Dielectric dispersion and absorption and proton spin-lattice relaxation at the phase transition in the layered crystal SnCl₂·2H₂O

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Measurements of the real and imaginary parts of the dielectric constant at audio frequencies and of proton spin-lattice relaxation in the laboratory and in the rotating frames in a single crystal around the ferroelectric-type phase transition are reported. The experimental results are related to the order-disorder critical dynamics of the protons in the two-dimensional hydrogen-bonded network and discussed, mainly in the light of the dynamical theories for planar lattices of interacting Ising spins. The occurrence of a nonclassical critical behavior, connected to the short range of the interactions and to the restricted dimensionality, has been put in evidence. The static uniform susceptibility diverges with a critical exponent close to 1.75. From $T_{1\rho}$ the relaxation time of the polarization fluctuations is evaluated $\tau_p \simeq 1.2 \times 10^{-5}$ sec at $T \simeq T_c + 50°K$, while from the dielectric dispersion $\tau_p \simeq 1.8 \times 10^{-2}$ sec at $T \simeq T_c + 2°K$, in agreement with a divergence with critical exponent around 2. For $T \lesssim T_c + 1.5°K$, however, τ_p decreases on approaching the transition, probably due to crossover towards three-dimensional antiferroelectrically correlated fluctuations. Finally, a polydispersive nature of the dynamical susceptibility near T_c is evidenced.

I. INTRODUCTION

Stannous chloride dihydrate (SCD) is a hydrogen-bonded crystal with layers of stannous chloride molecules alternating with layers of water molecules; each water molecule is bonded to three others in the same layer by hydrogen bonds about 2.8 Å long.[1] A phase transition at about 218 °K in SCD was first put in evidence[2] by a peak in the low-frequency dielectric constant along the $\vec{b}$ and $\vec{c}$ axes. The transition is related to the order-disorder rearrangement of the hydrogen atoms in the two-dimensional (2D) network of the hydrogen bonds. The specific heat exhibits[3] a symmetrical divergence, trademark of 2D phase transitions.

As will be discussed later, the phase transition in SCD appears to be of the ferroelectric type: The strong increase of the static dielectric constant can be related to the divergence of the in-plane $\vec{q} = 0$ dielectric response. The low-temperature phase, however, is probably antiferroelectrically three dimensionally (3D) ordered, a consequence of weak interlayer interactions.[4] The ferroelectric transition in SCD is very interesting. First of all, the short range of the interactions as well the restricted dimensionality should allow the investigation of the nonclassical critical region, which is normally difficult to investigate, in 3D ferroelectrics with dipolar long-range interactions. In addition, the 2D character of the transition allows an analysis of the experiments, in the light of theoretical evaluations that are more reli-

able than the 3D molecular-field-approximation (MFA) treatments, such as the exact solutions of 2D statistical models[5] and the predictions of the dynamical theories for planar lattices of interacting Ising spins.[6] Relevant modifications of the main conclusions of the MFA theories can be expected; in particular, the finite value, even at the critical point, of the real part of the dynamical uniform susceptibility $\chi(\vec{q} = 0, \omega)$ and the breakdown of the thermodynamical slowing-down assumption, according to which the critical exponent Δ for the divergence in the relaxation time of the polarization fluctuations $\tau_p \equiv \tau_{\vec{q}=0}$ is equal to the exponent γ describing the divergence of the uniform static susceptibility $\chi(\vec{q} = 0, 0)$. Further interest in investigating the critical dynamics in SCD is related to the extreme slowing down of the fluctuations, as will be pointed out. Finally, close to the transition temperature, the crossover from the regime of 2D ferroelectrically correlated fluctuations to the regime of 3D antiferroelectrically correlated fluctuations could be detected.

In addition to the more conventional dielectric dispersion and absorption techniques, the slowing down of the order-disorder critical dynamics can be studied by means of spin-lattice relaxation measurements in the laboratory frame (T_1). In the presence of slowing down of the fluctuations below the rf range, spin-lattice relaxation measurements in the rotating frame ($T_{1\rho}$) are particularly significant. The temperature and frequencey dependence of T_1 and $T_{1\rho}$ due to critical fluctuations be-

gin to be better understood,[7,8] and therefore interesting information can, in principle, be obtained.

In this paper measurements of the real and imaginary part of the dielectric constant at audio frequencies and of protons T_1 and $T_{1\rho}$ in a single crystal of SCD around the transition temperature are presented and discussed, mostly in light of the dynamical theories for 2D lattices of Ising spins. To combine dielectric and nuclear spin-lattice relaxation measurements appears useful. Dielectric dispersion and absorption give information on the $\vec{q} = 0$ collective proton dynamics, and the temperature behavior of $\chi(0, 0)$ and τ_p can be inferred. Spin-lattice relaxation, instead, is sensitive to the $\vec{q}$-integrated critical dynamics; by expressing the $\vec{q}$ dependence of $\chi(\vec{q}, 0)$ and of $\tau_{\vec{q}}^-$ according to the static and dynamical scaling hypothesis, T_1 and $T_{1\rho}$ can in turn be related to τ_p and $\chi(0, 0)$ and elucidating comparisons become possible.

An interpretation of the dielectric and proton spin-lattice relaxation data in SCD according to the above-outlined arguments is given in Sec. III of the paper. In Sec. II the measurements are presented and analyzed for the purpose of clarifying the role of the hydrogen critical dynamics.

II. EXPERIMENTAL RESULTS AND ANALYSIS

A. Experimental

The single crystals of SCD were grown from a saturated acid solution (8% HCl in water) slowly evaporating. The crystals for the measurements were cut from optically good parts of large crystals, selected by means of a polarizing microscope. A further selection was done by looking at the lowest dc conductivity and at the greatest dielectric constant at the transition. For the dielectric measurements good surfaces were obtained by lapping in the presence of a solution of a few percent of acetone in Freon. For the electrodes silver paint manufactured by G.C. Electronics was used.

The real and imaginary parts of the dielectric constant were measured mostly by means of an apparatus based on the General Radio Bridge models 1615A and 1621, during a slow warmup in the temperature range from 90 to 270 °K. Some measurements at very low frequencies were performed by means of a Scheiber bridge.[9] The amplitude of the electric field on the crystal was 4 V cm^{-1}. The temperature stabilization during the measurements was about 10^{-2} °K, and the temperature gradients on the crystal were estimated to be less than 5×10^{-2} °K.

Proton spin-lattice relaxation times T_1 and $T_{1\rho}$ were measured by means of a Bruker SXP pulsed spectrometer in a single crystal of SCD with the crystallographic $\vec{a}^*$ axis parallel to the constant

magnetic field $\vec{H}_0$ in the temperature range 200–310 °K. The usual pulse sequences were used for T_1 and $T_{1\rho}$. The resonance frequency was $\nu_0 = 20$ MHz and the amplitude of the rf field H_1 was varied in the $T_{1\rho}$ measurements from 10 to about 40 G. The temperature gradient on the crystal was estimated to be some tenths of a degree. Below 200 °K the measurements become difficult in view of the large T_1 (> 150 sec).

B. Dielectric measurements

The experimental results, at some representative frequencies, for a single crystal of $2 \times 5 \times 0.7$ mm^3 and along the $\vec{c}$ axis are shown in Fig. 1.

Two important contributions to the dielectric constant appear to be present: one contribution which is dominant in the high-temperature range and a second one which causes the narrow peaks around the phase transition. The contribution around the transition is not simply a dielectric anomaly related to the peak observed in the dc conductivity[2]; in fact, the real part of the conductivity, σ', practically independent of the frequency at low and high temperatures, shows a strong frequency dependence around the transition. In addition, a maximum in σ' at 10 and 20 Hz occurs above the temperature at which the real part of the dielectric constant exhibits its maximum. Therefore, the peaks in the dielectric constant must also be related to the critical dynamics of the hydrogens.

The experimental data were analyzed by writing

$$\epsilon'_{\text{expt}}(\omega, T) = \epsilon(\infty) + \epsilon'(0, \omega, T) + \epsilon'_c(\omega, T) , \qquad (1a)$$

$$\epsilon''_{\text{expt}}(\omega, T) = \epsilon''(0, \omega, T) + \epsilon''_c(\omega, T) , \qquad (1b)$$

where $\epsilon(0, \omega, T) = 1 + 4\pi\chi(\vec{q} = 0, \omega, T)$ is the contribution associated with the critical susceptibility and $\epsilon_c(\omega, T)$ is related to the conductivity of the charge carriers. For $T \leqslant 210$ °K and $T \geqslant 230$ °K the critical contribution is negligible and the experimental results can be fitted by the expressions

$$\epsilon'_c(\omega, T) = (4\pi/\omega)\sigma''_0 e^{-E_A/RT} , \qquad (2a)$$

$$\epsilon''_c(\omega, T) = (4\pi/\omega)\sigma'_0 e^{-E_A/RT} , \qquad (2b)$$

where a temperature-activated complex conductivity has been introduced. The best fit to the data on the basis of Eqs. (2) gives the values $E_A = 13.8$ kcal/mole, $\sigma'_0 = 2.5 \times 10^4$ Ω^{-1} cm^{-1}, and $\sigma''_0 = 3.9 \times 10^3$ Ω^{-1} cm^{-1}. The corresponding behavior of ϵ'_c and ϵ''_c is shown in Fig. 1 (solid lines).

As already suggested,[2] the dc conductivity is probably due to the protons of water molecules and should be related to Bjerrum faults and/or ionic defects.[5] The activation energy E_A is lower than that evaluated[2] from the dc conductivity (17 kcal/
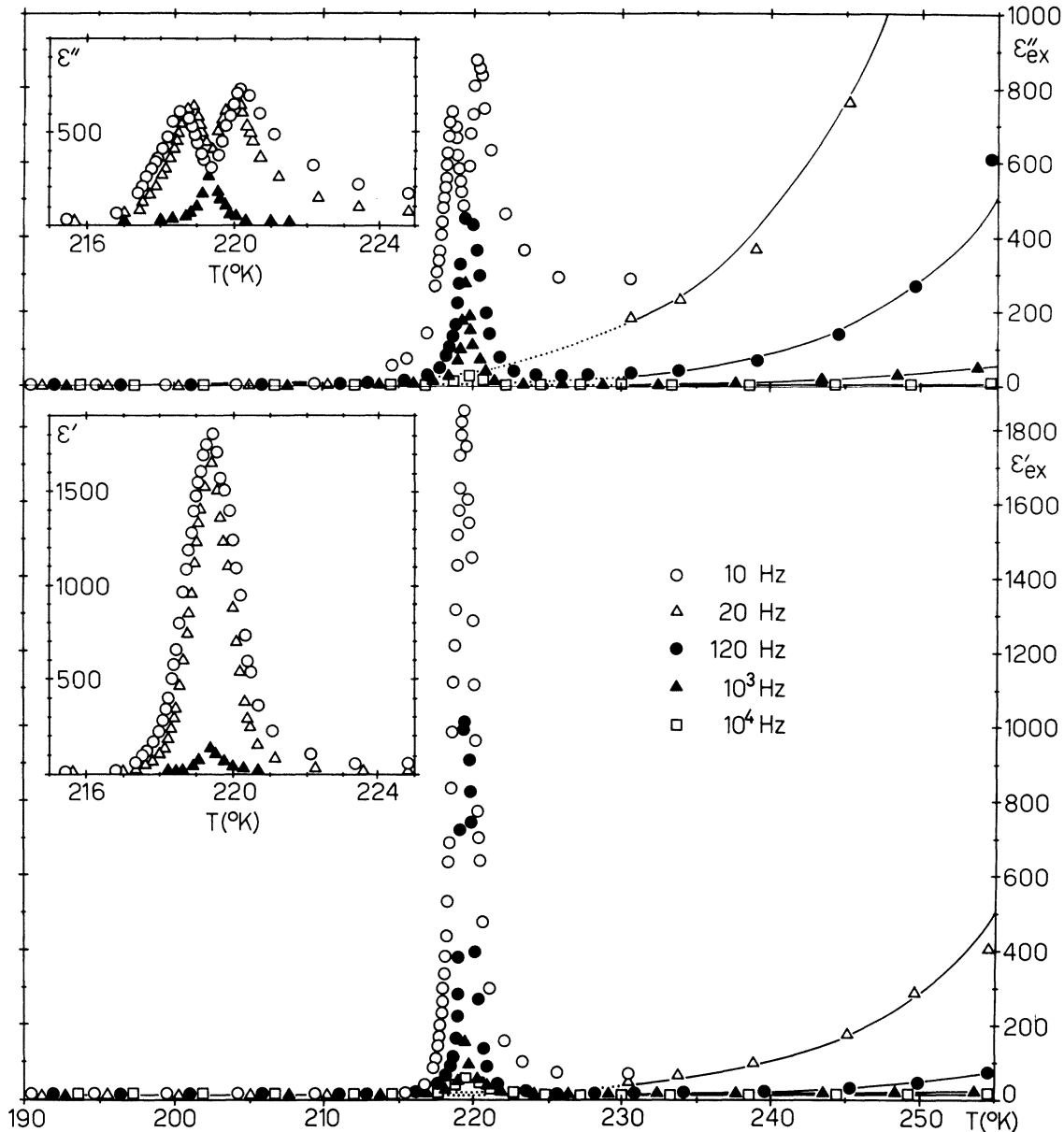
FIG. 1. Experimental results for the real and the imaginary parts of the dielectric constant in SCD along the $\vec{c}$ axis vs T, at various frequencies. The solid lines for $T < 210$ °K and $T > 230$ °K represent the best-fit behavior according to Eqs. (2) in the text. The critical parts ϵ' and ϵ'' at some representative frequencies are shown in the insets with expanded temperature scales.

mole). This is not surprising, since we observed E_A to be sample dependent.

In the temperature range $210 < T < 230$ °K the critical contribution ϵ' and ϵ'' [see Eqs. (1)] were determined by subtracting from the experimental results ϵ'_{expt} and ϵ''_{expt} the values of ϵ'_c and ϵ''_c. ϵ''_c was obtained by extrapolating to zero frequency the data obtained in the frequency range 0.5–5 Hz. ϵ'_c was evaluated from ϵ''_c, taking into account the

ratio σ'_0/σ''_0. In addition, $\epsilon(\infty) = 14$ was subtracted. In Fig. 1 the critical parts ϵ' and ϵ'' are shown for some representative frequencies.

C. Spin-lattice relaxation

1. Spin-lattice relaxation measurements

The experimental results[10] for protons T_1 and $T_{1\rho}$ in a single crystal of SCD are shown in Fig. 2
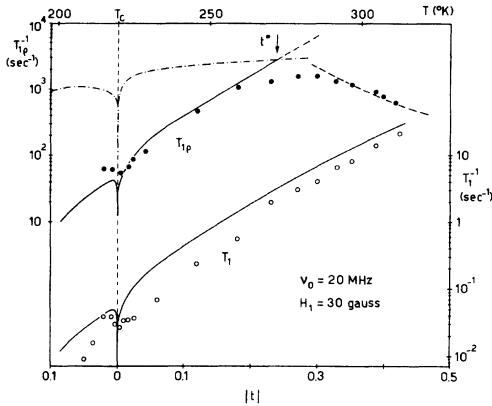
FIG. 2. Proton spin-lattice relaxation rates in the lab frame (O) and in the rotating frame (●) in a single crystal of SCD with the crystallographic $\vec{a}^*$ axis parallel to $\vec{H}_0$ as a function of the reduced temperature $t = (T - T_c)/T_c$, with $T_c = 219.45\,°K$. The solid lines give the plots of the theoretical expressions for the relaxation rates, as explained in the text.

as a function of the reduced temperature t $= (T - T_c)/T_c$, with $T_c = 219.45\,°K$ (see Sec. III). It can be observed that the recovery of the nuclear magnetization was exponential, within the experimental error, at all temperatures. This shows that the relaxation times of the various protons do not differ by more than a factor of 2 or 3, irrespective of whether they belong to the complexed water or to the crystallization water and independent of the orientations of the interprotonic vectors with respect to $\vec{H}_0$. By rotating the crystal about the $\vec{c}$ axis, a slight angular dependence of $T_{1\rho}$, of about 20%, was observed.

It must be emphasized that $T_{1\rho}$ was found to be independent of the amplitude H_1 of the rf field for $T \gtrsim 298\,°K$ ($t \gtrsim 3.6 \times 10^{-1}$), while for temperatures lower than about $258\,°K$ ($t \lesssim 1.8 \times 10^{-1}$) the law

$$T_{1\rho}^{-1} \propto \omega_1^{-2} \qquad (3)$$

($\omega_1 = \gamma H_1$) was observed to hold, to a good approximation. In the intermediate temperature range a more complex frequency dependence of $T_{1\rho}$ was observed; by reducing H_1, the broad maximum in $T_{1\rho}^{-1}$ is shifted to slightly lower temperatures. The maximum in $T_{1\rho}^{-1}$ at $t \simeq 2.7 \times 10^{-1}$ (for $H_1 = 30$ G) and the frequency dependence according to Eq. (3) indicate that for $T \lesssim 258\,°K$ the effective correlation time of the motions which drive the spin-lattice relaxation is much greater than ω_1^{-1}.

2. Proton spin-lattice relaxation mechanism

The proton relaxation in SCD is driven by the dipolar interaction. For the $T_{1\rho}$ data shown in Fig. 2, ω_1 was greater than the local dipolar frequency

ω_D [$\omega_D^2 = \frac{1}{3}\gamma^2 M_2$, where M_2 is the dipolar second moment; in SCD $M_2 \simeq 30$ G^2 (Ref. 2)]. Therefore, the well-known expressions for the relaxation rates in the weak-collision approach[11] can be used to write, for a given proton,

$$T_{1\rho}^{-1} = \frac{1}{4} A [J_0(2\omega_1) + 10 J_1(\omega_0) + J_2(2\omega_0)], \qquad (4a)$$

$$T_1^{-1} = A [J_1(\omega_0) + J_2(2\omega_0)], \qquad (4b)$$

where $A = \frac{9}{8}\gamma^4\hbar^2$. For uncorrelated fluctuations $J_\alpha(\omega)$ in Eqs. (4) is the sum of the spectral densities of the two-proton correlation functions $\langle F_\alpha^{(i,j)}(0) F_\alpha^{(i,j)*}(t) \rangle$ of the "lattice functions" $F_\alpha^{(i,j)}$, where

$$F_\alpha^{(i,j)} = a_\alpha Y_2^\alpha / r^3, \qquad (5)$$

with $a_0 = (\frac{16}{5}\pi)^{1/2}$, $a_1 = (\frac{8}{15}\pi)^{1/2}$, and $a_2 = (\frac{32}{15}\pi)^{1/2}$; Y_2^α are the second-order spherical harmonics of the polar angles describing the orientation of the internuclear vector $\vec{r}_{ij}(t)$.

Two types of motion could provide the main relaxation mechanisms: (i) the 180° flipping motion of the water molecule around its bisectrix (which is a typical mechanism in hydrated crystals); or (ii) the collective critical dynamics of the hydrogens (pseudo-spin-waves or Ising-type fluctuations in the double-minimum potential), with which the order-disorder phase transition is connected. The relevance of other motions can be ruled out on the basis of order-of-magnitude estimates and/or temperature and frequency dependence of the relaxation rates.[12]

By referring to the 180° flipping motion and by taking into account the theory for the dipolar relaxation driven by this mechanism,[13] the leading term for the relaxation rate in the rotating frame can be written [see Eq. (4a)]

$$T_{1\rho}^{-1} = \frac{A}{64} \sum_j {}'[\eta_0^{(i,j)} j(\omega_1) + 2\xi_0^{(i,j)} j(2\omega_1)], \qquad (6)$$

where

$$j(\omega) = 4W/(4W^2 + \omega^2), \qquad (7)$$

W being the probability per unit time that a spin jumps between equilibrium lattice sites; $\eta_0^{(i,j)}$ and $\xi_0^{(i,j)}$ are simply related to the values that the lattice function $F_0^{(i,j)}$ assumes in dependence on the positions of the two interacting spins taken into consideration (discussed below). It must be stressed that since the 180° flip does not change the intramolecular dipole-dipole Hamiltonian, only the interactions between protons in different water molecules could be responsible for this relaxation mechanism in SCD.

The experimental results for $T_{1\rho}$ shown in Fig. 2 cannot be fitted by means of Eqs. (6) and (7) with the usual assumption of a temperature-activated behavior for W. A satisfactory fitting can be ob-

tained only by introducing a distribution of transition probabilities. Assuming, for sake of illustration, a simple distribution of the form

$$I(W) = \begin{cases} \frac{1}{2}\ln b & \text{for } \overline{W}/b \le \overline{W} \le \overline{W}b \\ \\ 0 & \text{elsewhere ,} \end{cases}$$

Eq. (7) becomes

$$j'(\omega) = \int j(\omega) I(W)\, d(\ln W)$$

$$= (2\omega \ln b)^{-1} \arctan[\overline{W}\omega(b^2 - 1)/(\overline{W}^2 + \omega^2)b] .$$

$$(8)$$

The best fit to the data on the basis of Eqs. (6) and (8) is obtained with an activation energy for $\overline{W}$ equal to 10.5 kcal/mole and with $b \simeq 8$. However, such a wide distribution of the transition probabilities seems hard to justify.

Also, an order-of-magnitude numerical estimate seems to indicate that the $180°$ flipping of the water molecule is not the dominant relaxation mechanism. Let us refer to a pair of protons, one belonging to a H_2O molecule with O_I and the other to a H_2O molecule with O_{II}.[1] For a single crystal with $\vec{a}* \parallel \vec{H}_0$ one can write, from Eq. (5),

$$F_0^{(1,2)} = (1 - 3\cos^2\theta_{12})/r_{12}^3 \simeq r_{12}^{-3} ,$$

so that η_0 and ξ_0 in Eq. (6) become

$$\eta_0 = \frac{1}{2}\{[r(\beta, \beta)]^{-3} + [r(\delta, \delta)]^{-3}$$
$$- [r(\beta, \delta)]^{-3} - [r(\delta, \beta)]^{-3}\}^2 , \qquad (9a)$$

$$\xi_0 = \{[r(\beta, \beta)]^{-3} - [r(\delta, \delta)]^{-3}\}^2$$
$$+ \{[r(\beta, \delta)]^{-3} - [r(\delta, \beta)]^{-3}\}^2 , \qquad (9b)$$

where $r(\delta, \beta)$ means the interprotonic distance when the proton 1 is at its δ site and proton 2 at its β site.[12] From Eq. (6), taking into account Eq. (8) with $b = 8$ and Eq. (9) combined with the x-ray results,[1] the maximum in $T_{1\rho}^{-1}$ is evaluated

$$(T_{1\rho}^{-1})_{\max} \simeq 2 \times 10^2 \text{ sec}^{-1} , \qquad (10)$$

lower than the experimental result by a factor of about 10.

As regards the relaxation driven by the critical dynamics, we will point out in detail in Sec. III the good agreement of the theoretical estimates with the experimental results. For sake of illustration, assuming for the critical motions a correlation function of exponential type, with an effective correlation time $\tau \simeq (2\omega_1)^{-1}$, one obtains for the leading term of Eq. (4a)

$$(T_{1\rho}^{-1})_{\max} \simeq \frac{1}{4} A \Lambda_0 (2\omega_1)^{-1} \simeq 2.5 \times 10^3 \text{ sec}^{-1} , \qquad (11)$$

to be compared with Eq. (10). For the structural

factor Λ_0 in Eq. (11) the value $\Lambda_0 = 2.9 \times 10^{46}$ cm^{-6} was used [see Eqs. (21)].

In accordance with the above analysis, in Sec. III we will discuss the experimental results for protons T_1 and $T_{1\rho}$ in SCD with the assumption that the relevant relaxation mechanism is the critical dynamics in the hydrogen-bonded network.

III. DISCUSSION OF THE RESULTS IN LIGHT OF THE CRITICAL DYNAMICS

We will try to relate the temperature and frequency dependence of ϵ' and ϵ'' and of protons T_1 and $T_{1\rho}$ in SCD to the collective critical dynamics using an Ising-model approach. As is known, the dynamical Ising model applies quite well to order-disorder systems when the tunneling is negligible and nonpropagating diffusion modes, or polarization fluctuations, occur. In SCD the increase of the transition temperature by deuterium substitution[2] suggests that the tunneling affects the critical dynamics somewhat. However, the relaxational character of the dielectric response (discussed later) requires the occurrence of a strong damping of the pseudo-spin-waves, and in this limiting case an Ising model can be used, in any case, as a starting point. In addition, an Ising-type picture could be more applicable if the low-frequency part of the spectral density of the excitations is a "central-peak" tail of resonant pseudo-spin-wave modes.[14]

By applying the MFA treatment for the time-dependent statistics of Ising spins[15] to a system of electric dipoles[16] the dynamical susceptibility becomes

$$\chi(\vec{q}, \omega) = \chi(\vec{q}, 0)/(1 + i\omega\tau_{\vec{q}}^*) . \qquad (12)$$

Therefore a Debye-type dispersion relation holds, with a relaxation time $\tau_{\vec{q}}^*$ proportional to the static susceptibility. $\tau_{\vec{q}}^*$ is connected to the Fourier transform of the interaction $I(\vec{q})$ by the relation (in the paraelectric phase) $\tau_{\vec{q}}^* = \tau_0/[1 - I(\vec{q})/KT]$. For the relaxation time τ_0 for the flip-flop motion of an individual Ising unit a temperature behavior

$$\tau_0 = \tau_\infty e^{U/KT} \qquad (13)$$

can be assumed, where U is the height of the potential barrier between the two stable states of the dipole and where τ_∞ can be taken to be temperature independent.[17]

According to the theory of critial phenomena[18] the temperature behavior of the static homogeneous susceptibility and of the relaxation time of the polarization fluctuations, around the critical temperature, can be written

$$\chi(0, 0) = \chi_0 t^{-\gamma} , \qquad (14a)$$

$$\tau_p \equiv \tau_{\vec{q}=0} = \tau_0 t^{-\Delta} , \qquad (14b)$$

where $t = |T - T_0|/T_0$; T_0 is the stability limit of the slowing down. For a second-order transition T_0 is equal to the transition temperature T_c. In Eq. (14a) $\chi_0 = N\mu^2/KT$ is the susceptibility in the absence of interactions.

In the MFA theories one has for the critical exponents in Eqs. (14) $\gamma = \Delta = 1$. More advanced treatments[6] for the dynamics of interacting Ising spins in planar lattices give $\gamma = 1.75$ and $\Delta = 2$, with breakdown of the thermodynamical slowing-down condition ($\gamma = \Delta$). In addition, a polydispersive nature of the relaxation close to T_c and a finite $\chi'(0, \omega)$ even at the critical point are expected,[6,19] in contrast with the MFA treatments.

A. Dielectric dispersion and absorption: Critical effects

To give an empirical account of dispersion and absorption measurements in polydispersive systems one can refer[20] to the Cole-Cole relation and write

$$\epsilon'(\omega, t) = [\epsilon'(0, t) - \epsilon(\infty)](1 + bZ)/(1 + 2bZ + Z^2) , \qquad (15a)$$

$$\epsilon''(\omega, t) = \epsilon'(\omega, t) aZ/(1 + bZ) , \qquad (15b)$$

where $a = \sin(\tfrac{1}{2}\beta\pi)$, $b = \cos(\tfrac{1}{2}\beta\pi)$, and $Z = (\omega\tau_p)^\beta$. Here $\beta(0 < \beta \leqslant 1)$ is a constant which measures the width of the distribution of relaxation times. For $\beta = 1$ one obtains the Debye relations, consistent with the $\vec{q} = 0$ MFA susceptibility (12).

By plotting $\epsilon''(\omega)$ vs $\epsilon'(\omega)$, and then $[\epsilon''/(\epsilon' a - \epsilon'' b)]^{1/\beta}$ vs ω, $\epsilon(0)$, β, and τ_p were obtained. In Fig. 3 an illustrative example is shown, showing the good fit on the basis of Eqs. (15).

In Fig. 4 the static dielectric constant is reported, in a log-log plot, versus the reduced temperature. The transition seems slightly first order, with $T_c = 219.45$ °K; the static dielectric constants for $T > T_c$ are compared with the theoretical temperature behavior according to Eq. (14a), with $T_0 = T_c$ and $\gamma = 1.75$. While making an exact evalu-
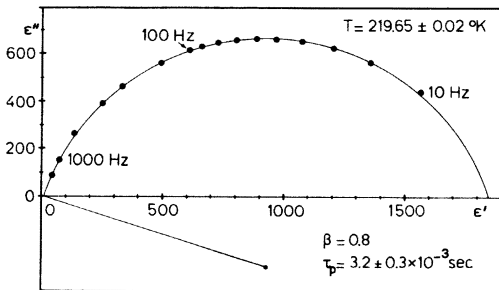

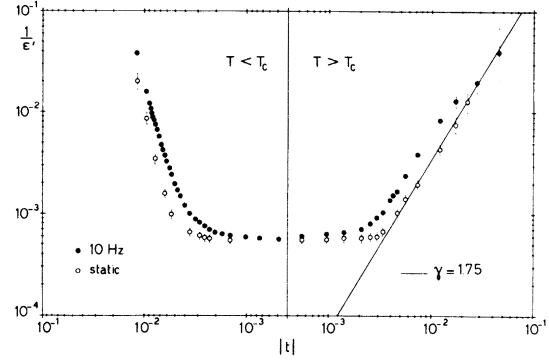
FIG. 4. Log-log plot of the inverse of the static dielectric constant vs $t = (T - T_c)/T_c$, with $T_c = 219.45$ °K. For comparison the experimental results at 10 Hz are also reported.

ation of γ is difficult (as usual when two adjustable parameters are present), the MFA value $\gamma = 1$ appears to be definitely ruled out.

The expected slowing down of the relaxation of the in-plane polarization fluctuations cannot be studied from the dielectric dispersion measurements. In fact, as shown in Fig. 5(a), τ_p decreases on approaching T_c. This could be due to the fact that interplanar interactions correlate the polarization flucutations antiferroelectrically. Therefore the homogeneous polarization decays more and more rapidly as the 3D-fluctuations regime occurs. A possible further indication in favor of the above interpretation is the flattening of $\epsilon(0)$ for $t \lesssim 2.5 \times 10^{-3}$ (see Fig. 4). In fact, sufficiently close to
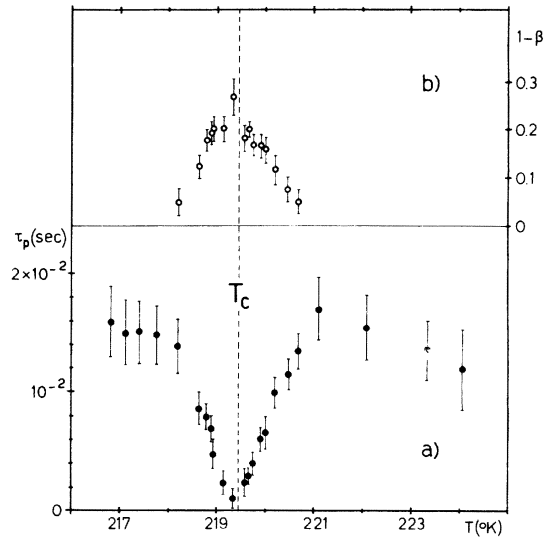

FIG. 3. Cole-Cole plot of ϵ'' vs ϵ' along the $\vec{c}$ axis in SCD.

FIG. 5. (a) Relaxation time of the polarization fluctuations and (b) width of the distribution $1 - \beta$, around the phase transition in SCD.

T_c the interplanar coupling could become strong enough to affect the static polarization also. A rounding of the parallel static susceptibility can be expected[21] by extending arguments[22] for anti-ferromagnets. However, no point of inflection in $\epsilon(0)$ is observed in our measurements.

B. Spin-lattice relaxation and critical dynamics

Let us derive the theoretical expressions for the proton relaxation rates in SCD within the framework of the picture for the critical dynamics already used for ϵ' and ϵ''. Since a quite narrow distribution of dielectric relaxation times seems to occur only close to T_c [see Fig. 5(b)], we will neglect here the polydispersive character of the dynamical susceptibility.

Let $s_i(t)$ indicate an order-disorder variable which assumes the values $+1$ or -1 according to the position of the hydrogen in the double-minimum potential. The lattice functions (5) can be written

$$F_\alpha^{(i,j)} = C_\alpha^{(i,j)} + D_\alpha^{(i,j)} s_i(t) + E_\alpha^{(i,j)} s_j(t)$$
$$+ G_\alpha^{(i,j)} s_i(t) s_j(t) , \qquad (16)$$

where:

$$C_\alpha^{(i,j)} = \tfrac{1}{4}(F_\alpha^{++} + F_\alpha^{+-} + F_\alpha^{-+} + F_\alpha^{--}) ,$$
$$D_\alpha^{(i,j)} = \tfrac{1}{4}(F_\alpha^{++} + F_\alpha^{+-} - F_\alpha^{-+} - F_\alpha^{--}) ,$$
$$E_\alpha^{(i,j)} = \tfrac{1}{4}(F_\alpha^{++} - F_\alpha^{+-} + F_\alpha^{-+} - F_\alpha^{--}) , \qquad (17)$$
$$G_\alpha^{(i,j)} = \tfrac{1}{4}(F_\alpha^{++} - F_\alpha^{+-} - F_\alpha^{-+} + F_\alpha^{--}) .$$

F_α^{+-} means F_α when the ith proton is at the $+$ position and the jth proton at the $-$ position. From Eq. (16) the time-dependent correlation function of F_α, for a given proton, can be written

$$\langle F_\alpha(0) F_\alpha^*(t) \rangle = \sum_i \Lambda_{a,\alpha}^{(i)} \langle s_i(0) s_i(t) \rangle$$
$$+ \sum_{i,j}' \Lambda_{p,\alpha}^{(i,j)} \langle s_i(0) s_j(t) \rangle + \cdots , \qquad (18)$$

where the auto- and pair-correlation factors $\Lambda_{a,\alpha}^{(i)}$ and $\Lambda_{p,\alpha}^{(i,j)}$ can easily be obtained in terms of C, D, E, and G given by Eqs. (17).

Three- and four-body correlation functions have been neglected in Eq. (18). By introducing the collective order-disorder variable

$$s_{\vec{q}}(t) = \frac{1}{\sqrt{N}} \sum_i e^{-i\vec{q}\cdot\vec{r}_i} s_i(t) ,$$

the spectral density $J_\alpha(\omega)$ of the correlation function (18) becomes, in the random-phase approximation,

$$J_\alpha(\omega) = \frac{1}{N} \sum_{\vec{q}} \left(\Lambda_{a,\alpha} + |\Lambda_{p,\alpha}|_{\vec{q}} \right) \int e^{-i\omega t} \langle s_{\vec{q}}(0) s_{-\vec{q}}(t) \rangle dt , \qquad (19)$$

where

$$\Lambda_{a,\alpha} = \sum_i \Lambda_{a,\alpha}^{(i)} ,$$

$$|\Lambda_{p,\alpha}|_{\vec{q}} = \sum_{i,j}' \Lambda_{p,\alpha}^{(i,j)} e^{i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)} ;$$

it can be assumed $|\Lambda_{p,\alpha}|_{\vec{q}} = |\Lambda_{p,\alpha}|_{\vec{q}=0}$. The spectral density (19) can be related to the imaginary part of the reduced ($\mu=1$) susceptibility (12) by means of the fluctuation-dissipation theorem. Therefore, from Eqs. (4) and (19), taking into account that $\omega_0^2 \tau_{\vec{q}}^2 \gg 1$ (see Sec. II C 1), the spin-lattice relaxation rates can finally be written

$$T_{1\rho}^{-1} = \frac{A\Lambda_0}{4} \frac{kT}{N^2} \sum_{\vec{q}} \frac{\chi(\vec{q},0) 2\tau_{\vec{q}}}{1 + 4\omega_1^2 \tau_{\vec{q}}^2} , \qquad (20a)$$

$$T_1^{-1} = 2A(\Lambda_1 + \tfrac{1}{4}\Lambda_2) \frac{kT}{N^2} \frac{1}{\omega_0^2} \sum_{\vec{q}} \frac{\chi(\vec{q},0)}{\tau_{\vec{q}}} . \qquad (20b)$$

The structure factors Λ_0, Λ_1, and Λ_2 in the above equations have been evaluated on the basis of the x-ray determinations.[1] For a single crystal of SCD with $\vec{a}^* \parallel \vec{H}_0$, by averaging over the various protons in the nonequivalent positions (in correspondence to the exponential recovery of the magnetization; see Sec. II C 1) a computer evaluation gives

$$\Lambda_0 = 2.9 \times 10^{-2} \text{ Å}^{-6} , \qquad \Lambda_1 = 0.5 \times 10^{-2} \text{ Å}^{-6} ,$$
$$\Lambda_2 = 17.5 \times 10^{-2} \text{ Å}^{-6} . \qquad (21)$$

In order to perform the $\vec{q}$ summation in Eqs. (20) we will apply the static and dynamical scaling hypotheses,[18] which allow us to write

$$\chi(\vec{q},0) = \chi_0 t^{-\gamma} f(q/\kappa) , \qquad (22a)$$

$$\tau_{\vec{q}}^{-1} = \tau_0^{-1} t^\Delta g(q/\kappa) , \qquad (22b)$$

where f and g are homogeneous functions of q/κ only, κ is the inverse correlation length, and

$$\kappa = \kappa_0 t^\nu , \qquad (23)$$

ν being the appropriate critical exponent.

In the disordered phase and in the temperature range in which $\omega_1^2 \tau_{\vec{q}}^2 \gg 1$, by referring to Eq. (20a) and by taking into account Eqs. (22) and (21) we have

$$T_{1\rho}^{-1} = \frac{A\Lambda_0 t^{(\Delta-\gamma)}}{8\omega_1^2 \tau_0} \frac{1}{N} \sum_{\vec{q}} fg$$

$$\simeq \frac{2 \times 10^9}{\omega_1^2 \tau_0} t^{(\Delta-\gamma)} , \qquad T > T_c , \quad \omega_1^2 \tau_{\vec{q}}^2 \gg 1 , \qquad (24)$$

where it has been assumed $g \simeq f^{-1}$ (in the MFA $g = f^{-1} = q^2/\kappa^2 + 1$); analogously

$$T_1^{-1} \simeq \frac{5.3 \times 10^{10}}{\omega_0^2 \tau_0} t^{(\Delta - \gamma)}$$

$$= 27.5 \left(\frac{\omega_1}{\omega_0}\right)^2 T_{1\rho}^{-1}, \quad T > T_c . \qquad (25)$$

According to Eqs. (24) and (25), for thermodynamical slowing down ($\Delta = \gamma$) the only temperature dependence of the relaxation rates is due to τ_0, as recently pointed out in a 3D MFA evaluation.[23]

For $T \gtrsim 260\,°K$ the condition $\omega_1^2 \tau_q^2 \gg 1$ does not apply. In the fast-motion region ($\omega_1^2 \tau_q^2 \ll 1$) the temperature behavior of $T_{1\rho}$ can, however, easily be obtained: since $\int f g^{-1} d\vec{q} \propto \kappa^d$, where d denotes the lattice dimensionality, Eq. (20a) gives

$$T_{1\rho}^{-1} \propto \tau_0 t^{(\nu d - \Delta - \gamma)}, \quad T > T_c, \quad \omega_1^2 \tau_q^2 \ll 1, \qquad (26)$$

i.e., the relaxation rate exhibits a divergence for $T \to T_0$ with a critical exponent that in the 3D molecular-field isotropic approximation is 0.5.[24] In the intermediate region of slowing down ($\tau_p \gtrsim \omega_1^{-1}$ while $\tau_0 \lesssim \omega_1^{-1}$) a complex expression for the relaxation rates holds. By assuming for f and g in Eqs. (22) Ornstein-Zernike-type expressions one would obtain,[8,25] approximately,

$$T_{1\rho}^{-1} \propto \omega_1^{-1/2} \tau_0^{1/2} .$$

For $T < T_c$ it can be assumed

$$\chi(\vec{q}, 0)/\tau_q^- = \chi_0 \tau_0^{-1} (- t)^{\Delta - \gamma} (1 - \langle s \rangle^2) .$$

From Eqs. (20), taking into account Eqs. (21), one has

$$T_{1\rho}^{-1} = \frac{2 \times 10^9}{\omega_1^2 \tau_0} |t|^{(\Delta - \gamma)} (1 - |t|^{2\beta})$$

$$= 3.6 \times 10^{-2} \left(\frac{\omega_0}{\omega_1}\right)^2 T_1^{-1}, \quad T < T_c, \qquad (27)$$

where β is the critical exponent for the order parameter $\langle s \rangle$.

In order to obtain from Eqs. (24), (25), and (27) the theoretical relaxation rates an evaluation of τ_0 is required. This can be achieved by setting $\tau_0 \simeq (2\omega_1)^{-1}$ for $t^* = 2.3 \times 10^{-1}$ (see Fig. 2), where the ratio $T_1/T_{1\rho}$ deviates with respect to the values at lower temperatures [thus indicating the breakdown of the condition $4\omega_1^2 \tau_q^2 \gg 1$; see Eqs. (20a), (24) and (25)]. According to Eqs. (24) and (25) with $\Delta = 2$ and $\gamma = 1.75$ one then obtains, at t^*, $T_{1\rho}^{-1} = 3.2 \times 10^3$ and $T_1^{-1} = 3.5$ sec^{-1}, in good agreement with the experimental data. It should be noted that no adjustable parameters are present.

In Fig. 2 the plots of the theoretical expressions for T_1 and $T_{1\rho}$ according Eqs. (24), (25), and (27) are reported, for $\gamma = 1.75$, $\Delta = 2$, $\beta = \frac{1}{8}$. The dash-dotted line refers to a temperature-independent τ_0, while the solid line refers to a temperature dependence according to Eq. (13) with $U = 0.25$ eV.

The dotted line for $t \gtrsim 3 \times 10^{-1}$ is the best-fitting behavior for $T_{1\rho}^{-1}$, according to Eq. (26) (with $d = 2$ and $\nu = 1$).

The temperature dependence of the relaxation rates compares quite well with theory. This agreement, however, does not allow one to conclude that the critical exponent for the relaxation time of in-plane polarization fluctuations is actually 2, in view of the weak temperature dependence predicted by Eqs. (24), (25), and (27) far from T_c; on the other hand, the narrow dips that according to the theoretical treatment are expected at T_c can be difficult to study in detail, due to the slightly first-order character of the transition and/or the temperature gradients on the sample.

A better indication of the temperature behavior of τ_p can be achieved by making comparisons among the data from $T_{1\rho}$ and those from dielectric dispersion. From $T_{1\rho}$, τ_0 at $T \simeq T_c + 50\,°K$ is obtained; on the basis of Eq. (14b) with $\Delta = 2$, one can evaluate the expected value of τ_p at $T = T_c + 2\,°K$ (slightly above the crossover to 3D antiferroelectrically correlated fluctuations). One obtains $\tau_p = 7.5 \times 10^{-3}$ sec if τ_0 is assumed temperature independent [$U = 0$ in Eq. (13)] and $\tau_p = 7.2 \times 10^{-2}$ sec for $U = 0.25$ eV. This is to be compared with $\tau_p \simeq 1.8 \times 10^{-2}$ sec obtained from the dispersion measurements at $T \simeq T_c + 2\,°K$ [see Fig. 5(a)].

IV. CONCLUSIONS

The results of dielectric dispersion and absorption and of proton T_1 and $T_{1\rho}$ measurements in a single crystal of layered SCD around the phase transition have been discussed on the basis of the dynamical theories for a planar lattice of interacting Ising spins.

The dielectric response has a relaxational character, with a polydispersive nature arising a few degrees before the transition. The static uniform susceptibility diverges with a critical exponent close to 1.75.

On the basis of the same picture of the critical dynamics used for the interpretation of the dielectric measurements, a theoretical treatment has been given for the proton relaxation rates. A gratifying agreement with the experimental results is obtained. The temperature dependence of the relaxation time for the in-plane polarization fluctuations cannot be obtained, over a wide temperature range, either from dielectric or proton spin-lattice relaxation. However, from $T_{1\rho}$ one can deduce $\tau_p \simeq 1.2 \times 10^{-5}$ sec at $T \simeq T_c + 50\,°K$, while from dielectric dispersion $\tau_p \simeq 1.8 \times 10^{-2}$ sec at $T \simeq T_c + 2\,°K$, in agreement with a slowing down described by a critical exponent around 2. From the frequency and temperature dependence of $T_{1\rho}$

the relaxation time τ_0 for the flip-flop motion of an individual hydrogen atom in the hydrogen bond, in absence of interaction, appears characterized by an activated temperature dependence, with a height of the potential barrier of about 0.25 eV. For $T \lesssim T_c + 1.5\,°\text{K}$, the relaxation time of the polarization decreases on approaching the transition, probably due to crossover towards three-dimensionally antiferroelectrically correlated fluctuations.

By summarizing, nonclassical critical effects that can be related to the short range of the interactions and to the restricted dimensionality have been demonstrated for the phase transition in layered SCD. These critical effects are in agreement with the main conclusions of the theories for the critical dynamics of interacting Ising spins in planar lattices.

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