Dynamic Critical Behavior of Ferroelectric Triglycine Sulfate from Dielectric Loss Measurements

R. García and J. A. Gonzalo
Departamento de Óptica y Estructura de la Materia, Universidad Autónoma de Madrid, Madrid 34, Spain
(Received 27 September 1982)

Measurements of the dielectric loss in triglycine sulfate are shown to yield information on the critical temperature dependence of the relaxation time, $\tau(t)$, where $t \equiv (T - T_c)/T_c$. The data indicate a power law $\tau^{-1}(t) \sim t^x$, where $x = 0.656 \pm 0.025 \simeq \frac{2}{3}$ for $7\times10^{-2} < \Delta T < 1.5$°C at $T > T_c$. $\tau(t)$ does not diverge at T_c, in accordance with theoretical considerations. For $T < T_c$ the data suggest a similar behavior. The role of logarithmic corrections is analyzed, and estimates of the correlation length amplitude $\xi_0 \simeq 7.86$ Å and the dipole-dipole constant $g \simeq 3.44\times10^{-7}$ Å^{-2} are obtained.

PACS numbers: 77.80.Bh, 64.60.Ht, 77.40.+i

The critical behavior of uniaxial dipolar ferroelectrics and ferromagnets has received recent considerable attention[1-5] in part because it makes possible comparisons with results from the renormalization-group theory of phase transitions, which predict mean-field behavior with logarithmic corrections[6] for dimensionality $d = d^* = 3$ (corresponding to the long-range dipolar interaction). Triglycine sulfate (TGS) can be considered a prototype uniaxial ferroelectric with a second-order transition at $T_c \simeq 49$ °C. The dielectric dispersion of TGS has been the object of several papers.[7-9] Luther and Muser's[8] data on this crystal show, in contrast to those of Hill and Ichiki,[7] a monodispersive behavior, with a single Debye relaxation time. Unruh and Wahl's[9] data confirm this monodispersive behavior and report a temperature dependence of the relaxation time $\tau_s \sim \epsilon_s{}^x \sim |(T - T_c)/T_c|^x$ with $x \simeq 1.08$. The data shown by the last authors (Fig. 2, Ref. 9) are not inconsistent with lower values for x as ϵ_s approaches $\epsilon_s(T_c)$.

Samples of thicknesses ranging from 0.5 to 7 mm and areas from 0.17 to 1.40 cm^2 were cut from a large single crystal of TGS grown from water solution. Gold leaf electrodes were attached directly to the main surfaces, perpendicular to the ferroelectric b axis. The sample holder, within a thick-walled aluminum container, was immersed in a temperature controlled bath, and the temperature was measured by means of a Chromel-Alumel thermocouple with a Fluke digital microvoltmeter. For measurements in the vicinity of T_c, the slow spontaneous cooling technique[10] was used. Successive temperature and time readings, the latter using a digital chronometer, defined with good accuracy the cooling rate, which was nearly linear in an interval of a few degrees above and below T_c, thus providing an improved relative definition of the temperature readings (approximately ± 0.001 °C). Simultaneous measurements of the capacitance, C, and the loss factor, $D \equiv R/|X|$, were obtained at each temperature with a universal Video-bridge (Electro-Scientific Industries model 2100) which gave digital readouts for both C and D with five or more significant figures. The relative accuracy for C and D in our range of measurements, according to the manufacturers, was better than 0.1%, and this is borne out by the small scatter of our data points. The 1-kHz field amplitude was fixed at about 2 V/cm, regardless of the thickness of the sample. The two main factors affecting the quality of the data are thought to be (a) thermal gradient from the lower to the upper surface of the samples and (b) charged-impurities gradient through the sample, producing a small effective field bias. A rough estimate of the thermal gradient for our experimental conditions gave ~ 0.01 K/mm. Inherently more difficult is to get an estimate of the presumable charged-impurities gradient in our samples, since its magnitude should change in going through T_c. Its associated internal bias should be no higher than ~ 1 V/cm at $T \simeq T_c$ in view of the values $\epsilon_{max} \sim 10^5$ observed.

The capacitance and the loss factor of three samples of different thickness (0.54, 2.19, and 6.94 mm, respectively) were measured between 56 °C and 40 °C at closely spaced temperature intervals, up to 0.005 °C, in the immediate vicinity of T_c. Rounding effects were noticeable within 0.1 °C of the peak temperature. Plots of ϵ^{-1} vs $t \equiv (T - T_c)/T_c$ were fitted to $\epsilon^{-1} \sim t$ (straight mean-field theory) and $\epsilon^{-1} \sim t\,|\ln t|^{-1/3}$ (three-dimensional dipolar Ising model). T_c was first optimized separately for both cases, using data points for which $0.1 < T - T_{peak} < 1.5$ °C. As might be anticipated, the goodness of the fit was similar, because of the uncertainties introduced by

the relatively large rounding observed.

Figure 1 shows data of inverse loss factor D^{-1} versus $\Delta T = T - T_c$ above T_c for the thickest sample ($d \simeq 6.94$ mm). It must be noted that the peak value of the loss factor, D_{max}, was almost independent of sample thickness. On the other hand, D values far away from T_c were much lower for the thickest sample, reflecting probably better the bulk characteristic conductivity of TGS. The log-log plot of Fig. 1, for which T_c was first determined separately, under the assumption only of a power law with an as yet unspecified critical exponent, indicates that D^{-1} remains finite as ΔT goes to zero, and can be fitted very well by $D^{-1} \sim t^x$, with $x = 0.656 \pm 0.025$ for $0.07 < \Delta T < 1.5$ °C, i.e., within a considerable span in ΔT, involving a more than twentyfold increase. The digital readout for D implies convenience and accuracy not easily attainable with conventional bridges. As stated before the relative accuracy was always better than 0.1% and, within one degree of T_c, better than 0.05%.

The q-dependent susceptibility of a dipolar ferroelectric along the polar axis can be written[1] as

$$\chi_q = \chi/(1 + q^2\xi^2 + g\xi^2 - hq^2\xi^2), \tag{1}$$

where $h < 1$, g is a dipole-dipole coupling constant, $\chi \sim t^{-1}|\ln t|^{1/3}$ is the zero-field susceptibility for spatially homogeneous polarization, and ξ is the correlation length. When we take into account that

$$\xi_\perp = \xi_0 t^{-1/2}|\ln t|^{1/6}, \quad \xi_\parallel = g^{1/2}\xi_0{}^2 t^{-1}|\ln t|^{1/3},$$

the overall correlation length can be written as

$$\xi = (\xi_\parallel \xi_\perp{}^2)^{1/3} = g^{-1/2}(g\xi_0{}^2)^{2/3} t^{-2/3}|\ln t|^{2/9} \simeq g^{-1/2}(g\xi_0{}^2)^{2/3} t^{-2/3}. \tag{2}$$

On the other hand, the frequency dependence of the dielectric constant of TGS near T_c appears to be well described by a single, temperature-dependent, Debye relaxation time τ_r.[8,9] Hence we have, for $\omega\tau_r \ll 1$,

$$\frac{1}{D} \equiv \frac{|X|}{R} = \frac{\epsilon'(\omega)}{\epsilon''(\omega)} = \frac{\epsilon_\infty{}^+(\epsilon_0 - \epsilon_\infty)/(1+\omega^2\tau_r{}^2)}{\omega\tau_r(\epsilon_0 - \epsilon_\infty)/(1+\omega^2\tau_r{}^2)} \simeq \frac{[\epsilon_\infty/(\epsilon_0 - \epsilon_\infty)] + 1}{\omega\tau_r}. \tag{3}$$

Furthermore, taking into account that

$$\mathrm{Re}[\epsilon^{-1}(\omega)] \equiv (4\pi\chi_q)^{-1} = (4\pi\chi_0)^{-1}[1 + (1-h)q^2\xi^2/(1+g\xi^2)], \tag{4}$$

where $\chi_0 \equiv \chi/(1+g\xi^2)$, and that, according to Debye's theory,

$$\mathrm{Re}[\epsilon^{-1}(\omega)] = (\epsilon_0 - \epsilon_\infty)^{-1}(1+\omega^2\tau_r{}^2), \tag{5}$$

one can combine Eqs. (1) and (3)–(5) to get, at a given frequency,

$$D^{-1} = \text{const} \cdot \tau_r{}^{-1} = (1-h)^{-1/2} q^{-1} g^{1/2}(1 + 1/g\xi^2)^{1/2} = D_{max}{}^{-1}(1 + 1/g\xi^2)^{1/2}, \tag{6}$$

where it has been assumed that $\epsilon_0 \gg \epsilon_\infty$ and $4\pi\chi_0 \gg 1$, so that $\epsilon_0 \sim 4\pi\chi_0$. Then, sufficiently away from T_c, when $g\xi^2 \ll 1$,

$$D^{-1} = D_{max}{}^{-1} g^{-1/2}\xi^{-1} \simeq D_{max}{}^{-1}(g\xi_0{}^2)^{-2/3} t^{2/3} \tag{7}$$

which is consistent with a critical exponent $x = \frac{2}{3}$ for the inverse relaxation time, while for $g\xi^2 \gg 1$,

$$D^{-1} \simeq D_{max}{}^{-1}, \tag{8}$$

which corresponds to a finite $D^{-1}(T_c) \equiv D_{max}{}^{-1} \simeq 4.87$ in our data.

The dimensionless product $g\xi_0{}^2$ can be obtained directly from the data in Fig. 1 with use of Eq. (6). The result is

$$g\xi_0{}^2 \simeq 2.127 \times 10^{-5} \text{ (dimensionless)}. \tag{9}$$

On the other hand, as shown by Aharony and

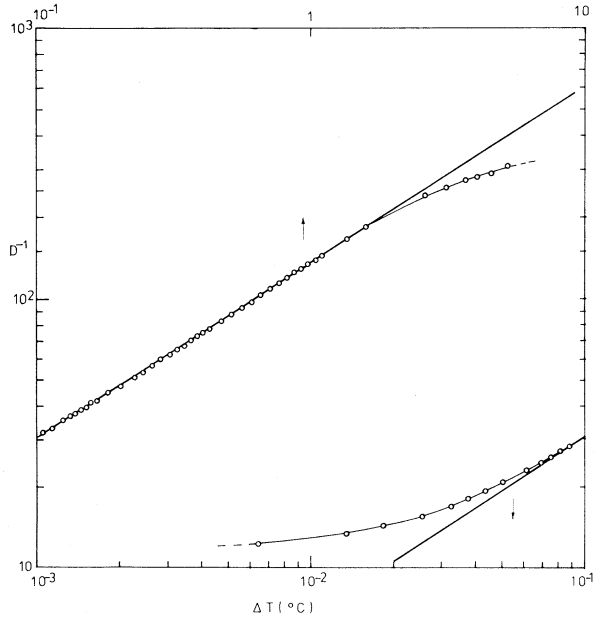

FIG. 1. Log-log plot of inverse dielectric loss factor, D^{-1}, vs $\Delta T \equiv T - T_c$ for TGS sample of thickness d = 0.694 cm.

Halperin,[1] specific-heat data provide a universal relation involving g and ξ_0, which is given by

$$g^{1/2}\xi_0^4 \simeq k_B D |\ln t|^{1/3}/C \simeq k_B D/A, \quad (10)$$

where k_B is Boltzmann's constant, $D = 3/32\pi$, and C is the singular part of the specific heat, which may be approximated in the close vicinity of T_c, for $T > T_c$, by

$$C \simeq A |\ln t|^{1/3}. \quad (11)$$

Existing data on C for TGS by Ema, Hamano, and Ikeda[11] can be fitted to Eq. (11) for $0.15 < \Delta T < 10$ °C. A good fit is obtained with $A \simeq 0.207$ (arbitrary units) $\simeq 1.671 \times 10^6$ erg/cm^3 °C, with[12] $C_{max} \simeq 0.68$ (arbitrary units) $\simeq 0.325$ J/g and $\rho = 1.69$ g/cm^3. We note that the background specific heat from this fit comes out considerably lower than that estimated by Ema, Hamano, and Ikeda in their paper. Substituting numerical values for A and the other constants in Eq. (10) we get

$$g^{1/2}\xi_0^4 \simeq 2.242 \times 10^{-24} \text{ cm}^3. \quad (12)$$

Now, combining Eqs. (9) and (12), we get

$$\xi_0 \simeq 7.86 \times 10^{-8} \text{ cm}, \quad g \simeq 3.44 \times 10^9 \text{ cm}^{-2}. \quad (13)$$

The numerical value obtained for the correlation length amplitude at about 0 K is hence of the order of the nearest-neighbor dipole-dipole distance in TGS.[13] The corresponding parameters for the uniaxial ferromagnet $LiTbF_4$ were obtained by Ahlers, Kornblit, and Guggenheim.[14]

The dynamic scaling hypothesis[15,16] implies that the characteristic relaxation time associated with fluctuations near a phase transition can be expressed as

$$\tau_k = \xi^z f(k\xi), \quad (14)$$

where the subscript k denotes the pertinent wave vector, z is a critical exponent, and $f(k\xi)$ is independent of t. Taking into account that, according to our data, $\tau_k(t) \sim t^{-2/3}$, and that $\xi(t) \sim t^{-2/3}$, these data appear to imply a dynamic exponent $z = 1$.

Figure 2 shows data of D^{-1} as a function of T for T below as well as above T_c from the sample with intermediate thickness ($d = 2.19$ mm) given in a different, linear representation. Substituting Eq. (2) into Eq. (6) and rearranging terms, one obtains

$$[(D^{-1}/D_{max}^{-1})^2 - 1]^{3/4} = (g\xi_0^2)^{-1} t \sim \Delta T. \quad (15)$$

The data seem to fulfill this relation very well near T_c, both above and below the transition, and are consistent with the same critical exponent $x \simeq \frac{2}{3}$ in both temperature regions. Similar results were obtained with the thin sample ($d = 0.54$ mm).

It may be concluded that *dynamic* critical behavior, previously sought but not found, consistent with that predicted by RG theory for a three-dimensional dipolar Ising system, has been observed for the first time in a uniaxial ferroelectric.

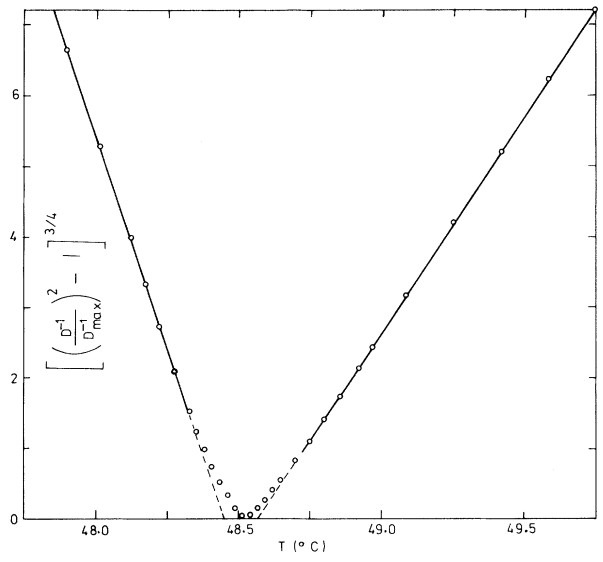

FIG. 2. Plot of $[(D^{-1}/D_{max}^{-1})^2 - 1]^{3/4}$ vs temperature for TGS sample of thickness $d = 0.219$ cm ($D_{max}^{-1} = 6.01$ at $T \simeq T_c$).

[1]A. Aharony and B. J. Halperin, Phys. Rev. Lett. 35, 1308 (1975).

[2]K. Binder, G. Meissner, and H. Mais, Phys. Rev. B 13, 4890 (1976).

[3]K. Imai, J. Phys. Soc. Jpn. 43, 1320 (1977).

[4]D. Stauffer, Ferroelectrics 18, 199 (1978).

[5]V. B. Laux, G. Meissner, and Ch. Vester, Ferroelectrics 35, 223 (1981).

[6]A. I. Larkin and D. E. Khmelnizkii, Zh. Eksp. Teor. Fiz. 56, 2087 (1969) [Sov. Phys. JETP 29, 1123 (1969)].

[7]R. M. Hill and S. K. Ichiki, Phys. Rev. 128, 1140 (1962).

[8]G. Luther and H. E. Muser, Z. Naturforsch. 24a, 389 (1969).

[9]H. G. Unruh and H. J. Wahl, Phys. Status Solidi (a) 9, 119 (1972).

[10]Some of the best data on $\epsilon_s(T)$ at $T \simeq T_c$ have been obtained by this technique; see, for instance, E. Naka-

mura, T. Nagai, K. Itoh, and T. Mitsui, J. Phys. Soc. Jpn. 28, 271 (1970), and references therein.
[11]K. Ema, K. Hamano, and Y. Ikeda, J. Phys. Soc. Jpn. 46, 345 (1979).
[12]R. Tobon and J. E. Gordon, Ferroelectrics 17, 409 (1977).
[13]See, for instance, F. Jona and G. Shirane, *Ferroelectric Crystals* (MacMillan, New York, 1962).
[14]G. Ahlers, A. Kornblit, and H. J. Guggenheim, Phys. Rev. Lett. 34, 1227 (1975).
[15]B. I. Halperin and P. C. Hohenberg, Phys. Rev. 177, 952 (1969).
[16]S. Ma, *Modern Theory of Critical Phenomena* (Benjamin, Reading, Mass., 1976).