PHYSICAL REVIEW B VOLUME 40, NUMBER 1 1 JULY 1989

Mn^{2+} EPR study of the phase transition in an ammonium sulfate single crystal: Existence of two inequivalent sublattices

Sushil K. Misra, Jiansheng Sun,* and Stanislaw Jerzak†
Physics Department, Concordia University, 1455 de Maisonneuve Boulevard West, Montreal, Quebec, Canada H3G 1M8

(Received 14 December 1988)

Angular variations of X-band EPR spectra, for the magnetic field orientations in three mutually perpendicular planes, of a single crystal of Mn^{2+}-doped $(NH_4)_2SO_4$, have been recorded from 113 to 398 K. Two Mn^{2+} centers, the principal axes of whose zero-field splitting tensors (b_2^m) are found to be oriented very close to each other, exhibit ferroelectric phase transitions of entirely different natures, although occurring at the same transition temperature ($T_c=223$ K). At T_c, the EPR lines corresponding to one center exhibit a jump (first-order transition), while those for the other a continuity (second-order transition). For both the centers each EPR hyperfine line splits into two below T_c. The Mn^{2+} spin-Hamiltonian parameters in $(NH_4)_2SO_4$ are evaluated at room temperature, using a rigorous least-squares-fitting procedure, combined with numerical diagonalization of the spin-Hamiltonian matrix. The present EPR data confirm the existence of two inequivalent sublattices in the $(NH_4)_2SO_4$ crystal. The unusual crossing of the EPR line positions, below T_c, for the Mn^{2+} center which undergoes a first-order phase transition at T_c, has been related to the reversal of the spontaneous polarization. The dynamic behavior of the two Mn^{2+} centers, in this ferroelastic crystal, has here been interpreted to be due to the deformation of the ${SO_4}^{2-}$ groups and the spontaneous strain produced by the acoustic mode. The critical exponent β has been determined, for both the centers, to be 0.49 ± 0.03, from the line splitting below T_c. It has been verified that the scaling law and Rushbrooke inequality are well satisfied in $(NH_4)_2SO_4$.

I. INTRODUCTION

Ammonium sulfate [$(NH_4)_2SO_4$] (AS, hereafter) has been found to undergo a phase transition, becoming ferroelectric below 223 K, by Matthias and Remeika.[1] Unusual ferroelectric properties, e.g., a low value of the Curie-Weiss constant,[2] a large spontaneous strain,[3,4] provided a great deal of interest in AS. In order to understand the transition mechanism responsible for the phase transition, many experimental techniques, e.g., dielectric measurement,[5] neutron diffraction,[6] NMR,[7] EPR,[8–20] infrared,[21] and Raman spectroscopy,[22] have been used to study AS. Theoretically, different mechanisms, e.g., order-disorder,[23] displacive,[24] improper-ferroelectric,[5] "coupled-oscillator-relaxator" model,[25] two-inequivalent ferroelectric sublattices,[26] and, more recently, the molecular-distortion model[27] and weakly first-order Landau-type-transition model,[20] have been invoked to explain the mechanism of the phase transition in AS. Despite so many studies, the phase-transition mechanism in AS still remains controversial. Even the transition temperature T_c, the spontaneous polarization P_s, and its temperature dependence, have been reported to have different values; as well, the various explanations provided are at variance from each other. Hoshino *et al.*[3] reported that P_s was almost temperature independent in the neighborhood of the ferroelectric "Curie" temperature T_c (223 K), while Ikada *et al.*[5] found the same result at a lower temperature (153 K). They explained it by the use of a phenomenological theory. Later, Unruh *et al.*[4] reported that P_s was strongly temperature dependent, changing the sign below 85 K; this was explained by Sawada *et al.*[26] to be due to the existence of two-inequivalent sublattices in AS. In the two-inequivalent-sublattices model, also referred to as the ferroelectric model, Sawada *et al.*[26] proposed that the two ${NH_4}^+$ ions in the unit cell of AS are crystallographically inequivalent, possessing different dipole moments, which are likely to be antiparallel along the c axis. Sawada *et al.*[26] further proposed that all the ${SO_4}^{2-}$ ions in AS are equivalent.

The AS crystal is ferroelastic, both in the paraelectric ($T>T_c$) and ferroelectric ($T<T_c$) phases.[28] Makita *et al.*[28] reported that, at room temperature, AS crystals consisted of three domains, separated by $\{011\}$ and $\{031\}$ twin planes. These domains can be switched amongst themselves by an external stress. Group-theoretical analysis[29] of AS crystal symmetry suggests that the pseudohexagonal orthorhombic symmetry P_{nam} ($Z=4$) in the paraelectric phase may be derived by a hypothetical phase transition of AS from a hexagonal (prototype) structure of symmetry $P6_3/mmc$ ($Z=2$), supposed to exist at high temperatures.

EPR has been used in the study of the phase-transition mechanisms, in AS because of its high sensitivity to the local changes in the environment around the paramagnetic ions doped as microscopic probes. Many different paramagnetic ions, such as Mn^{2+},[8–10] Cu^{2+},[11–13] ${SeO_3}^-$,[14,15] VO^{2+},[16,17] ${CrO_4}^{3-}$,[18] $(CrO_4)^{2-}$,[19] and ${NH_3}^+$ [14,20] have been used to this end. However, some of these studies have been confined to either temperatures above T_c, or both above and below T_c, but not systematically as a function of temperature in the range including T_c.[11,13,17,19] Similar to the findings of the other techniques, a lot of controversy exists in the EPR results on AS as well.

Mn^{2+} is an important EPR probe of the environment around it since its spin ($S=5/2$), being greater than 1/2, experiences the crystalline field directly via the spin-Hamiltonian (SH) parameters b_2^m, b_4^m. As for the EPR studies of Mn^{2+}-doped AS single crystal, Abdulsabirov *et al.*[8] found four physically equivalent Mn^{2+} centers, (i.e., only one type of Mn^{2+} center); the magnitudes of the angles between the Z axes, defined to be the principal axis of the zero-field splitting tensor b_2^m, of the four Mn^{2+} centers and the crystallographic axes (a,b,c) were found to be about the same. The respective Z axes, were deduced to be along the $NH_4{}^+$(I)-$NH_4{}^+$(II) directions, depending on which $NH_4{}^+$ ion is replaced by the Mn^{2+} ion, with a type-1 charge-compensation mechanism being effective.[30] The temperature variation of the value of the zero-field splitting parameter (b_2^0) was found by Abdulsabirov *et al.*[8] to be discontinuous at 215 K; thus implying the occurrence of a first-order phase transition at 215 K. This temperature was assumed to be T_c, 8 K lower than the well-accepted value (223 K). Shrivastava[9] also found the existence of only one type of Mn^{2+} center, corresponding to four physically equivalent Mn^{2+} complexes in the AS crystal, associated with a transition temperature of 217.5 K, 5.5 K lower than the accepted value of T_c. He observed that the EPR lines just split below 217.5 K without experiencing any jump in their positions; implying that AS undergoes a second-order phase transition at 217.5 K. Based on the data of Ref. 9, Misra and Shrivastava[10] estimated the critical exponent β for this second-order transition from the line splitting (ΔB) below T_c: $\Delta B \propto (T_c - T)^\beta$, with $\beta=0.5$ and $T_c=217.5$ K. Both Abdulsabirov *et al.*[8] and Shrivastava[9] estimated the Mn^{2+} spin-Hamiltonian parameters in AS at room temperature, the differences between their values are significant (Table I). Furthermore, the parameters were evaluated, employing perturbation expressions, using the line positions obtained for one direction of the external magnetic field ($\mathbf{B}\|\hat{\mathbf{Z}}$) by Shrivastava,[9] while for three directions ($\mathbf{B}\|\hat{\mathbf{Z}},\hat{\mathbf{X}},\hat{\mathbf{Y}}$) by Abdulsabirov *et al.*[8]

The present paper reports yet much more detailed and systematic EPR experimental study on the Mn^{2+}-doped AS single crystal. The purpose is to verify the existence of two different Mn^{2+} centers, to determine T_c, to study the nature of the phase transition of AS at T_c (first and/or second order), to evaluate the room-temperature spin-Hamiltonian parameters for Mn^{2+} in AS by the use of a rigorous least-squares-fitting procedure employing exact numerical diagonalization of the spin-Hamiltonian matrix,[33] and to interpret the temperature dependences of the EPR spectra for the two Mn^{2+} centers. A detailed discussion of the dynamic behavior of the two different Mn^{2+} centers is provided. In addition, the value of the critical exponent β has been estimated from the line splittings of the two Mn^{2+} centers below T_c. As well, the validity of the scaling law and Rushbrooke inequality has been examined.

II. EXPERIMENTAL ARRANGEMENT, SAMPLE PREPARATION, AND CRYSTAL STRUCTURE

The EPR spectra were recorded on a X-band Varian V4506 spectrometer, consisting of a 12-in. Varian Associates electromagnet, a Varian power supply, and a Bruker

TABLE I. Room-temperature Mn^{2+} spin-Hamiltonian parameters in $(NH_4)_2SO_4$ crystal, as evaluated by the use of a rigorous least-squares-fitting procedure.[33] The results of Abdulsabirov *et al.*[8] and Shrivastava[9] are also included for comparison. The unit for b_l^m, A and B vaues is GHz, while that for χ^2, GHz^2 [$\chi^2 \equiv (|\Delta E_j| - h\nu_j)^2$; here ΔE_j is the calculated energy difference between the pair of levels participating in resonance for the jth line position, ν_j is the corresponding klystron frequency, and h is Planck's constant]. n is the number of lines fitted simultaneously. For the data of Abdulsabirov *et al.*[8] and Shrivastava[9], χ^2 are as calculated using their reported parameters and the line positions observed presently.

Parameters	Present work	Abdulsabirov *et al.* (Ref. 8)	Shrivastava (Ref. 9)
$g_\parallel$	2.0014±0.0004	$g_z=2.0009$	$g=1.9959$
$g_\perp$	2.0176±0.0079	$g_x=2.0009$	
		$g_y=2.0014$	
b_2^0	2.153 ±0.003	−2.183	1.454
b_2^2	−0.714 ±0.027	1.108	−0.717
b_4^0	0.001 ±0.001	0.008	−0.006
b_4^2	0.699 ±0.045	0.000	
b_4^4	−0.281 ±0.180	0.039	
A	−0.258 ±0.003	0.259	−0.256
B	−0.281 ±0.003	0.263	−0.250
C		0.263	
χ^2/n	0.003	0.096	3.064
n	140	140	140

field controller (B-NM-2). The crystal was placed inside a TE_{102} Varian cavity. Temperatures, above and below room temperature, were maintained at the sample by gently blowing nitrogen gas, passing respectively through the heater coils and coils immersed in liquid nitrogen, of a Varian temperature-controller unit (model E4540). The temperature stability was better than 0.5 K, as measured by an Omega Engineering Inc. microprocessor-based thermocouple meter (model 680), with a temperature resolution of 0.1 K.

The AS crystals, used for measurements, were grown by slow evaporation at room temperature of an aqueous solution of $(NH_4)_2SO_4$ to which a small amount of $MnSO_4$ (0.5 at. %) was added. Good-quality crystals with dimensions suitable for measurements (about $3\times2\times8$ mm^3) were obtained after about eight weeks. It was found that Mn^{2+} does not enter the crystal lattice of AS in large amounts. Thus the actual amount of Mn^{2+} in AS crystals is much less than that present in the mother liquor. The crystals so obtained were colorless, had excellent cleavage in the (100) plane, and were almost ferroelastically monodomain, as verified under a polarizing microscope.

The growth habit of AS crystals is shown in Fig. 1. The crystal structure of AS has been determined by Schlemper and Hamilton,[6] by neutron diffraction; it is the same as that of K_2SO_4. At room temperature, the crystal possesses orthorhombic symmetry (space group P_{nam}), with the unit-cell parameters being $a=7.782$, $b=10.64$, and $c=5.993$ Å.[6] (Some AS crystals show a superstructure at room temperature, i.e., characterized by the b and c dimensions doubled.[31]) Below T_c, the reflection planes of the AS crystal disappear, changing the space group to P_{na2_1}, while the crystal still possesses orthorhombic symmetry; the c axis becomes the axis of electric polarization. The unit-cell parameters of AS below T_c are $a=7.837$, $b=10.61$, and $c=5.967$ Å.[6]

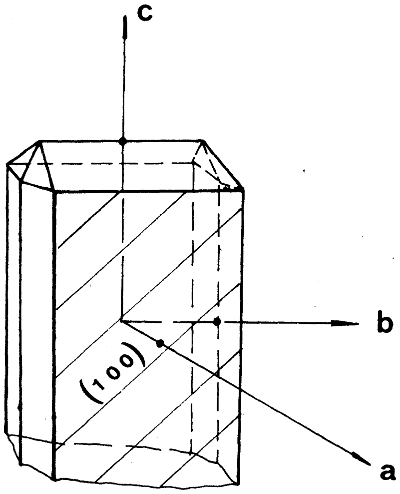

FIG. 1. The growth habit and crystallographic axes a, b, and c of $(NH_4)_2SO_4$ single crystal. The {100} plane, which exhibits a perfect cleavage, is shaded by oblique lines.

At room temperature, the unit cell of AS contains four formula units ($Z=4$). There are present two crystallographically different NH_4^+(I) and NH_4^+(II) ions. NH_4^+(I) ions, with five SO_4^{2-} ions surrounding them, are designated as α ammonium ions, while NH_4^+(II) ions, located in the middle of a distorted octahedra of SO_4^{2-} ions, are designated as β ammonium ions. The directions of the two NH_4^+(I)-NH_4^+(II) (or α-β) pairs make the following angles, relative to the crystallographic axes:[8] $(\hat{\mathbf{a}},\hat{\mathbf{Z}})=\pm71.2°$, $(\hat{\mathbf{b}},\hat{\mathbf{Z}})=\pm55.5°$, and $(\hat{\mathbf{c}},\hat{\mathbf{Z}})=\pm40.5°$. These directions are found to be almost coincident with the magnetic Z axes corresponding to the two Mn^{2+} centers, as seen in Sec. III below.

III. ROOM-TEMPERATURE EPR SPECTRA

EPR spectra were recorded for the orientations of the external magnetic field (**B**) in the ab, ac, and bc planes. Figure 2 exhibits the high-field EPR spectrum for the orientation of **B** in the ab plane, at 23° from the a axis; six strong hyperfine lines of almost equal intensity, corresponding to the highest-field fine-structure sextets $M=5/2\leftrightarrow3/2$ for the two Mn^{2+} centers, designated as I and II, are clearly visible. [For Mn^{2+}, $S=I=5/2$, where S and I are the electronic and nuclear spins, respectively. Therefore, for each Mn^{2+} center, the EPR spectrum consists of five allowed sextets $(M,m)\leftrightarrow((M-1),m)$, where M and m are, respectively, the electronic and nuclear magnetic quantum numbers.] The small difference in EPR line heights for Mn^{2+} centers I and II, as seen in Fig. 2, results from a slightly larger linewidth of center II, as compared with that for center I (17 G for center II and 14 G for center I). This suggests a somewhat bigger distortion of the surrounding of Mn^{2+} center II as compared to that of center I. The equality of the intensities of the EPR lines corresponding to centers I and II imply that the occupation probabilities of the sites available to centers I and II are about the same. (It is noted that there were observed, in addition, two other centers of very weak intensity designated as III and IV; these are, most likely, due to additional ferroelastic domains of AS crystal, which were, however, not detected under a polarizing microscope, because of their negligible volume. Centers III and IV have not at all been studied in the present paper because of their extremely weak intensities.)

Figure 3 shows the angular variation of the highest-field resonant lines for centers I and II for the orientation of **B** in the ab plane. The lines corresponding to the two magnetically inequivalent Mn^{2+} centers (I and II) are clearly visible in Fig. 3. This is possible because the principal axes and magnitudes of the zero-field splitting tensors b_2^m, corresponding to the two centers, are at definitive variance, albeit small, from each other.

Figures 4 and 5 exhibit the angular variation of EPR spectra for the orientation of **B** in the bc and ac planes, respectively; they are found to be symmetric about the b and c axes, respectively, for the two centers, in accordance with the crystal symmetry. Figures 4 and 5 confirm that there indeed exist two physically inequivalent Mn^{2+} centers with almost the same intensity

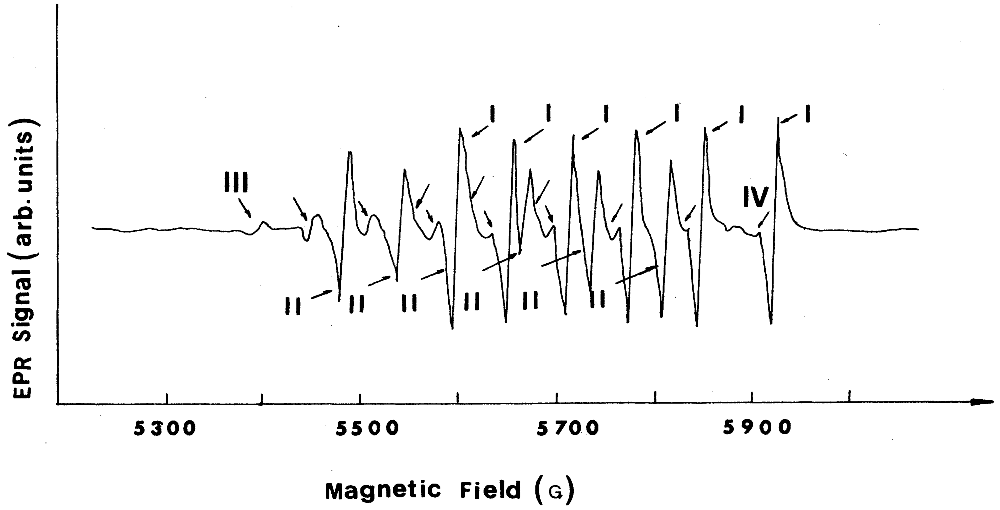

FIG. 2. EPR spectrum (first derivative) of Mn^{2+}-doped $(NH_4)_2SO_4$ crystal for **B** in the *ab* plane, 23° from the *a* axis, showing the highest-field hyperfine sextets (fine-structure transition $5/2 \leftrightarrow 3/2$), corresponding to the two Mn^{2+} centers, marked as I and II. The two centers have almost the same intensity. There are also seen two weak centers, marked as III and IV; these are due to another ferroelastic domain of relatively small volume.

but slightly different directions of the respective principal axes and the values of the zero-field splitting tensors b_2^m. These relative differences did not change much upon increasing the temperature from room temperature to 398 K, except that the EPR line positions moved slightly towards higher magnetic fields for both the centers.

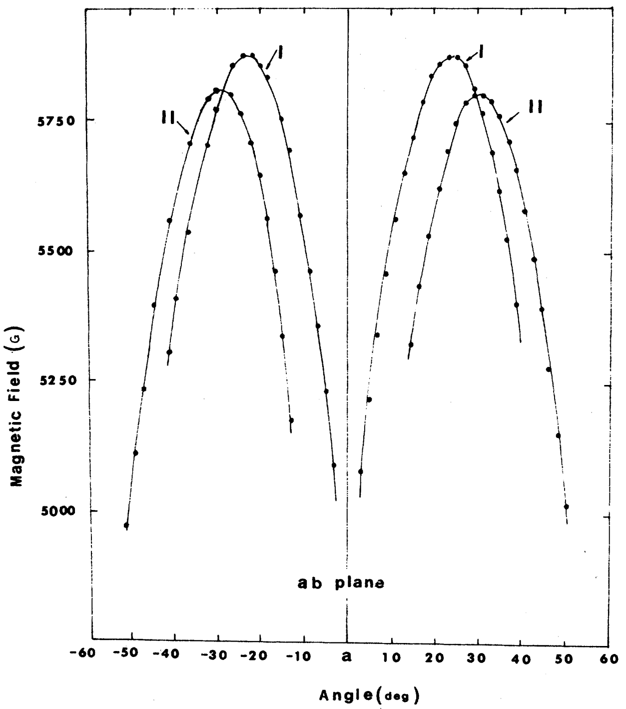

FIG. 3. Angular variation of the highest-field line of the highest-field hyperfine sextet for Mn^{2+} centers I and II in Mn^{2+}-doped $(NH_4)_2SO_4$ crystal at room temperature for the orientation of **B** in the *ab* plane. The continuous lines are smooth curves that connect data points.

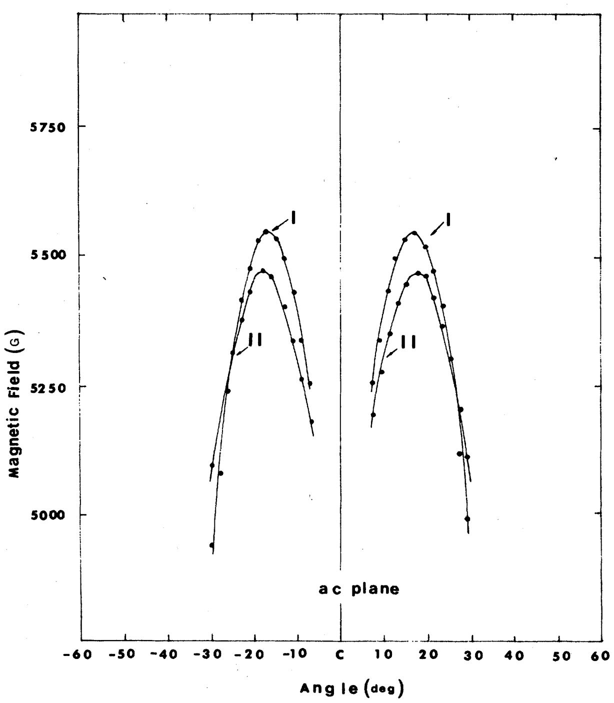

FIG. 4. Angular variation of the highest-field line of the highest-field hyperfine sextet for Mn^{2+} centers I and II in Mn^{2+}-doped $(NH_4)_2SO_4$ crystal at room temperature for the orientation of **B** in the *ac* plane. The continuous lines are smooth curves that connect data points.

The orientations of the principal axes of the zero-field splitting tensor b_2^m (i.e., the magnetic Z axes) corresponding to centers I and II can be determined from the angular variation of spectra in the three mutually perpendicular planes. (The magnetic Z, X, and Y axes of a Mn^{2+} complex are defined to be those directions of **B** for which the overall separations of the allowed lines exhibit extrema; of these three, the overall separations occur in decreasing order for **B** along the Z, X, and Y axes, respectively.) The results are as follows. Center I: $(\hat{\mathbf{Z}},\hat{\mathbf{a}})=75.6°\pm0.5°$, $(\hat{\mathbf{Z}},\hat{\mathbf{b}})=57.9°\pm0.5°$, and $(\hat{\mathbf{Z}},\hat{\mathbf{c}})=35.9°\pm0.5°$. Center II: $(\hat{\mathbf{Z}},\hat{\mathbf{a}})=74.5°\pm0.5°$, $(\hat{\mathbf{Z}},\hat{\mathbf{b}})=62.8°\pm0.5°$, and $(\hat{\mathbf{Z}},\hat{\mathbf{c}})=32.2°\pm0.5°$. Furthermore, using the crystallographic data,[8] it is found that the Z axis for center I is almost coincident with the direction of one of the two $NH_4{}^+$(I)-$NH_4{}^+$(II) pairs (within 5°); while that for center II deviates slightly from this direction (about 9°). The angle between the Z axes corresponding to Mn^{2+} centers I and II is about 6°.

Unlike the previous findings[8,9] of the presence of only one type of Mn^{2+} center in AS, two different types of Mn^{2+} centers have, indeed, been detected to exist simultaneously in the present studies; each of these two Mn^{2+} centers are characterized by EPR spectra which are symmetrical about c, b, and a axes, for **B** in the ab, ac, and bc planes, respectively (Figs. 3, 4, and 5). (The term, "Mn^{2+} center" here refers to a complex consisting of a Mn^{2+} ion with surrounding $SO_4{}^{2-}$ groups and a nearest vacancy; see Sec. V for more details.)

IV. ROOM-TEMPERATURE SPIN-HAMILTONIAN PARAMETERS

In order to evaluate the spin Hamiltonian (SH) parameters, the EPR spectra were, specifically, recorded, at room temperature, for various orientations of the external magnetic field in the magnetic ZX plane, corresponding to the Mn^{2+} center I. The following spin Hamiltonian, appropriate to orthorhombic symmetry, is applicable to Mn^{2+} in AS[32]:

$$\mathcal{H}=\mu_B[g_{\parallel}B_zS_z+g_{\perp}(B_xS_x+B_yS_y)]+\tfrac{1}{3}(b_2^0O_2^0+b_2^2O_2^2)+\tfrac{1}{60}(b_4^0O_4^0+b_4^2O_4^2+b_4^4O_4^4)+AS_zI_z+B(S_xI_x+S_yI_y)$$
$$+Q'[I_z^2-\tfrac{1}{3}I(I+1)]+Q''(I_x^2-I_y^2)\ . \tag{4.1}$$

In Eq. (4.1), μ_B is the Bohr magneton, and the O_l^m are spin operators, as defined by Abragam and Bleaney.[32] A rigorous least-squares-fitting (LSF) procedure,[33] utilizing numerical diagonalization of the SH matrix on a digital computer, in which all clearly-resolved allowed Mn^{2+} line positions, observed for several orientations of **B** in its ZX plane, were simultaneously fitted to evaluate the nine SH parameters $g_{\parallel}$, $g_{\perp}$, b_2^0, b_2^2, b_4^0, b_4^2, b_4^4, A, and B. (The parameters Q' and Q'' could not be determined since the allowed line positions do not depend upon them to first-order in approximation.) The errors of the parameters were determined by the use of a statistical method.[34] Finally, a total of 140 line positions were used to evaluate the nine SH parameters. This included, generally, all the six lines of each of the first, second, fourth, and fifth hyperfine (hf) sextets for each of the orientations of **B** close to, and including, the Z axis (at 0°, 2°, 4°, 6°, 8°, and 10° from the Z axis), and all the six lines of each of the first and fifth hf sextets for each of the orientations of **B** close to, and including, the X axis (at 0°, 2°, 4°, 6°, and 8° from the X axis). (Here, the sextets are referred to in increasing values of the Zeeman field, i.e., the first hf sextet lies at the lowest values of B, while the fifth hf sextet lies at the highest values of B.) The values of the SH parameters, so evaluated, are listed in Table I, which also include the SH parameters reported by Abdulsabirov *et al.*[8] and by Shrivastava.[9] As for the absolute signs of the parameters, they could not be determined from the present data since no relative-intensity data were available at liquid-helium temperature. The sign of b_2^0 was, then, assumed to be positive. The signs of the other fine-structure parameters, relative to that of b_2^0, as yielded by the LSF procedure, are correct. The signs of the hyperfine parameters A, B were chosen to be negative, in accordance with the hyperfine-interaction data.[35]

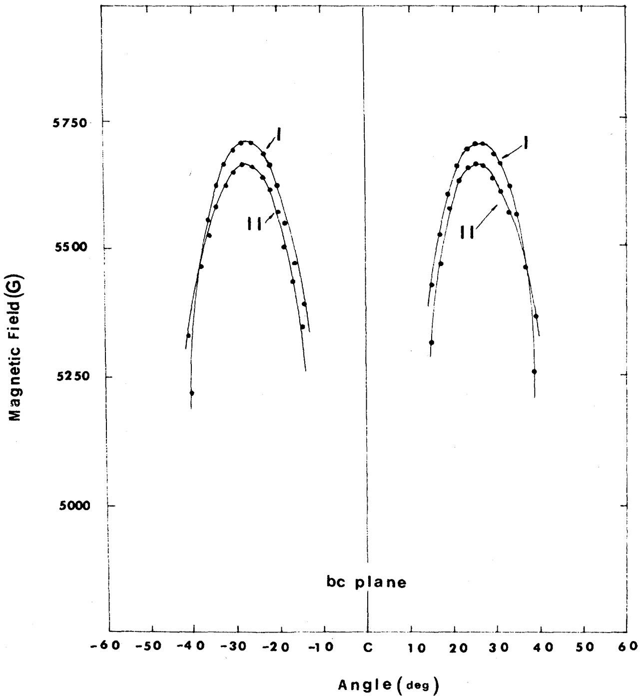

FIG. 5. Angular variation of the highest-field line of the highest-field hyperfine sextet for Mn^{2+} centers I and II in Mn^{2+}-doped $(NH_4)_2SO_4$ crystal at room temperature for the orientation of **B** in the bc plane. The continuous lines are smooth curves that connect data points.

Although the values of the SH parameters as evaluated presently are for Mn^{2+} center I, those for center II are expected not to be much different from these because of the very close proximity of the environments of the two centers, as discussed in Sec. V below.

V. INTERPRETATION OF Mn^{2+} CENTERS I AND II

A. Two Mn^{2+} centers

According to Abdulsabirov *et al.*,[8] when the Mn^{2+} ion replaces a $NH_4{}^+$ ion in AS, a neighbor $NH_4{}^+$ is displaced to create a vacancy for charge compensation; this is referred to as a type-1 charge-compensation mechanism.[30] The same charge-compensation mechanism was suggested by Chaddha,[11] for the case when Cu^{2+} replaces NH_4^+ in AS. Abdulsabirov *et al.*[8] did not specify which of the NH_4^+ ions, in the α or β position, was replaced by Mn^{2+}, reporting the observation of only one Mn^{2+} center, with four physically equivalent orientations. However, in the present work, two physically inequivalent Mn^{2+} centers were, indeed, observed (Figs. 3, 4, and 5). This can be understood as follows. There exist two inequivalent, NH_4^+(I) and NH_4^+(II), ions in AS as verified by neutron-diffraction measurement.[6] When a NH_4^+(I) ion is replaced by Mn^{2+}, a different Mn^{2+} center is created from that when the Mn^{2+} ion replaces a NH_4^+(II) ion. This is due to the smaller space available around the NH_4^+(I) ion (α position); the substitution of Mn^{2+} for NH_4^+(I) causes greater distortion of the coordinations with the surrounding ligands than that caused when Mn^{2+} substitutes for the NH_4^+(II) ion. Assuming that the larger EPR linewidth of Mn^{2+} center II is due to the more distorted coordination, it appears from the present experimental results that the Mn^{2+} ion, in center II, is in the α position, which is surrounded by five SO_4^{2-} ions with the β position left as a vacancy. The Mn^{2+} ion in center I replaces a NH_4^+(I) ion, which is in the β position surrounded by six SO_4^{2-} ions forming a distorted octahedron with the α position left as a vacancy. The α position can also be considered, equivalently, to be surrounded by six SO_4^{2-} ions, one of them lying a little farther from the NH_4^+ ion as compared with the remaining five SO_4^{2-} ions. Therefore, the environments of the α and β positions appear to be very close to each other.

Using the geometrical orientations of the SO_4^{2-} ions,[26] and the assumption that the SO_4^{2-} ions, being heavier than the NH_4^+ ions, are responsible for the occurrence of the spontaneous strain (acoustic mode) in the AS crystal, it is presently concluded that there also exist two-inequivalent SO_4^{2-} groups. This inequivalence may be caused by the *hypothetical* ferroelastic phase transition from hexagonal to orthorhombic symmetry which is expected to take place at a temperature higher than 630 K in the AS crystal.[29] [Although, actually, $(NH_4)_2SO_4$ changes into $(NH_4)HSO_4$ above 630 K, it is known that the other two isomorphous crystals, K_2SO_4 and K_2SeO_4, do, in fact, undergo such transitions at 860 and 745 K.[29]] The NH_4^+ ions also respond to this hypothetical transition, resulting in the creation of two-inequivalent α and β cations. It is, therefore, likely that the two-inequivalent SO_4^{2-} groups, which ligand to Mn^{2+} ions, are responsible for the creation of two different Mn^{2+} centers in AS.

B. Two inequivalent sublattices

It is likely that the Mn^{2+} centers I and II belong to two-inequivalent sublattices. Different EPR linewidths, and different temperature dependences of the EPR spectra for the two Mn^{2+} centers (Sec. VI), imply different distortions and different dynamic behaviors of these two sublattices. This conclusion is a logical consequence of the presence of two crystallographically inequivalent NH_4^+ ions in the unit cell, which implies that there also exist two sets of inequivalent SO_4^{2-} ions in the lattices of AS, since the two α- and β-NH_4^+ groups are surrounded by different SO_4^{2-} groups. The existence of two-inequivalent sublattices in AS has also been proposed from the temperature dependence of the reported spontaneous polarization, and the softening of a coupled-lattice vibration mode by Fujimoto *et al.*[16] As for the EPR studies on AS, the two-sublattices model was proposed only from the EPR of SeO_3^- ions in AS, namely, from the observation of two-inequivalent SeO_3^- ions, which substitute for the SO_4^{2-} ions by Fujimoto and Jerzak.[15].

VI. FERROELECTRIC PHASE TRANSITION AT 223 K

A. EPR spectra

Figure 6 exhibits the variation of the highest-field line position of the highest-field hyperfine sextet corresponding to center I, as well as that of the lowest-field line position of the highest-field hyperfine sextet corresponding to center II, for the orientation of the external magnetic field **B** in the *ab* plane, 25° away from the *a* axis, in the temperature range 113–398 K. (These hyperfine lines are particularly chosen, because they are not flanked by other lines, and are easy to identify.) It is clearly seen from Fig. 6 that, as the temperature is decreased, the line positions corresponding to center I show an abrupt jump to higher magnetic fields at $T_c = 223$ K, thereafter, each line split-

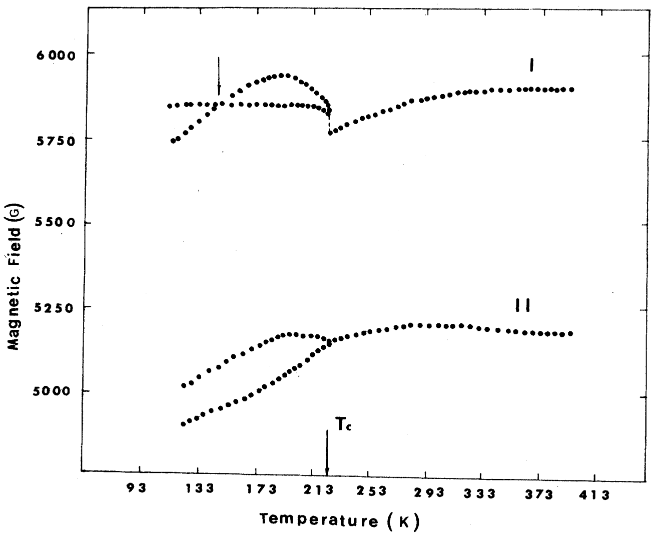

FIG. 6. Variation of the highest-field and the lowest-field hyperfine EPR line positions for the highest-field hyperfine sextets for Mn^{2+} centers I and II, respectively, as functions of temperature, from 113 K to 398 K, for **B** in the *ab* plane, 25° from the *a* axis. At $T_c = 223$ K, different natures of the phase transitions, i.e., a jump of the line position for center I and a continuous change of line position for center II, are clearly exhibited. As well, unusual crossing of split lines for Mn^{2+} center I at 147 K is distinctly visible.

ting into two lines below T_c, characterizing a first-order phase transition of the sublattice of AS crystal to which it belongs. On the other hand, the line positions corresponding to center II do not at all undergo any jumps at T_c, as the temperature is decreased, each of them experiences only a splitting into two lines below T_c; this indicates a second-order phase transition of the sublattice of AS, to which center II belongs. Furthermore, as seen from Fig. 6, the splittings of the lines corresponding to center I exhibit a unique feature *never* reported previously; the line splitting first increases with decreasing temperature below T_c, then it starts to diminish, finally becoming zero at about 147 K. It splits again below 147 K in the opposite direction. This feature is not exhibited by the splitting of the EPR lines, which correspond to center II.

Figure 7 exhibits detailed EPR spectra for **B** in the *ab* plane, 25° from the *a* axis, over a temperature region, including T_c, confirming the conclusions drawn from Fig. 6. Another feature that is apparent from Fig. 7 for center I, is that at 223.5 K (just above T_c), some weak lines of the ferroelectric phase that exists below T_c are also observed, although the EPR lines of the paraelectric phase that exist above T_c, are dominant. This indicates a coexistence of the paraelectric and ferroelectric phases just above T_c. Figure 8 displays a detailed temperature dependence of the EPR spectra, for **B** in the *ab* plane, 25° from the *a* axis, over a temperature region including 147 K; the EPR lines corresponding to center I show crossing of split lines, in accordance with that exhibited by Fig. 6. On the other hand, the lines corresponding to center II continue to remain split, without reversing their splitting, or crossing, at all temperatures below T_c.

Variable-temperature EPR measurements were made for the orientation of **B** in the *bc* and *ac* planes also; similar results to those observed for the orientation of **B** in the *ab* plane were found, except for the fact that no crossing of split lines was observed below T_c for any Mn^{2+} center.

B. Critical exponents

For both the centers I and II, the critical exponent β is presently found to be 0.49 ± 0.03 from the line splitting (ΔB), in the region $[0<(T_c-T)<10\ \mathrm{K}]$. This is clear from Fig. 9, exhibiting log-log straight-line plots of ΔB versus (T_c-T), the slopes being β. The result for center II is in agreement with that reported by Misra and

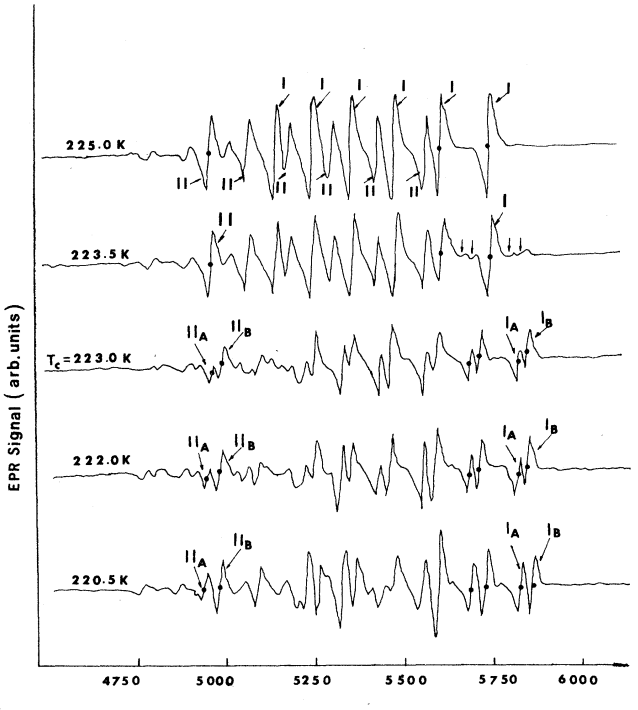

FIG. 7. EPR spectra (first derivative), for the highest-field Mn^{2+} sextet in $(NH_4)_2SO_4$ single crystal, in the temperature range, covering the ferroelectric transition temperature T_c $(=223\ \mathrm{K})$, for **B** in the *ab* plane, 25° from the *a* axis. As the temperature is lowered, the lines corresponding to Mn^{2+} center I show a jump at T_c, then each splits into two lines; the lines corresponding to Mn^{2+} center II, on the other hand, show only a splitting of each line into two at T_c, without undergoing jumps in line positions. (Some weak lines, indicated by arrows, belonging to the ferroelectric phase are also observed just above T_c.) I_A and I_B indicate the two subsublattices to which center I belongs below T_c; the same applies to II_A and II_B for center II.

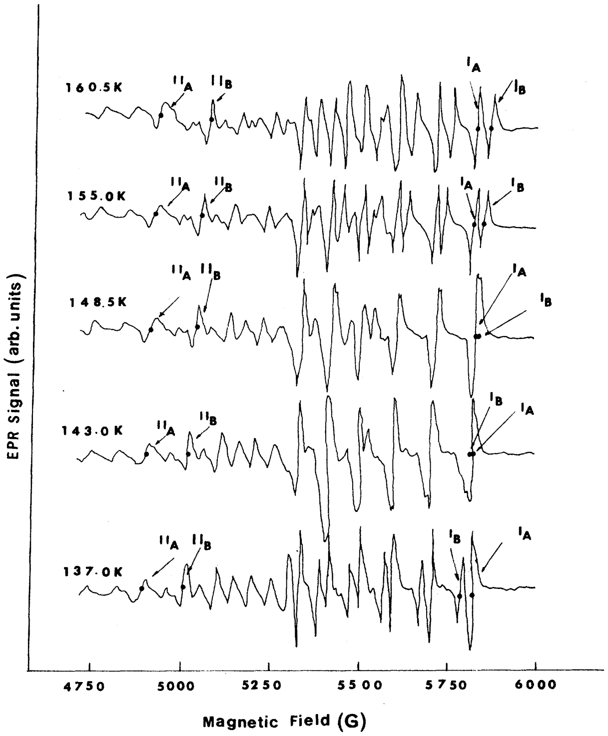

FIG. 8. EPR spectra (first derivative) for the highest-field Mn^{2+} hyperfine sextet in $(NH_4)_2SO_4$ single crystal in the temperature range covering 147 K, for **B** in the *ab* plane, 25° from the *a* axis. It is clearly seen that Mn^{2+} center I exhibits an unusual crossing of split lines at 147 K, as indicated by the relative positions of the solid circles identifying the lines corresponding to center I on the highest-field side, as functions of temperature. I_A and I_B indicate the two subsublattices to which center I belongs below T_c; the same applies to II_A and II_B for center II.

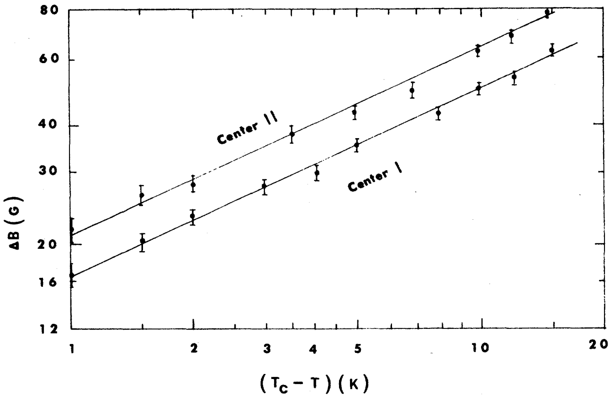

FIG. 9. Log-log plot of the temperature dependence of the line splitting, ΔB, for Mn^{2+} centers I and II, below the ferroelectric phase transition temperature, T_c. The straight lines show that $\Delta B \propto (T_c - T)^\beta$, with $\beta = 0.49 \pm 0.03$ and $T_c = 223$ K, for both the centers in the range 0 K $< (T_c - T) <$ 10 K, consistent with Landau theory (Ref. 36).

Shrivastava,[10] where a second-order transition was considered, while that for center I is in agreement with that reported by Bhat *et al.*[18] for $CrO_4{}^{3-}$-doped AS crystal for the $CrO_4{}^{3-}$ center, which undergoes a first-order phase transition.

C. Scaling law and Rushbrooke inequality

There exists a relation, $(\alpha + 2\beta + \gamma) = 2$, involving the critical exponents α and γ for $T > T_c$ and β for $T < T_c$, known as a *scaling* law.[36] It is interesting to examine the fulfillment of this law for AS. The critical exponent $\beta = 0.5$, as determined presently. The critical exponents α and γ are defined, for $T > T_c$, from the relations $C \propto (T - T_c)^{-\alpha}$ and $\chi \propto (T - T_c)^{-\gamma}$, where C and χ are specific heat and susceptibility, respectively.[38] For AS crystal, γ has been reported to be ~ 1.0.[37] As for α, it has been determined by Hoshino *et al.*[3] to be almost 0.0, for $T > T_c$. Thus, for AS, $\alpha + 2\beta + \gamma \cong 2$. This is in agreement with the scaling law. For $T < T_c$, there exists only an inequality: $\alpha' + 2\beta + \gamma' \geq 2$,[38] known as the Rushbrooke inequality. Here the exponents α' and γ' are defined from the relations $C \propto (T_c - T)^{-\alpha'}$ and $\chi \propto (T_c - T)^{-\gamma'}$.[38] For the AS crystal, γ' and α' have been reported to be ~ 1.0,[37] and ~ 0.2,[3] respectively. Thus for AS, $\alpha' + 2\beta + \gamma' \cong 2.2$. This is in good agreement with the Rushbrooke inequality.

D. Mechanism for phase transition

Unruh *et al.*[4] concluded from their measurement of the spontaneous polarization, P_s, of AS, that P_s could not be treated as the order parameter of the phase transition and thus called the transition *ferrielectric*, implying that the two sublattices contribute differently to the resultant spontaneous polarization. Since P_s, which is related to the optic mode of lattice vibration, is not the order parameter, some other mode must be responsible for the occurrence of the phase transition. This other mode is presently suggested to be the acoustic mode, related to the existence of ferroelasticity in the paraelectric phase of the AS crystal above T_c. The high value of the spontaneous strain may cause additional crystal distortion leading to ferroelastic domains. This creates additional weak lines in the Mn^{2+} spectra at room temperature in AS over and above those already mentioned. It is likely that the coupling to the spontaneous strain (acoustic mode) is different for the two sublattices. It is suggested presently that the sublattice to which Mn^{2+} center I belongs, which undergoes first-order transition, is strongly coupled to the acoustic mode while the sublattice to which center II belongs, which undergoes second-order transition, is only weakly coupled to the acoustic mode. This explains qualitatively why Mn^{2+} ions belonging to different sublattices behave differently at T_c. Bhat *et al.*[18] also noticed the coexistence of discontinuous (the same as that of center I) and continuous (the same as that of center II), behavior of the EPR lines in $CrO_4{}^{3-}$-doped AS crystal at T_c. However, they did not invoke the two-inequivalent-sublattices model, which would have provided the correct explanation of their spectra.

The reversal of the sign of polarization, P_s, at low temperatures, as observed by Unruh,[4] can be explained as follows. As the temperature is lowered below T_c, the sublattice, to which center I belongs, splits further into two sublattices with opposite polarizations; these polarizations exhibit different temperature dependences. The crossing of split lines for center I occurs when these two polarizations are equal and opposite, i.e., at 147 K (Fig. 8).

The two-inequivalent-sublattices model, as proposed presently, is not the same as that postulated by Sawada,[26] in which no further splittings of the sublattices below T_c was predicted, contrary to the present finding for AS, wherein each of the two sublattices above T_c splits into two sub-sublattices below T_c. Otherwise, the observed polarization behavior below T_c could not be correctly explained, as discussed above. In the model proposed presently, the $SO_4{}^{2-}$ ions are also considered to be inequivalent, contrary to the assumption of Sawada *et al.*[26] The $SO_4{}^{2-}$ ions play an important role in the splitting of each of two sublattices, which exist above T_c, into two sublattices below T_c. The effectiveness of $SO_4{}^{2-}$ ions in the ferroelectric phase transition has also been suggested by Sawada *et al.*[29] and by Bhat *et al.*[18]

The present results and interpretation are similar to those drawn by Fujimoto and Jerzak[15] from the EPR of $SeO_3{}^-$ ions in the AS crystal. According to them, two inequivalent centers of the $SeO_3{}^-$ radical in AS belong to two coupled sublattices; the EPR lines above T_c of one center are very strongly temperature dependent, while those of the other are almost temperature independent.

VII. LINEWIDTH

The EPR linewidths for Mn^{2+} were estimated for the two centers in the temperature range 113–398 K. Center II is characterized by a slightly larger linewidth than that of center I. The EPR linewidth for center I is 14±1 G above T_c, while it is 16±1 G below T_c. On the other hand, the linewidth for center II remains 17±1 G at all temperatures. The fact that only the linewidth corresponding to center I experiences a change at T_c supports the contention that only one sublattice in AS, namely, the one to which center I belongs, is responsible for the onset of ferroelectric phase transition; the other sublattice, the one to which center II belongs, just follows this transition.

VIII. CONCLUDING REMARKS

It has been possible here to identify the presence of the two different Mn^{2+} centers only because of the high sensitivity of the Mn^{2+} fine-structure EPR lines to even very small changes in the configuration of the $SO_4{}^{2-}$ ligands to Mn^{2+} ions; the configurations of the surroundings of the α and β positions are quite close to each other.

The following are the salient features of the present study.

(i) Two different Mn^{2+} centers, belonging to two inequivalent sublattices undergoing first- and second-order phase transitions, have been simultaneously observed in AS. Previously, either center I, or center II, but not both together, was observed.

(ii) Above T_c, there exist two inequivalent sublattices in AS for each of the $NH_4{}^{+}$ and $SO_4{}^{2-}$ ions which are coupled to each other; each of these split further into two subsublattices below T_c.

(iii) The ferroelectric phase transitions of different natures for the two sublattices are caused by couplings of different strengths of the two sublattices to the acoustic mode, effected by the spontaneous strain.

(iv) The unusual crossing of split lines, observed for Mn^{2+} center I below T_c, has not been reported previously in AS crystals, whether doped by Mn^{2+} or by any other paramagnetic ion.

(v) Only one sublattice is responsible for the temperature variation of the spontaneous polarization, P_s, since only one center exhibits a crossing of split EPR lines as the temperature changes.

(vi) The ferroelectric phase transition temperature T_c, presently determined to be 223 K, is in agreement with the well-accepted value.

(vii) The room-temperature Mn^{2+} spin-Hamiltonian parameters, as reported presently, have been evaluated by the use of a rigorous least-squares-fitting procedure.

(viii) The ferroelectric phase transition in AS is found to satisfy both the scaling law and Rushbrooke inequality.

ACKNOWLEDGMENTS

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support (Grant No. A4485). The facilities of the Concordia University Computer Center were used to compute the spin-Hamiltonian parameters.

---

*On leave of absence from Center of Materials Analysis, Nanjing University, Nanjing, Jiangsu, People's Republic of China.

†Present address: Physics Department, York University, North York, Ontario, Canada M3J 1P3.

[1] V. T. Matthias and J. P. Remeika, Phys. Rev. **103**, 262 (1956).

[2] H. Ohshima and E. Nakamura, J. Phys. Chem. Solids **27**, 481 (1966).

[3] S. Hoshino, K. Vedam, Y. Okaya, and R. Pepinsky, Phys. Rev. **112**, 405 (1958).

[4] H. G. Unruh, Solid State Commun. **8**, 1951 (1970).

[5] T. Ikada, K. Fujibayashi, T. Nagai, and K. Kobayashi, Phys. Status Solidi A **16**, 279 (1973).

[6] E. O. Schlemper and W. C. Hamilton, J. Chem. Phys. **44**, 4498 (1966).

[7] R. Blinc and I. Levstek, J. Phys. Chem. Solids **12**, 295 (1960).

[8] R. Yu. Abdulsabirov, Yu. S. Greznev, and M. M. Zaripov, Sov. Phys.—Solid State **14**, 2894 (1973).

[9] K. N. Shrivastava, Phys. Status Solidi A **1**, K101 (1970).

[10] S. K. Misra and K. N. Shrivastava, Phys. Rev. B **37**, 2255 (1988).

[11] G. Chaddha, J. Phys. Soc. Jpn. **24**, 976 (1968).

[12] F. J. Owens, Chem. Phys. Lett. **38**, 106 (1976).

[13] C. V. Manjunath and R. Srinivasan, Phys. Status Solidi A **44**, 687 (1977).

[14] N. Shibata, R. Abe, and I. Suzuki, J. Phys. Soc. Jpn. **41**, 2011 (1976).

[15] M. Fujimoto and S. Jerzak (unpublished).

[16] M. Fujimoto, L. A. Dressel, and T. J. Yu, J. Phys. Chem. Solids **38**, 97 (1977).

[17] K. Chu, J. Magn. Reson. **21**, 151 (1976).

[18] S. V. Bhat, N. C. Mishra, and R. Srinivasan, J. Phys. Chem. Solids **43**, 1157 (1982).

[19] C. V. Manjunath and R. Srinivasan, Phys. Status Solidi B **87**, 395 (1978).

[20] B. Rakvin and N. S. Dalal, J. Chem. Phys. **85**, 6060 (1986).

[21] Y. S. Jain, H. D. Bist, and G. C. Upreti, Chem. Phys. Lett. **22**, 572 (1973).

[22] Z. Iqbal and C. W. Christoe, Solid State Commun. **18**, 269 (1976).

[23] D. E. O'Reilly and T. Tsang, J. Chem. Phys. **46**, 1291 (1967).

[24] A. Sawada, Y. Takagi, and Y. Ishibashi, J. Phys. Soc. Jpn. **34**, 748 (1973).

[25] J. Petzelt, J. Grigas, and I. Myerova, Ferroelectrics **6**, 225 (1974).

[26] A. Sawada, S. Ohya, Y. Ishibashi, and Y. Takagi, J. Phys. Soc. Jpn. **38**, 1408 (1975).

[27] Y. S. Jain, P. K. Bajpai, R. Bhattachajee, and D. Chowdhury, J. Phys. C **19**, 3789 (1986).

[28] Y. Makita, A. Sawada, and Y. Takagi, J. Phys. Soc. Jpn. **41**, 167 (1976).

[29] A. Sawada, Y. Makita, and Y. Takagi, J. Phys. Soc. Jpn. **41**, 174 (1976).

[30] G. D. Watkins, Phys. Rev. **113**, 79 (1959).

[31] Y. Okaya, K. Vedam, and R. Pepinsky, Acta Crystallog. **11**, 307 (1958).

[32] A. Abragam and B. Bleaney, *Electron Paramagnetic Reso-*

nance of Transition Ions (Clarendon, Oxford, 1970).

[33]S. K. Misra, J. Magn. Reson. **23**, 403 (1976); Physica B **121**, 193 (1983).

[34]S. K. Misra and S. Subramanian, J. Phys. C **15**, 7199 (1982).

[35]A. Steudel, *Hyperfine Interactions* (Academic, New York, 1970), p. 182.

[36]F. J. Owens, in *Magnetic Resonance of Phase Transitions*, edited by F. J. Owens, C. P. Poole, Jr., and H. Farach (Academic, New York, 1979).

[37]*Numerical Data and Functional Relationship in Science and Technology,* Vol. 16 of *Landolt-Börnstein Series,* edited by T. Mitsui and E. Nakamura (Springer-Verlag, Berlin, 1982), p. 105.

[38]R. B. Griffiths, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1972).