perpendicular to the a axis. The samples, of size approximately 5 mm^3 , were irradiated at 77 K with x-rays (75 kV; 15 mA) for 2 h and transferred at the same temperature to the cryostat-cavity set-up.

The angular dependence of the EPR spectra of Tl^{2+} was investigated in the paraelectric phase (227 K) and in the ferroelectric phase (85, 210 and 220.5 K). It is

observed that the intensity of the spectra decays above approximately 150 K, because of the instability of the Tl^{2+} defect.

Figure 1 shows the angular dependence of the EPR spectra at 227 K (paraelectric phase) for H on the ab , bc and cd planes. On the bc and ac planes the spectrum is formed by two pairs of lines and on the ab plane each line splits into two. It is observed that line A is weaker than line B, which indicates that there are a larger number of substitutional Tl^{2+} ions of type B and that, therefore, the substituted NH_4^+ radical has a weaker bonding. The larger anisotropy of line A, observed in the angular dependence, suggests that ions surrounding the corresponding site are nearer. Both facts lead to the conclusion that lines A correspond to Tl^{2+} in site $\text{NH}_4(\text{I})$ and lines B to Tl^{2+} in site $\text{NH}_4(\text{II})$.

Figure 2 shows the angular dependence of the EPR spectra in the ferroelectric phase at 210 K. Lines corresponding to site A split on the ab , bc and ca planes, as expected from the symmetry analysis. However, the lines corresponding to site B did not split on the bc plane. This unpredicted degeneracy resulted by accident, as shown from our analysis of the spectra, and not from any preserved symmetry. It is probably an unresolved splitting rather than a true degeneracy. Anyhow, the experimental results confirm our *ansatz* that the symmetry of the NH_4^+ site is preserved by the Tl^{2+} impurity; the tensors of the paraelectric phase have mirror symmetry (ab plane) belonging to the space group $Pnam$ and the tensors of the ferroelectric phase have the symmetry C_1 , belonging to the space group $Pna2_1$. This gives a privileged status to the Tl^{2+} centre as a paramagnetic probe in EPR studies of the phase transition on AS, compared with other probes previously used, including Cu^{2+} [6], Mn^{2+} [7, 8], VO^{2+} [9], NH_3^+ [10, 11], SeO_3^- [12], CrO_4^{3-} [13] and CrO_4^{2-} [14]. One can reasonably expect that the changes in the g - and A -tensors of the spin Hamiltonian below the phase transition reflect with some fidelity the changes in the vicinity of the NH_4^+ sites.

A centres, those with less intense resonance lines, are more anisotropic, as shown in figures 1 and 2, and therefore their orientations can be obtained more precisely. Most of our discussion from now on is related to the reorientation of these centres. Table 1 shows the orientation of the A - and g -tensors for one of the A centres in the paraelectric phase and at two temperatures in the ferroelectric phase. From these data we can obtain the rotations of the tensors in the ferroelectric phase with respect to their orientation in the paraelectric phase. At 210 K we found that the tensors are rotated by $\theta = 11^\circ$ around the $R = 0.67i + 0.71j - 0.20k$ axis. One should note that this axis is very close to $(\sqrt{2}/2)(i + j)$. At 85 K the tensors are rotated by $\theta = 33^\circ$ around the $R = 0.30i + 0.94j + 0.15k$ axis. Again, it should be noted that this axis is very close to $1j$. The behaviour of the centre is unusually complicated. The rotations have a very large amplitude and the rotation axis is not fixed for all temperatures. It should not be too far from the truth to say that at the phase transition the centre has an abrupt rotation around the $(\sqrt{2}/2)(i + j)$ axis and that, for decreasing temperature, it presents an increasing rotation around the $1j$ axis.

Similar results, i.e. large and increasing rotations, are obtained for the B centres, although they are much less precise owing to the small anisotropy of these centres. It is very clear, however, that the reorientation of the B centres is very different from that observed for the A centres. These observations strongly support the idea that the order parameter of the phase transition on AS is some kind of molecular reorientation and that two sublattices are involved, each having a distinct behaviour. In fact, our data strongly suggest that the order parameter is composed mainly of rotations of

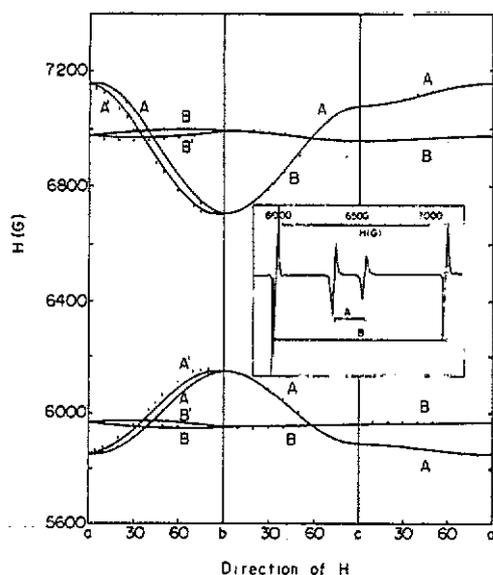


Figure 1. Angular dependence of the EPR spectra of $(\text{NH}_4)_2\text{SO}_4:\text{Tl}^{2+}$ in the paraelectric phase (227 K) at 8917 MHz. Lines A and A' correspond to site NH_4^+ (I) and lines B and B' to site NH_4^+ (II). Only the angular dependences of A and B centres were adjusted to the experimental points; the continuous lines corresponding to A' and B' were obtained by symmetry operations. The inset shows the EPR spectrum in the b direction.

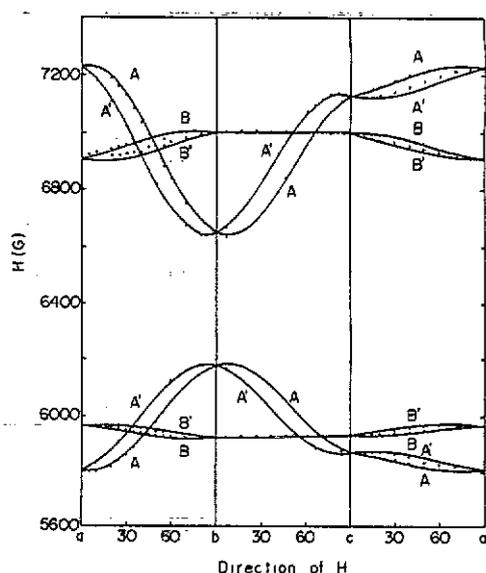


Figure 2. Angular dependence of the EPR spectra of $(\text{NH}_4)_2\text{SO}_4:\text{Tl}^{2+}$ in the ferroelectric phase (210 K) at 8916 MHz. The comments in the caption for figure 1 are also valid here.

Table 1. Spin-Hamiltonian tensors \mathbf{g} and \mathbf{A} of one of the A centres at three temperatures.

Temperature (K)	Regime	Component	\mathbf{g}	\mathbf{A} (MHz)	Cosine directors		
227	Paraelectric	X	1.989	114845	0.997	-0.071	0
227	Paraelectric	Y	1.996	115422	0.071	0.997	0
227	Paraelectric	Z	1.993	114947	0	0	1
210	Ferroelectric	X	1.989	110585	0.983	-0.100	-0.154
210	Ferroelectric	Y	1.998	111475	0.119	0.986	0.119
210	Ferroelectric	Z	1.991	110739	0.139	-0.135	0.981
85	Ferroelectric	X	1.986	107872	0.852	0.056	-0.521
85	Ferroelectric	Y	1.998	109145	0.025	0.989	0.147
85	Ferroelectric	Z	1.983	108103	0.523	-0.139	0.841

the ammonium ions. This is in agreement with the theoretical model of Sawada *et al* [15], which associates the transition with the softening and condensation of a B_{1u} mode composed of librational motion of the ammonium radicals. Two previous EPR studies by Fujimoto *et al*, using NH_3^+ [10] and VO^{2+} [9] as probes, produced evidence along the same lines. As both these centres break the local symmetry, however, their

indications on phase transition reordering are qualitative.

3. Discussion

Our findings are in sharp contrast with the conclusion of a recent investigation [8] where crossing of the EPR lines of Mn^{2+} at 147 K is related to the reversal of the polarization. We also observed crossing of resonance lines which occur for different A or B centres and at different temperatures, depending on the orientation of the magnetic field. Figures 3 and 4 show the temperature variation in the splitting of the low-field resonance lines for two orientations. For H on the ab plane, at 45° from the axes, the lines related to the A centres cross each other at 145 K, as shown in figure 3. For H on the ac plane, at 45° from the axes, the splitting of lines A keeps increasing at low temperatures, whereas lines B cross each other at about 175 K. The source of these complications is the fact that the axes of rotation of the tensors, and not just the amplitude of the rotation, change with change in temperature. Because of this, any projection of the tensors can give an erroneous idea of their temperature evolution.

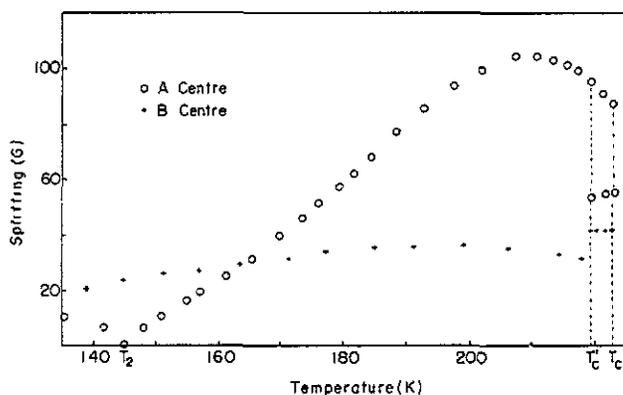


Figure 3. Splitting of the low-field resonance lines of A and B centres for H on the ab plane, midway between the axes. The lines are already split in the paraelectric phase, as shown in figure 1. Note the discontinuous change at T_c and the coexistence of the two phases between T_c and $T'_c = T_c - 4$ K. The splitting of the A-centre lines goes to zero at 145 K.

Another fact that is the object of conflicting reports in the literature is the behaviour of the splittings just at the transition temperature. Shibata *et al* [12] observed that all EPR lines of both the NH_3^+ and the SeO_3^- radicals split discontinuously at T_c , whereas Misra *et al* [8] observed that an EPR line of the Mn^{2+} centre on site I has discontinuous splitting at T_c and another line of that centre on site II behaves continuously. Our data show that the spin-Hamiltonian tensors of both A and B centres behave discontinuously at T_c . However, depending on the orientation of the magnetic field, one can observe nearly continuous behaviour for the splitting of one of the lines, as shown in figure 4.

Dielectric constant [4, 5] and electrical conductivity [5] measurements have indicated the existence of another phase transition some 8 K below the well known transition at 223 K. We have not observed that new transition, although some attention was paid to this possibility. Thus, we conclude that, if that transition exists, it

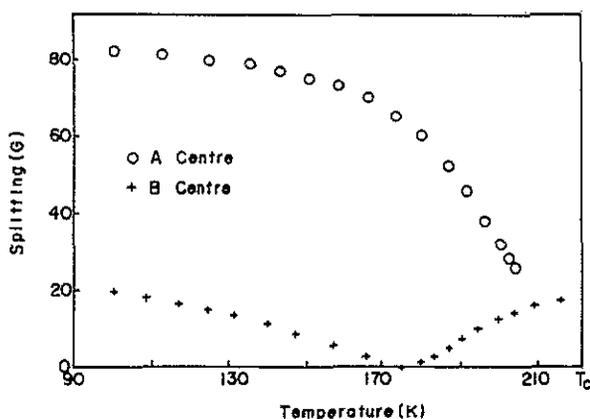


Figure 4. Splitting of the low-field resonance lines of A and B centres for H on the ac plane, midway between the axes. The splitting is zero in the paraelectric phase. The splitting of the A lines is almost continuous at T_c . The splitting of the B lines is a maximum at T_c , after a discontinuous change, and goes to zero at 175 K.

has little effect on the orientation of the ammonium radicals. However, we observed the coexistence of the paraelectric and ferroelectric phases at about 4 K below T_c in circumstances that were not clear to us. The lines of the coexisting phases are shown in figure 3. The coexistence of two phases has also been reported in [11]. We failed to observe thermal hysteresis, in agreement with results of Siamaprasad and Vallabhan [5] and in conflict with the report of Yoshihara *et al* [4]. Our speculative explanation is that the ferroelectric transition in AS is diffuse in the presence of some impurities, resulting in the coexistence of two phases, which may mask the thermal hysteresis.

Acknowledgments

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