

EPR determination of the critical exponent of Mn^{2+} -doped $(\text{NH}_4)_2\text{SO}_4$ below the ferroelectric phase transition

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(Received 11 March 1987)

The Mn^{2+} EPR line splitting in $(\text{NH}_4)_2\text{SO}_4$ has been exploited to determine the critical exponent β for the electric polarization below the ferroelectric phase-transition temperature. The estimated value of $\beta=0.5$ is consistent with the exactly solvable spherical model for spatial dimension $d=3$.

Recently the technique of EPR has been employed to investigate the temperature dependence of the order parameter of phase transitions by means of the line splitting. For example, Waplak, Schmidt, and Drumheller¹ found the critical exponent $\beta=0.5$ below the ferroelectric phase-transition temperature (T_c), using the line splitting for the fine-structure component of the Cu^{2+} tetramer, in monoclinic CsH_2PO_4 (CDP). A similar study has been published by Müller and Berlinger.²

The present paper reports the EPR determination of the critical exponent β for Mn^{2+} -doped (0.005 at.%) $(\text{NH}_4)_2\text{SO}_4$ single crystal by studying the temperature dependence of the splitting of EPR lines below the phase-transition temperature. $(\text{NH}_4)_2\text{SO}_4$ crystal is characterized by the space group $Pnam$ (orthorhombic) at room temperature, while in the low-temperature ferroelectric

phase, below 217.5 K, the space group describing³ the crystal is $Pna2_1$ (orthorhombic). At room temperature, there are only two hydrogen bonds of $\text{O}\cdots\text{H}$ distance less than 2 Å, whereas in the ferroelectric phase there are six. The mean distance of hydrogen bonds $\text{O}\cdots\text{H}$ is decreased by 0.1 Å in the latter phase, although the range of distances remains the same. The bond lengths in each phase are listed quantitatively by Schlemper and Hamilton.³

X-band EPR studies reporting the spin-Hamiltonian parameters of Mn^{2+} in $(\text{NH}_4)_2\text{SO}_4$ have been previously published.^{4,5} At room temperature, four sets of typical thirty-line Mn^{2+} EPR spectra corresponding to four physically inequivalent, but magnetically equivalent, Mn^{2+} complexes, with electronic spin $S=\frac{5}{2}$ and nuclear spin $I=\frac{5}{2}$, are observed. The features of the spectrum remain

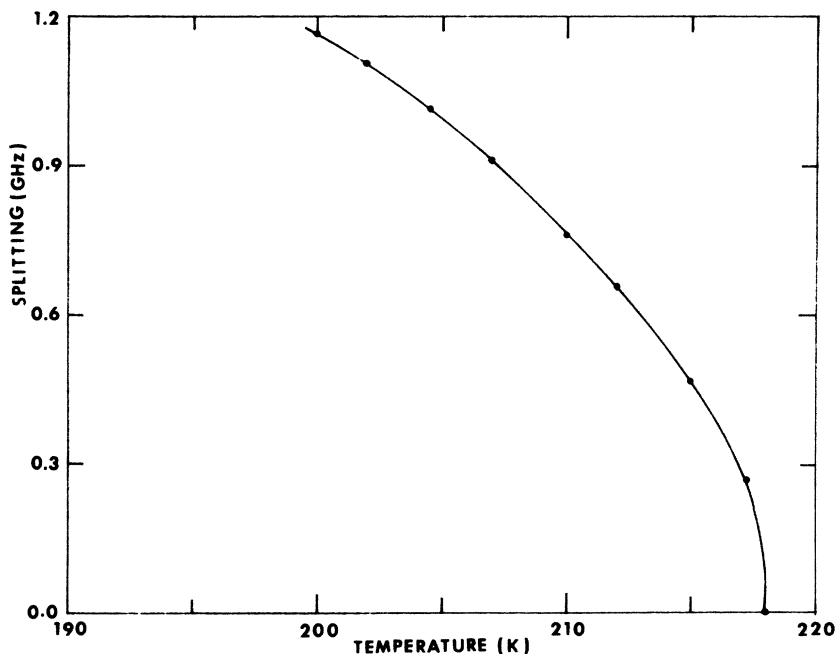


FIG. 1. The temperature variation of the splitting of the $-\frac{3}{2}, \frac{5}{2} \leftrightarrow -\frac{5}{2}, \frac{3}{2}$ transition of Mn^{2+} in $(\text{NH}_4)_2\text{SO}_4$ below the phase-transition temperature. The measured values are shown by the dots. The continuous line describes the calculated values corresponding to Eq. (1) with $H_0=4.053$ GHz, $T_c=218$ K, and $\beta=0.5$.

the same down to the phase-transition temperature $T_c = 217.5 \pm 0.5$ K, below which each of the thirty lines splits into two in the ferroelectric phase of $(\text{NH}_4)_2\text{SO}_4$. This is due to ferroelectric polarization, rotation of NH_4 molecules, and distortion, along with strengthening of hydrogen bonds.

No detailed study of temperature dependence of EPR line splitting below T_c of Mn^{2+} -doped $(\text{NH}_4)_2\text{SO}_4$ has been published so far. The temperature dependence of the splitting observed previously^{3,4} using a Varian 4502 spectrometer equipped with a Varian temperature-control unit, will here be examined in detail. Figure 1 exhibits ΔH , the splitting of the highest-field line $(-\frac{5}{2}, \frac{5}{2} \leftrightarrow -\frac{3}{2}, \frac{3}{2})$ for \mathbf{H} along the principal z axis of the b_2^m tensor for Mn^{2+} doped $(\text{NH}_4)_2\text{SO}_4$ in energy units (by multiplying the splitting of the line in gauss with $g\mu_B$ where $g=2$ and μ_B is the Bohr magneton). The data can be fitted very accurately (Fig. 1) to

$$\Delta H = H_0[(T_c - T)/T_c]^\beta, \quad (1)$$

with $H_0 = 4.053$ GHz, $T_c = 218$ K, and $\beta = 0.5$.

That the exponent in Eq. (1) is β is, indeed, established by the fact that, as shown in the Appendix, the EPR line splitting depends linearly on the differences of the values of the spin-Hamiltonian parameters corresponding to the two sets of spectra. These are determined by the polarization P , the latter varying near the phase transition⁶ in the ferroelectric phase as $(T - T_c)^\beta$. The other critical exponents α , γ , and δ are defined, respectively, by the variations of the specific heat C , the electric field E , and susceptibility χ as follows: $C \sim (T - T_c)^{-\alpha}$, $P \sim E^{1/\delta}$, $\chi \sim (T - T_c)^{-\gamma}$. From these definitions, along with $P = \chi E$, it follows that $\gamma = \beta(\delta - 1)$. Theoretical calculations of α , β , γ , and δ have been made. According to the mean-field theory⁶ $\beta = 0.5$, $\delta = 3$, $\gamma = 1$, while the exactly solvable spherical model for spatial dimension $d = 3$ gives $\beta = 0.5$, $\gamma = 2$, $\delta = 5$.^{7,8} On the other hand, the Gaussian approximation yields $\alpha = 2 - d/2$, $\beta = 0.5$, $\gamma = 1$, $\delta = 3$.

The exponent η of Green's function is described by $G(k) \sim k^{-2+\eta}$ where k is the wave vector;⁹ η is related to β by the relation

$$\beta = \nu(d - 2 + \eta)/2 \quad (2a)$$

or

$$\beta = \gamma(d - 2 + \eta)/(2 - \eta), \quad (2b)$$

using the relation $\nu = \gamma/(2 - \eta)$.^{6,9} In Eqs. (2a) and (2b) ν is defined by the exponent of the correlation length as $\xi \sim |T - T_c|^{-\nu}$. Usually $\eta \ll 1$. Thus, neglecting η in Eq. (2) one obtains $\gamma = 2$ for $d = 3$ and $\beta = 0.5$. (Note that if $\beta > 0$ and $\eta \sim 0$, d should be > 2 .) These values are consistent with those found for the spherical model for spatial dimension $d = 3$, as listed above.

In conclusion, the value of $\beta = 0.5$ as estimated from the EPR line splitting of $(\text{NH}_4)_2\text{SO}_4$ corresponds to $d = 3$, in-

TABLE I. The spin-Hamiltonian parameters for Mn^{2+} -doped $(\text{NH}_4)_2\text{SO}_4$ single crystal at room temperature, and at temperatures just above and just below the ferroelectric phase-transition temperature $T_c = 217.5$ K. The parameter g is dimensionless, while the remaining parameters are expressed in units of GHz. A site I above T_c splits into two sites (I_a and I_b) below T_c .

Parameter	300 K Site I	218 K Site I	217 K Site I_a	217 K Site I_b
g	1.996	1.996	2.001	1.998
B_2^0	0.485	0.482	0.483	0.448
B_2^2	-0.239	-0.287	-0.279	-0.293
B_4^0	-0.00009	0.00001	-0.00022	-0.00053
A	-0.256	-0.256	-0.262	-0.259
B	-0.250	-0.250	-0.249	-0.249

dicating the existence of three-dimensional correlations in $(\text{NH}_4)_2\text{SO}_4$.

APPENDIX

The EPR spectrum corresponding to one of the physically inequivalent, of the four magnetically equivalent complexes of Mn^{2+} in $(\text{NH}_4)_2\text{SO}_4$ is described, in the notation of Abragam and Bleaney,¹⁰ by the following spin Hamiltonian:

$$\mathcal{H} = g\mu_B \mathbf{H} \cdot \mathbf{S} + B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0 + AS_z I_z + B(S_x I_x + S_y I_y). \quad (3)$$

In Eq. (3), g , B^m , A , and B are the spin-Hamiltonian parameters (SHP), while the O_l^m are the spin operators.¹⁰ The SHP, as determined from line positions obtained for the external magnetic field orientation along the principal axis of the B_2^m tensor at room temperature, at 218 K and at 217 K, are listed in Table I.^{4,5}

Using the calculated magnetic field values for the various transitions¹⁰ from the eigenvalues, estimated to second order of perturbation, one can express the splitting of a line below T_c as follows:

$$\Delta H = \sum_i C_i \Delta a_i, \quad (4)$$

where the Δa_i represent the differences of the corresponding SHP below T_c for the two sets of the spectra and C_i are constants. In writing Eq. (4), it has been assumed that there are no large changes in the SHP a_i for $200 \text{ K} < T < 217 \text{ K}$, so that even though some of the a_i may appear in the C_i , the C_i are still very nearly constant.

It is well known that the polarization of the surrounding ions determines the SHP of an ion, see, e.g., calculations of SHP based on the point charge and induced-dipole model.^{11,12} Thus, ΔH , as given by Eq. (4), is proportional to the polarization P . Hence, $\Delta H \sim (T - T_c)^\beta$.

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