Order-disorder dynamics of the ferroelectric phase transition in tris-sarcosine calcium chloride crystals

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(Received 25 October 1985)

Critical anomalies in the Mn^{2+} impurity spectra near the ferroelectric phase transition in tris-sarcosine calcium chloride (TSCC) crystals have been interpreted in terms of a collective fluctuation in the polar pseudospin system representing Ca(sarcosine)$_6$ complexes in the lattice. The anomalous line broadening in the paraelectric phase was found to be closely related to the splitting of the line below the transition temperature T_c. At temperatures close to T_c in the ferroelectric phase the line shape was asymmetrical, indicating that sinusoidally distributed pseudospins were randomly sampled by Mn^{2+} impurities. The time scale of EPR measurements modified the line shape, where the presence of a slow fluctuation between the pair of lines was evident. Contrary to recent spectroscopic and dielectric results on TSCC crystals, the critical anomalies in the Mn^{2+} spectra were well resolved to give grounds for the order-disorder dynamics of the transition.

I. INTRODUCTION

The phase transition in *tris-sarcosine calcium chloride* (TSCC) crystals at 130 K has been a subject of many investigations in recent years, providing a model case of a uniaxial ferroelectric phase transition. Although the molecular mechanism is still unveiled, Makita's early dielectric results[1] suggested that the transition was order-disorder, while the presence of underdamped soft modes in the noncritical region[2–4] is clear evidence for a displacive mechanism. Lacking a direct proof for the former, the latter seems to be overwhelming; however, the details of the transition have not yet been fully understood.

To gain an insight into the mechanism, dielectric properties of TSCC crystals have recently been remeasured by Deguchi and co-workers[5] and Sawada and Horioka[6] at uhf and microwave frequencies. According to these investigators, the dielectric anomalies are attributed to overdamping of the soft modes that are coupled to a *relaxator* in the critical region. Sugo and co-workers[7] have given support to this view on the basis of the Raman scattering data, while Chen and Schaack[8] have shown in contrast that their infrared and Raman results can be interpreted in terms of pseudospins coupled with phonons. In these experiments however, the details of the transition were not sufficiently resolved to disclose the mechanism. In our opinion, it is a matter of the models that has led to these different views. Chen and Schaack[8] have proposed in their work a molecular model for the active group consisting of a collective sarcosine orientation.

Windsch[9] first carried out EPR studies on the phase transition in TSCC crystals, reporting that a critical anomaly was observed in the Mn^{2+} impurity spectra near the transition temperature ($T_c \simeq 130$ K). Fujimoto[10] studied VO^{2+} impurity spectra in TSCC crystals, which exhibited a symmetry representing closely the Ca(sarcosine)$_6$ complex. Although no critical effect was detected in the ^{51}V-hyperfine structure, the sarcosine displacement inferred from the change in the VO^{2+} spectra was indeed consistent with the model of Chen and Schaack. However, the order-disorder mechanism was not necessarily verified in these EPR results, except when the dynamics of the transition was observed in its favor. In the noncritical region, a displacive feature dominated these spectra, while the critical anomaly was not sufficiently studied to reveal the nature of the transition. Therefore, we have examined these spectra in further detail[11] and found that the dynamics in the ligand field reflect sensitively in the fine-structure tensor. Divalent Mn^{2+} ions, among others, exhibit a particularly simple spectrum, which is suitable for studying the critical anomaly. Moreover, the Mn(sarcosine)$_6$ complex is supposed to be free from such a charge defect as that accompanying a trivalent impurity, representing the host lattice with less ambiguity. From these points of view, we studied the critical anomaly mainly in the Mn^{2+} spectra. As a result, the anomaly was attributed to the fluctuation of Ca(sarcosine)$_6$ complexes between two distinct orientations, manifesting an order-disorder mechanism of the transition.

While considered as a model ferroelectric, the properties of TSCC crystals are somewhat unusual. The small value of the Curie constant ($C = 58$ K) and the relatively high T_c suggest that the short-range force plays an essential role in the phase transition.[4] Although the long-range dipolar force cannot be ignored, we consider that the short-range interaction among spins is primarily responsible for the ordered complex arrangement. If so, the fluctuation in the pseudospin system should appear in the spectra, depending on the time scale of EPR measurements. To observe the critical dynamics, we studied the Mn^{2+} spectra with X- and Q-band spectrometers, and ob-

tained a significant difference. Assuming a pseudospin coupling of the Heisenberg type, we can show that two competing interactions in the TSCC lattice yield an incommensurate distribution of pseudospins along the ferroelectric b axis. We consider that such distributed spins represent premature domains in the critical region below T_c and their dynamics reflects the characteristics of observed anomalies.

Bornarel and Schmidt[12] have shown in their dielectric studies that the ferroelectric transition in TSCC crystals can be modified substantially by an externally applied electric field. In fact, prior to this work, Windsch[13] had already observed that the Mn^{2+} spectra responded sensitively to the *bias* field. We have further investigated the electric field effect and interpreted it as suppressing the polar mode fluctuation. As a result, we have concluded that the pseudospin defined for the deformed Ca(sarcosine)$_6$ complex is dipolar.

In this paper, we present EPR evidence for the order-disorder dynamics of the phase transition in TSCC crystals. Essential features of the Mn^{2+} spectra are summarized in Sec. II to deal with the phase transition, where the pseudospin is defined for the change in the fine-structure tensor. In Sec. III, the relation between the linewidth anomaly in the paraelectric phase and the splitting in the ferroelectric phase is discussed, in justification of the mechanism. In Sec. IV, the anomalous line shape observed below T_c is described and interpreted in terms of a modulation of the polar mode. In Sec. V, the electric field on Mn^{2+} spectra is summarized and the role of the long-range dipolar force is discussed. In Sec. VI, the nature of short-range interaction in TSCC crystals is discussed in light of a model inferred from the x-ray and EPR data.

II. Mn^{2+} SPECTRA AND THE ORDER PARAMETER

Details of the Mn^{2+} spectra in TSCC crystals have already been discussed in the literature,[9,13] and only the essential features are summarized here to deal with the phase transition.

Magnetic properties of the Mn(sarcosine)$_6$ complex are described by the spin Hamiltonian

$$H=g\beta\mathbf{B}\cdot\mathbf{S}+\mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S}+K\mathbf{S}\cdot\mathbf{I}+H' , \quad (1)$$

where all the notations are conventional. The g factor and the ^{55}Mn hyperfine splitting K are practically constant within experimental errors, whereas the fine-structure splitting determined by the **D** tensor is anisotropic, showing a significant change with temperature. The **D** tensor characterizes an orthorhombic distortion of the nearly octahedral Ca(sarcosine)$_6$ complex. In terms of the **D** tensor, only a quadrupolar distortion can be dealt with, while the higher-order spin terms expressed by H' in Eq. (1) are not significant for allowed EPR transitions in the first-order approximation. With a Mn^{2+} impurity substituted for the Ca^{2+} ion, the complex is further deformed, but we assume that the change in the **D** tensor $\Delta D=D-D_0$, where $|D|=D_0$ at $T=T_c$, provides us with an adequate description of the phase transition.

In the unit cell there are four magnetically inequivalent impurity sites, which are related by symmetry operations of the crystal. Therefore, the number of resonance lines is reduced substantially when the static field **B** is applied in crystallographic planes (100), (010), and (001). In the paraelectric phase, two distinct spectra were observed in the (010) plane, whereas only one was observed in the other planes of rotation. In Fig. 1 are shown angular variations of the fine-structure splittings in these planes. The directions of the principal axes are schematically illustrated in Fig. 2. It is noticed that in the paraelectric phase the two unique Z axes are distinguishable only in the (010) plane. The angle between them is small and only 9.0° at room temperature (22.5 °C) and bisected by the a axis. We have found that this small angle diminishes further with increasing temperature, representing the pseudosymmetry in the paraelectric phase. The results of our study on the ferroelasticity of TSCC crystals have been reported in a separate paper.[14]

In the ferroelectric phase, the Mn^{2+} spectra exhibited a splitting into two components, except in the mirror (010) plane. As shown in Fig. 1, there was no splitting when the static field was perpendicular to the b axis. A similar ferroelectric splitting was also observed from VO^{2+} impurity complexes whose unique hyperfine axes lie in the

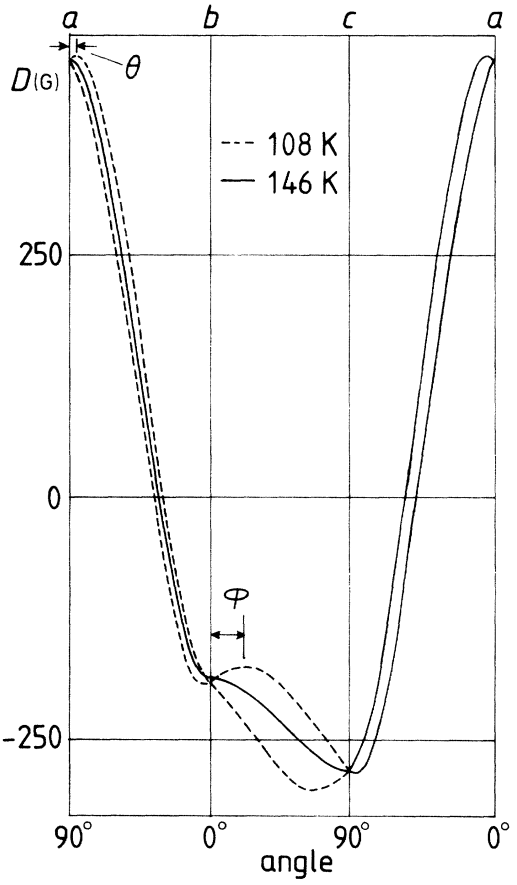

FIG. 1. Angular dependences of the fine-structure splitting in the Mn^{2+} spectra from TSCC crystals. The solid and dashed lines were obtained at 108 and 146 K, respectively. Notice that in the (010) plane no splitting occurs in the ferroelectric phase.

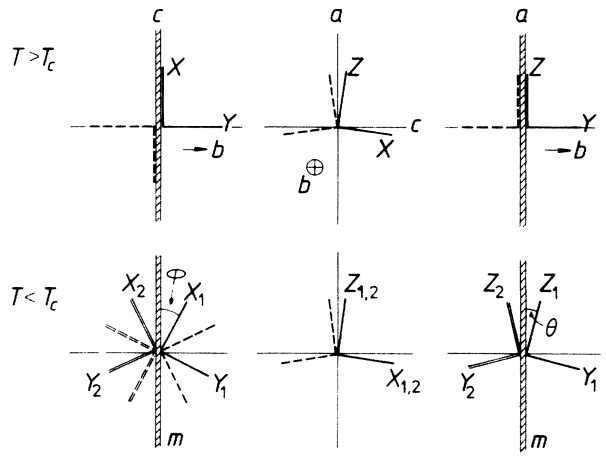

FIG. 2. Principal directions of the D tensor for $T > T_c$ and $T < T_c$. The cross-hatched areas represent the mirror plane. The subscripts 1 and 2 are designated for the two ferroelectric domains with opposite polarizations. Notice that two domains are distinguishable in the Mn^{2+} spectra only in the (001) plane.

mirror plane [$VO^{2+}(I)$ in Ref. 10]. In these spectra the ferroelectric transition is characterized by two-way shifts of the unique axes in the direction normal to the (010) plane. In a uniaxial ferroelectric crystal, such a splitting represents two ferroelectric domains with opposite polarizations, signifying the loss of the mirror symmetry in each domain. In this case, the domain volumes are represented by intensities of the components, as can be verified by a hysteresis study with an electric field applied parallel to the b axis. In the Mn^{2+} spectra, however, such a domain distinction was possible only in the (001) plane. In the other planes of rotation, (100) and (010), the intensity consists of complementary contributions from two domains and is independent of the change in domain volumes. This is precisely a consequence of the domain symmetry.

At the transition point, a structural change takes place, which may be described by angle $\pm\theta$ and $\pm\phi$ defined in Fig. 1. While the angle θ indicates the shift of the Z axis from the mirror plane, the angle ϕ represents a rotation of the complex around the Z axis. According to the above domain identification, the rotations $\pm\phi$ occur in each domain without violating the crystal symmetry, whereas the angular shifts $\pm\theta$ are assigned to each domain when the mirror symmetry is lost. The temperature dependences of these angles should be identical, provided that the complex is regarded as a rigid body. However, the Ca(sarcosine)$_6$ complex is by no means rigid in the ferroelectric phase, as indicated by the change of the fine-structure asymmetry $E=\frac{1}{2}(D_x-D_y)$ below T_c.[9] Assuming that $\theta \propto (T_c-T)^{\gamma}$ and $\phi \propto (T_c-T)^{\gamma'}$, the values of the exponents were evaluated: these are $\gamma=0.42\pm0.02$ and $\gamma'=0.22\pm0.02$. While such an exponent description for the approach to T_c may not represent any physically meaningful process,[4] these different exponents obtained from the complex suggest the presence of a mechanism beyond the rigid-body assumption. It is clear that the angle $\pm\phi$ have no macroscopic significance by symmetry, whereas θ corresponds to a displacement to break the mirror reflection symmetry. Furthermore, the value of γ agrees within experimental error to that determined from the soft-mode frequencies.[2] Therefore, we consider that the angle θ represents the order parameter, which may be defined by an electric dipole moment induced by distortion of the complex below T_c. Although directly undetectable in magnetic measurements, it may be observed through the change of the quadrupole axis, which occurs as the dipole of the complex is rotated by an internal electric field. Such a rotation of the complex may be interpreted as caused by the local piezoelectric stress. In fact, the dipolar character of the pseudospin has been substantiated in the electric field effect, as described in Sec. V.

In the case of the Mn^{2+} complex in TSCC crystals, we have considered that the relations

$$\Delta D \propto \phi^2, \quad \Delta D \propto \theta$$

hold approximately in the (100) and (001) planes, respectively. In this case, the empirical relation between these exponents, i.e., $\gamma \approx 2\gamma'$, may not have been accidental, and the order parameter is represented by ϕ^2 and θ in these phases. In general, for a linear fluctuation, one can write[15]

$$\Delta D = A\sigma , \tag{2}$$

where A is an anisotropic factor and σ the order parameter. Then the above assignment of the angular parameters to the order parameter can be justified at least to the lowest-order approximation. The order parameter for the phase transition can thus be defined by the pseudospin representing the Ca(sarcosine)$_6$ complex. The change in the **D**-tensor value from D_0 to $D_0 \pm A\sigma$ signifies the ferroelectric transition.

III. ANOMALOUS LINEWIDTHS ABOVE T_c AND THE RELATION TO FERROELECTRIC SPLITTINGS

In the noncritical region above T_c, the linewidths for allowed EPR transitions in the Mn^{2+} spectra were practically constant and independent of the quantum numbers. However, lines in the $(\pm\frac{5}{2},\pm\frac{3}{2})$ and $(\pm\frac{3}{2},\pm\frac{1}{2})$ transitions exhibited increasing widths, when the transition T_c was closely approached from above. This critical broadening was most appreciable in the $(\pm\frac{5}{2},\pm\frac{3}{2})$ transitions and less so in the $(\pm\frac{3}{2},\pm\frac{1}{2})$ lines, whereas the linewidths in the $(\pm\frac{1}{2},\mp\frac{1}{2})$ transitions were virtually unchanged. The line shape was approximately Gaussian, signifying that the fine-structure splittings became distributed in this region, as the fluctuation slowed down near T_c.

Primarily, the critical broadening was thought to occur in proportion to the slope of the angular variation curve of the fine-structure splitting, i.e., $\Delta D/\Delta\alpha$, where α is the angle of rotation. The broadening was thus anisotropic and noticeable between crystallographic axes, suggesting that an angular fluctuation of the D-tensor axes was responsible for the anomaly. The critical anomaly in the Mn^{2+} spectra was not as much as that in the Cr^3 and Fe^3 spectra, but significant enough to deal with the phase

transition. In fact, larger anomalies in the latter were attributed to larger values of fine-structure splittings in these ions. Figure 3 shows temperature-dependent linewidths measured in the hyperfine line of the $(\pm\frac{5}{2},\pm\frac{3}{2})$ transitions for a direction in the (100) plane. Figure 4 illustrates angular dependences of the critical linewidths in the (100) and (001) planes at $\Delta T=T-T_c=6$ and 0.3 K. In the (010) plane, in contrast, there was no anomaly observed at all. Also shown in Fig. 4 for comparison are curves of the squares of the ferroelectric splitting at 120 K, i.e., $(D_1-D_2)^2$ calculated from the spectra. We have noticed that there is a striking similarity between the broadening above T_c and the squared splitting below T_c. In the mirror plane, the absence of critical broadenings above T_c corresponds significantly to the absence of splittings below T_c. It is clear from this correspondence that the broadening above T_c is the precursor of the ferroelectric splitting. This result suggests that the critical fluctuation occurs in such a manner as to lead to the splitting into D_1 and D_2, representing two opposite domains in the ferroelectric phase.

Therefore, the anomalous linewidths can be expressed by

$$\Delta B(\pm\tfrac{5}{2},\pm\tfrac{3}{2})=4\langle\Delta D^2\rangle/g^2\beta^2+\Delta B_i\ ,$$

$$\Delta B(\pm\tfrac{3}{2},\pm\tfrac{1}{2})=2\langle\Delta D^2\rangle/g^2\beta^2+\Delta B_i\ ,$$

and

$$\Delta B(\pm\tfrac{1}{2},\mp\tfrac{1}{2})=\Delta B_i\ ,$$

where ΔB_i is the contribution from an intrinsic mechanism other than the **D**-tensor fluctuation. $\langle\Delta D^2\rangle$ is the average value of the squared fluctuation and $\langle\Delta D\rangle=0$ in the paraelectric phase. In the anomalous region, the pseudospin variable is considered to be a function of time t. For a random fluctuation of ΔD, one can write

$$\langle\Delta D^2\rangle=A^2\sigma(0)^2\tau\ , \tag{3}$$

where τ is the characteristic correlation time for pseudospins. τ is usually defined by the relation

$$\langle\sigma(0)\sigma(t)\rangle=\sigma(0)^2\exp(-t/\tau)\ . \tag{4}$$

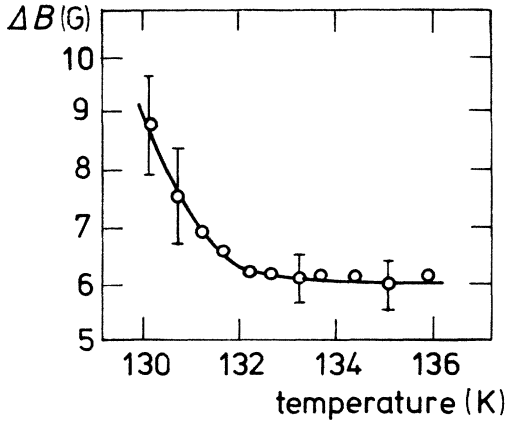

FIG. 3. Critical line broadenings in the $(\pm\frac{5}{2},\pm\frac{3}{2})$ transitions of the Mn^{2+} complex in TSCC crystals.

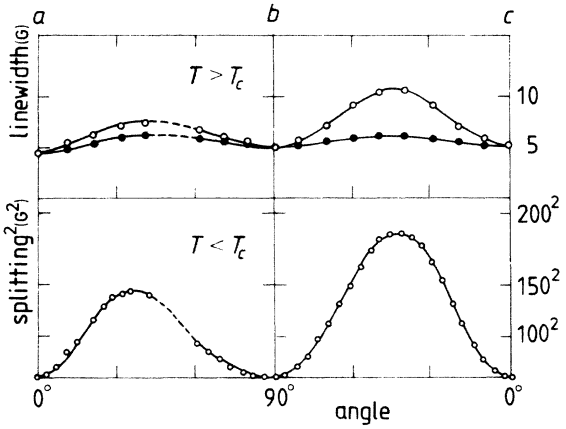

FIG. 4. Angular dependences of the linewidth of a hyperfine line in the $(\pm\frac{5}{2},\pm\frac{3}{2})$ transitions at $\Delta T=6.0$ and 0.3 K, which are indicated by ● and ○, respectively. Also shown are calculated values of the squared splittings $(D_1-D_2)^2$ from the spectra at 120 K for comparison.

In the above expressions for linewidths, we have assumed that the fluctuation in the critical region is dominated by low frequencies $\omega\ll 1/\tau$.

According to Eq. (3), the critical broadening is essentially due to τ, which becomes longer as the transition is approached. Empirically, we have found that the linewidth of Mn^{2+} lines remains *finite* at T_c, implying that the fluctuation is slowed down but still oscillatory at a low frequency. This corresponds to the nonzero value of the soft-mode frequency at T_c. If the soft mode is overdamped, the fluctuation would cease at T_c and the splitting should then follow displacively. We consider that the presence of a slow fluctuation is significant for the transition to be order-disorder.

IV. ANOMALOUS LINE SHAPE BELOW T_c

In the narrow temperature range of about 1 K below T_c, the Mn^{2+} spectra exhibited a splitting into three lines, changing to two with decreasing temperature. Figure 5 shows a sequence of hyperfine lines in the $(\pm\frac{5}{2},\pm\frac{3}{2})$ transitions at successive temperatures in this region observed at conventional X band frequencies (9.2 GHz). At temperatures very close to T_c, the spectra are dominated by a center line denoted by p, which is accompanied by weak side lines f_1 and f_2. On lowering the temperature, the side lines gain intensities at the expense of the center line.

Windsch[9] considered in his early work that this anomaly in the Mn^{2+} spectra was attributed to the coexistence of para- and ferroelectric phases. However, this interpretation is in conflict with the trivalent Cr^{3+} and Fe^{3+} spectra where the center line is absent. Moreover, we observed that the change was reversible, and that the transition is likely to be second order, as reported in the literature.[1]

At the ferroelectric transition, a pair of lines f_1 and f_2 start to appear, emerging from the fluctuation above T_c. Thus, the ferroelectric phase is characterized by a nonvan-

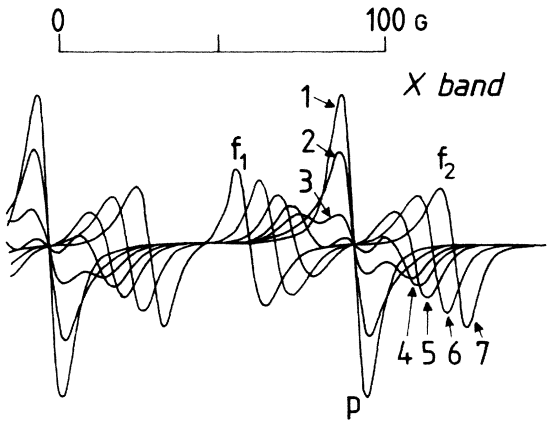

FIG. 5. Critical anomalies in a Mn^{2+} spectrum below T_c. Two hyperfine lines are recorded in the $(\pm\frac{5}{2},\pm\frac{3}{2})$ transitions observed at X band frequencies ($\sim$9.2 GHz). The temperatures corresponding to these spectra numbered from 1 to 7 are $\Delta T=T_c-T=-0.63$, -0.15, $+0.18$, $+0.25$, $+0.41$, $+0.76$, and $+1.49$ K, respectively. Here we took $T_c=131$ K.

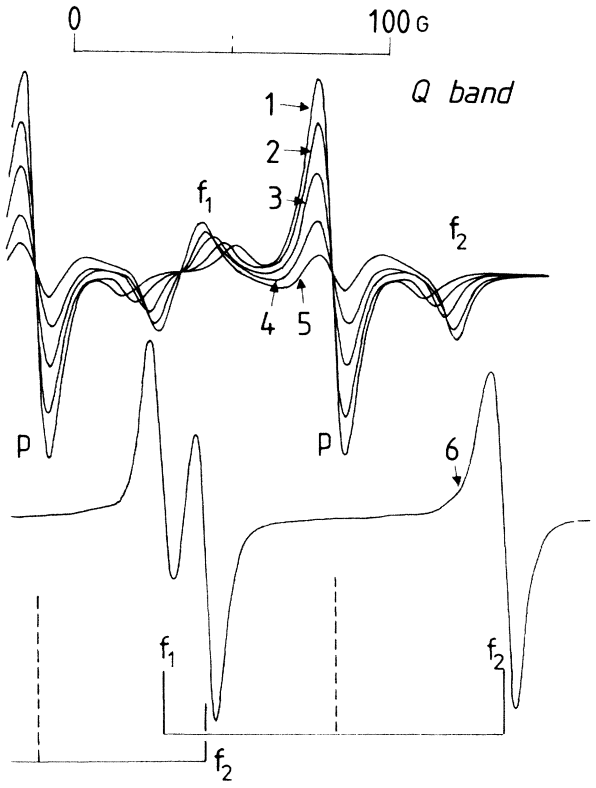

FIG. 6. Critical anomalies observed at Q band frequencies ($\sim$36 GHz). The temperatures for those spectra numbered from 1 to 5 are $\Delta T=+0.14$, $+0.27$, $+0.32$, $+0.36$, and $+0.41$ K, respectively. The spectrum 6 was observed at 110 K in the noncritical region. A slight asymmetry is noticed in these well-separated doublet lines.

ishing average of the fluctuation ΔD. Equation (2) suggests that neither averages of $\langle A\rangle$ nor $\langle\sigma\rangle$ should be zero in the general direction of the static field. While $\langle\sigma\rangle$ describes the average value of the pseudospin, the average $\langle A\rangle$ increases with increasing long-range order. Indeed, the fluctuation turns out to be a well-separated splitting in the noncritical region, representing the temperature dependence of the spontaneous polarization.[9]

We have assumed that in the critical region below T_c the TSCC crystal becomes inhomogeneous in a sense that the pseudospins are in a collective motion in some parts while still disordered in the others, and are represented by the lines (f_1,f_2) and p, respectively. Although this assumption may lead to a view similar to the two phases, we consider that the presence of a dynamical process makes the *spin-cluster* concept different from the thermodynamical phase. If this is the case, the absence of a disordered region in TSCC crystals doped with trivalent impurities should be explained with an additional mechanism related to charge defects in the lattice (see Sec. V).

When looking closely at the spectrum in Fig. 5, it is noticed that the line shape of f_1 and f_2 is slightly asymmetrical. This asymmetry is even more pronounced in the corresponding spectrum observed at Q band frequencies (36 GHz), as shown in Fig. 6. In addition, the separation between f_1 and f_2 is noticeably wider at Q band frequencies than at X band frequencies. While these differences can be attributed to a slow fluctuation observed in different time scales, the asymmetrical line shape is another significant feature of the anomaly below T_c.

Such asymmetrical lines imply that the complex orientations are distributed sinusoidally in the lattice, as typically observed in incommensurate phases. In the present case, the lines f_1 and f_2 emerge from the fluctuation between two tensors D_1 and D_2, and should be characterized by a dynamical feature of the pseudospin system. While related by symmetry operations of the point group, these tensors in the TSCC lattice are not related by translational symmetry, except when the fluctuation occurs independently at each Ca^{2+} site. The fluctuation between inequivalent sites should therefore be characterized by a $\mathbf{k}$ vector that is not given by any reciprocal-lattice point.

We postulate that the random fluctuations of pseudospins turns out a collective motion as the temperature is lowered through the transition point. Such a fluctuation may be described by an incommensurate wave

$$\sigma=\sigma_0\cos(\mathbf{k}\cdot\mathbf{r}-\Omega t+\phi_0)\ ,$$

where $\mathbf{k}\cdot\mathbf{r}\neq 2\pi n$ (n are integers) gives a variety of phases for a Mn^{2+} ion to be located at various Ca^{2+} sites $\mathbf{r}$. ϕ_0 is a phase constant; whereby an incommensurate $\mathbf{k}$ and the corresponding frequency Ω signify the phase distribution. The fluctuation in the $\mathbf{D}$ tensor is then given by Eq. (2) as

$$\Delta D=A\sigma_0\cos(k\cdot r-\Omega t+\phi_0)\ . \tag{5}$$

Considering ΔD as a perturbation, the resonance frequencies for the $(\pm\frac{5}{2},\pm\frac{3}{2})$ transitions are expressed by

$$\omega=\omega_0+4\omega_1\langle\cos(\mathbf{k}\cdot\mathbf{r}-\Omega t+\phi_0)\rangle$$

where

$\omega_0=(1/\hbar)(g\beta B+4D_0+KM_I)$ $(M_I=\frac{5}{2},\frac{3}{2},\ldots,-\frac{5}{2})$

and $\omega_1=(1/\hbar)A\sigma_0$. Here, the angular brackets around the cosine signify the time average over the time scale $\tau=2/\pi/\omega_m$ of EPR measurements.

The phase constant ϕ_0 is, in fact, thermally distributed due to the phase pinning mechanism. Therefore, we consider that in EPR measurements, such a distribution should be observed *adiabatically* with a deviation

$$\Delta\phi_0=\phi_0(t+\tau)-\phi_0=\phi_0'(t)\tau\ .$$

In this case, the value of the above time average is also distributed. Writing for the distribution as $f(\Delta\phi_0)$, the Gaussian assumption yields

$$f(\Delta\phi_0)=f(0)\exp(-\langle\Delta\phi^2\rangle)\ , \tag{6}$$

while $\langle\Delta\phi\rangle=0$.

It is elementary to show that

$$\langle\cos(\mathbf{k}\cdot\mathbf{r}-\Omega t+\phi_0)\rangle=\frac{1}{\tau}\int_t^{t+\tau}\cos(\mathbf{k}\cdot\mathbf{r}-\Omega t'+\phi_0)dt'$$
$$=\frac{2}{(\Omega-\phi_0')\tau}\sin\frac{(\Omega-\phi_0')t}{2}$$
$$\times\cos\left[\mathbf{k}\cdot\mathbf{r}-\Omega t+\phi_0-\frac{(\Omega-\phi_0')\tau}{2}\right].$$

Using Eq. (6), we obtain the expression for the modulated frequency

$$\omega=\omega_0+4\langle\omega_1\rangle\cos(\mathbf{k}\cdot\mathbf{r}-\Omega t+\phi_1)\ , \tag{7}$$

where $\phi_1=\phi_0-(\Omega\tau/2)$ is just another phase constant and the amplitude of the modulation $\langle\omega_1\rangle$ is smaller than ω_1 by a factor

$$\frac{\langle\omega_1\rangle}{\omega_1}=\frac{2}{\Omega\tau}\sin\frac{\Omega\tau}{2}\exp(-\sigma^2\tau^2)\ \text{ for } \Omega\ll\omega_m\ , \tag{8}$$

where $\sigma^2=\langle\phi'(t)^2\rangle$.

In the ensemble of Mn^{2+} ions, the resonance frequency ω has distributed values determined by the phase $\phi=\mathbf{k}\cdot\mathbf{r}-\Omega t_0+\phi_1$ for each ion. In fact, the phase ϕ as a nearly continuous distribution and the corresponding frequency $\omega-\omega_0$ derived from Eq. (7) is distributed between two edge singularities at $\pm4\langle\omega_1\rangle$. Such a frequency distribution is expressed by

$$f(\omega-\omega_0)d\omega=\frac{\text{const}\times d\omega}{[\langle4\omega_1\rangle^2-(\omega-\omega_0)^2]^{1/2}}\ . \tag{9}$$

The two singularities can be resolved if $\Omega<8\langle\omega_1\rangle$; otherwise, they are unresolved or averaged out, depending again on the time scale of measurements.

It should be noted that $\langle\omega_1\rangle=\omega_1$ for $\tau=0$ in the limit of $\Omega\to0$ (static). As shown in Figs. 5 and 6, different separations between the singularities when observed at different frequencies can be taken as evidence for a low but nonzero Ω. The value of Ω was evaluated at several temperatures in the anomalous region from the edge separations measured at X and Q band frequencies. The result shows that Ω is temperature dependent, changing to lower frequencies toward the noncritical region. For example, $\Omega=6.2\pm0.3$ and 4.8 ± 0.3 GHz at $\Delta T=0.2$ and 0.4 K, respectively. In this evaluation of Ω, the Gaussian factor $\exp(-\sigma^2\tau^2)$ was ignored. However, it is essential for the different line shapes at X and Q band spectra. This factor is less significant at Q band frequencies and therefore the anomalies related to the edge singularities are more pronounced in the Q band spectrum. The presence of a slow fluctuation implies a dynamical switching process between D_i and D_2 in the critical region. As long as a strong polarization is not established, these two tensors represent oppositely polarized parts of the crystal. The size of these *prematurely* polarized parts should be of the order of one-half wavelength $\lambda/2=\pi/k$. While the dispersion relation for the modulated fluctuation is unknown, it is clear experimentally that $\Omega\to0$ and $\mathbf{k}\to0$, when the anomalous asymmetry fades out with decreasing temperature.

Blinc and co-workers[16–18] have investigated incommensurate systems extensively and observed quadrupole-perturbed NMR spectra of ^{87}Rb transitions in Rb_2ZnBr_4 crystals showing a very similar feature to Mn^{2+} EPR spectra in the ferroelectric TSCC lattice. These authors have considered that the incommensurate phase is composed of two parts, which are distinguishable in terms of the *pinning* of the modulation wave. In the present case, we have postulated the emergence of dynamical pseudospin order at the critical temperature extending to a range of the order $2\pi/k$. The fluctuation in such a pseudospin cluster is time dependent, whereas the modulated structure in an incommensurate phase is *static*. The frequency of the cluster motion is so slow that the line shape appears as if it were due to a static distribution of pseudospin within the time scale of EPR measurements.

Leblé and co-workers[19] have reported the result of EPR observation of the order-disorder transition in NH_4AlF_4 crystals using Fe^{3+} impurities substituted for Al^{3+} ions. We have noticed that the line shape of the Fe^{3+} spectrum in the critical region is practically identical to anomalous Mn^{2+} lines in TSCC crystals. They proposed a model of local relaxation due to surrounding NH_4^+ groups to explain their spectra. However, the dynamical aspect of the transition was not taken into account in their interpretation. While the analysis was different from ours, the striking similarity between those anomalies observed in entirely different systems should be a manifestation of the universality for the transitions in which a common type of mechanism is involved. The collective behavior of NH_4^+ groups in NH_4A/F_4 crystals should be a part of the responsible lattice mode, and therefore we believe that their model shares a common feature with the one we propose for TSCC crystals.

V. EFFECT OF AN APPLIED ELECTRIC FIELD

In EPR spectra from a crystal in equilibrium, parameters in the spin Hamiltonian represent the state of the impurity ion in its molecular surroundings in the long-range (ensemble) average. In this work, we have investigated a fluctuation between those two states specified by long-range order. In the ferroelectric TSCC lattice, the spon-

taneous polarization represents the long-range parameter.

Bornarel and Schmidt[12] have shown in their dielectric studies that the phase transition can be modified substantially by an external electric field applied parallel to the b axis. Windsch[13] had already noticed prior to this work that in Mn^{2+} spectra the transition appeared to be diffused when subjected to a bias field. We have reinvestigated the electric field effect on the Mn^{2+} spectra and found that the spectra change as if the polarization were enhanced by an external field.

Figure 7 shows the electric field effect on the Mn^{2+} spectra, when applied parallel to the b axis. Here, to observe maximum effect, the static magnetic field was applied exactly in between the crystallographic axes in the (100) plane, and the behavior of a hyperfine line in the $(\pm\frac{5}{2},\pm\frac{3}{2})$ transitions was traced against temperature. First, we notice that the crystal is polarized by an applied field even in the paraelectric phase, as indicated by the splitting above T_c and by the outward shifting below T_c. This substantiates the assumption in Sec. II that the pseudospin is accompanied by an electric dipole moment of the Ca(sarcosine)$_6$ complex. Secondly, the effect of an electric field was observed in the limited temperature range in the vicinity of T_c. In the region above T_c, the polarization fluctuation is suppressed along the b axis, owing to the uniaxial nature of the dielectric properties. Consequently, the dipole moment should be in a relatively shallow potential and hence susceptible to the applied electric field. In fact, in the Mn^{2+} spectra the splitting occurs in this region just as an extension of the lines f_1 and f_2. In the region below T_c, on the other hand, the resultant pseudospin force is softened and therefore each spin becomes sensitive to the applied field, provided that it carries an electric dipole.

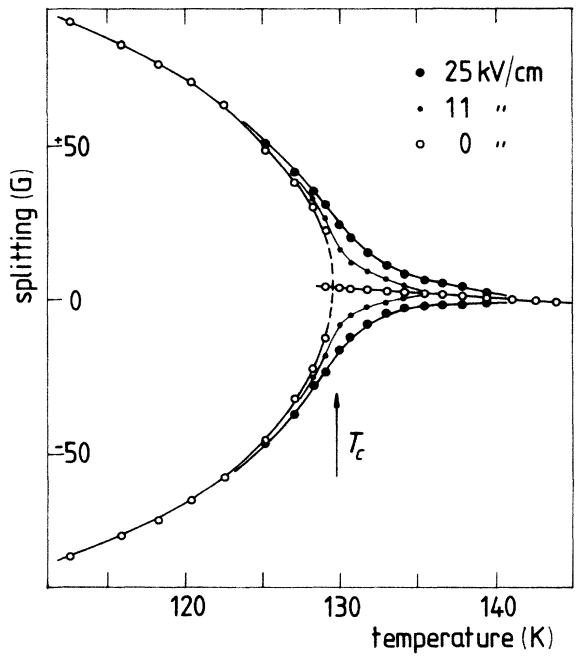

FIG. 7. Splittings of a Mn^{2+} hyperfine line in the $(\pm\frac{5}{2},\pm\frac{3}{2})$ transitions with bias electric fields.

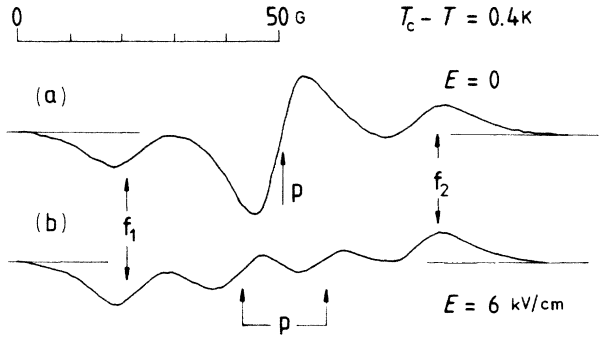

FIG. 8. An electric field effect observed on a hyperfine line in the $(\pm\frac{5}{2},\pm\frac{3}{2})$ transitions at $T=T_c-0.4$ K. The static field B was applied in the direction 30° from the a axis in the (001) plane. (a)$E=0$, (b)$E=6$ kV/cm ($E\|b$). With the field E turned on, the center line p splits in two with slightly unequal intensities. Although not shown, the asymmetrical intensities were reversed by switching the field E to the opposite direction.

The sensitivity of the dipolar spin in this region was further confirmed by observing the central line which is split in two by a weak electric field of the order of 6 kV/cm (see Fig. 8). In this case, the side lines f_1 and f_2 were just slightly shifted outward. A dipolar nature of the complex distortion is therefore believed to have been verified by these results. In this model, the spontaneous polarization is clearly a consequence of the pseudospin ordering, for which the short-range interaction is responsible.

In the spectra of Cr^{3+} and Fe^{3+} impurities substituted for the Ca^{2+} ion in TSCC crystals, we have observed a pair of asymmetrical lines in the critical region below T_c as reported in our previous paper.[11] Unlike in the Mn^{2+} spectra, there were no central lines in the Cr^{3+} and Fe^{3+} spectra. In light of the electric field effect, the anomalies in Cr^{3+} and Fe^{3+} spectra may be attributed to the presence of positive charge defects responsible for an electric field. It is interesting to note that there is a center line p in the Cr^{3+} and Fe^{3+} spectra observed by Leblé *et al.*[19] in the critical region of the order-disorder transition in NH_4AlF_4 crystals. In this case, no effect of charge defects is expected for these impurity ions substituted for Al^{3+}, and hence the pseudospin dynamics should be identical to that in TSCC crystals.

VI. SHORT-RANGE PSEUDOSPIN INTERACTIONS IN TSCC

In the analysis described in Sec. IV, we have considered an incommensurate fluctuation between pseudospins at lattice sites unrelated by translational symmetry. The anomalous line shape due to a sinusoidally modulated pseudospin distribution is clear evidence for the incommensurate fluctuation. The short-range interaction between pseudospins should be responsible for the correlated distribution, for which we are compelled to assume the interaction of the Heisenberg type. The wave vector for the sinusoidal fluctuation should be characterized by an irra-

tional value in the reciprocal lattice.

A possible incommensurate distribution of pseudospins is inferable from the model of short-range interactions in TSCC crystals, as shown in Fig. 9. In the ferroelectric phase at a temperature well below T_c, where the, spontaneous polarization is fully developed, the interactions J_b, J_c, and J_a should be dominant in the parallel arrangement of pseudospins. In the critical region, by contrast, these interactions are weak and comparable to the cross interaction J_d. Under these circumstances, the wave vector $\mathbf{k}$, to minimize the local interaction energy, is not necessarily given by a rational magnitude, but determined by the equation

$$\cos(k_b b) = -J_d/2J_b \ ,$$

where k_b is the component of the $\mathbf{k}$ vector along the b axis. If so, the irrational k_b occurs in the range $0 < -J_d/2J_b < 1$, depending on the values of these interactions. While speculative, such an argument is conceivable to justify the incommensurate pseudospin distribution in the critical region.

At the transition temperature, since Ω is nonzero, the corresponding $\mathbf{k}$ vector is likely to be nonzero. This appears to be contradictory to the fact that the phase transition occurs at the Brillouin-zone center. However the long-time average $\langle k_b \rangle$ should be zero statistically, and therefore there is no conflict. It is interesting that in the paraelectric TSCC crystals, the uniaxial dielectric properties were interpreted on the basis of the suppressed fluctuation along the b axis, yielding a significance of $\langle k_b^2 \rangle$ above T_c. In fact, such a mechanism is responsible for the logarithmic anomaly in the static susceptibility as measured by Sandvold and Courtens.[20]

In the presence of a bias field, the $\mathbf{k}$ vector should shift along the k_b axis, owing to the dipolar nature of the pseudo spin. As a result, we have observed a pair of edge singularities with an asymmetrical shape, indicating nonzero wave vectors at and above T_c. We may therefore describe the phenomenon as the *pinning* of the incommensurate modulation wave by an applied electric field. In the ferroelectric phase with no bias field, it is the internal electric field originating from the spontaneous polarization which pins the modulation wave. When the polarization value increases, the value of $\langle \omega_1 \rangle$ increases, resulting in a condition close to a static pinning. In the limit of $\Omega \rightarrow 0$, k becomes zero, establishing the complete order with $\lambda \rightarrow \infty$.

In the ferroelectric phase of TSCC crystals, the internal field $\mathbf{E}_{\text{int}} \propto \mathbf{P}$ plays a significant role in making one of the singularities dominant in each domain. The static dipolar energies $\pm\sigma \cdot \mathbf{E}_{\text{int}}$ should be added to the minima of the double minimum potential for the pseudospin σ, making it asymmetrical. Owing to the nonvanishing frequency Ω, the domain will eventually be dictated by the lower minimum as the temperature is lowered.

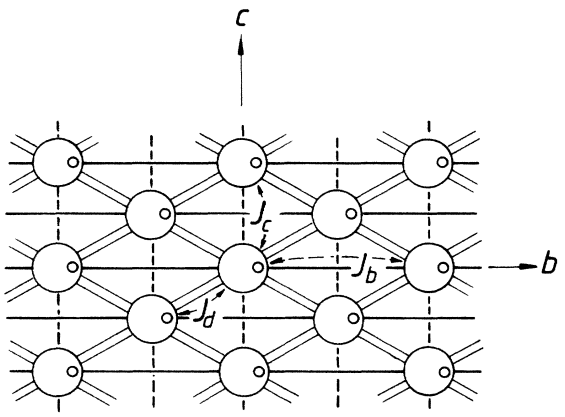

FIG. 9. A model for the short-range interaction in the TSCC lattice. It shows an ordered arrangement of pseudospins in the (100) plane, where the interaction J_a is not included. Here, the interactions are denoted by J's in the pseudospin couplings of the Heisenberg type.

VII. CONCLUSIONS

While the ferroelectric phase transition in TSCC crystals appear to be displacive in the noncritical region, the critical anomalies in the Mn^{2+} impurity spectra have revealed the presence of an order-disorder mechanism. The result manifests a changeover from displacive to order-disorder characters in the transition region, in which the phonon instability is taken over by an incommensurate collective pseudospin motion at low frequencies, representing *domain walls* in the critical region.

The pseudospin is associated with an electric dipole moment of the Ca(sarcosine)$_6$ complex induced by distortion, which was verified by the external electric field effect on the EPR spectra. Accordingly, the pseudospin order yields spontaneous polarization in the ferroelectric phase.

ACKNOWLEDGMENTS

The experimental work was performed independently at the two universities in Guelph and Leipzig. During a conference, two of us (M. F. and W. W.) discussed the subject matter and agreed to this joint publication. We express our sincere thanks to Professor J. Stankowski of the Polish Academy of Sciences, Poznan, for providing us with this opportunity for cooperation. The work at Guelph has been supported by a grant from the Natural Sciences and Engineering Council of Canada.

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