Dynamics of Freezing Electric Dipoles

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Dielectric relaxation measurements are reported in $KTaO_3$:Li and interpreted in terms of a Gaussian distribution of logarithmic relaxation times. The center and width of this distribution depend continuously on temperature, and reveal no signs of critical effects at the freezing temperature. It is suggested that the same mechanism governs freezing in $KTaO_3$:Li, spin-glasses, the quadrupole glass KBr:CN, and the tunneling-dipole glass KCl:OH.

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Electric, magnetic, and elastic moments occupying random sites in a crystalline host lattice may freeze into an apparently stable configuration. In their frozen state, these moments do not exhibit long-range order, and the question is being debated whether their state can be described by an order parameter characteristic of a thermodynamic phase transition, or else whether freezing is governed by slowing down of random clusters containing relatively few individual moments.

Numerous experiments on *spin*-glasses have contributed to the understanding of frozen disorder without settling the dispute.[1,2] A very recent report on the *orientational* glass Br appears to present data in favor of the slow-cluster model.[3] On the other hand, models have been proposed whose solution, implying a thermodynamic phase transition, might not apply to real systems since spin-spin interactions were assumed to have an infinite range.[4] These investigations are supplemented by computer-simulation studies on finite systems,[5] and by dynamic theories of spin-glasses.[6]

A model for an *electric-dipole* glass has been advanced on the basis of a self-consistent equation for the conjugate-field distribution.[7] It predicts a widening of the electric-field distribution below a certain temperature and possible freezing. An alternate approach, based on dipolar interaction in a strongly polarizable lattice, raises the possibility of ferroelectric order at sufficiently high concentrations.[8] Indeed, it is still debated whether experimental results in $KTaO_3$:Li should be explained in terms of a ferroelectric[9] or a dipole glass.[10]

The purpose of this Letter is to establish experimentally the range of validity of these theories and, in particular, to show that a transition point between the paraelectric and the glass phase does not exist. The main argument against the transition is the observation of fluctuations of Li dipoles in $KTaO_3$ which *slow down* progressively and *continuously* in the very temperature range where a condensed phase appears to be established.

To underline the similarity between random-site spin and electric-dipole systems, the customary plot of the absolute values of the susceptibility is given as a function of temperature for several frequencies $f = \omega/2\pi$. Figure 1 shows that the peaks of the susceptibility of $K_{0.974}Li_{0.026}TaO_3$ shift to lower temperature upon lowering the frequency of the applied field, just as in spin-glas-

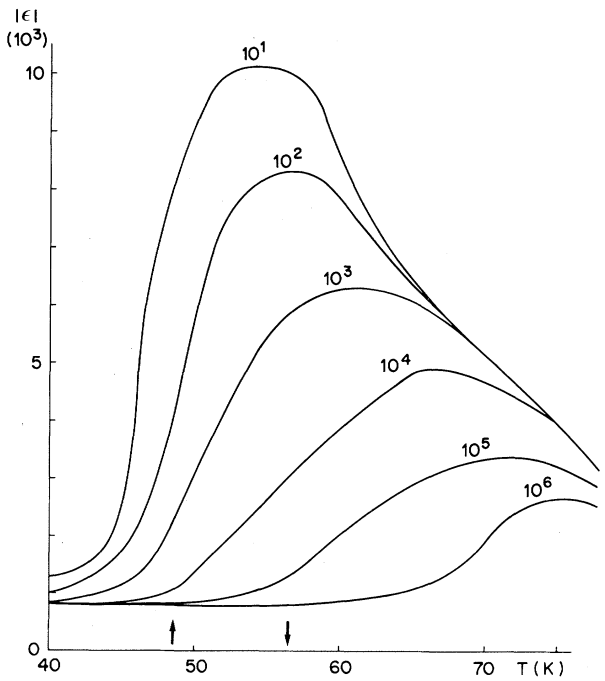

FIG. 1. Dielectric susceptibility of $KTaO_3$:Li as a function of temperature. Labels stand for the measuring frequencies, arrows for the maximum of the dielectric dispersion step (49 K) and the stability limit of remanent polarization (56 K) (see also Fig. 3). Li concentration is 0.026.

ses. The susceptibility above lattice background is attributed to the Li dipoles pointing in one of the six equivalent [100] directions and following the applied ac field over a barrier v_B with a characteristic time lag[11] τ_0. The dielectric bridge method allows for precise determination of the imaginary part ϵ'' of ϵ. It is shown as a function of $s=\ln(\omega\tau_0)$ in Fig. 2. Only the high-frequency part of the practically symmetric bell-shaped curve is given. The width of the curve clearly exceeds that attributed to Debye relaxation,

$$\epsilon''/(\epsilon_0-\epsilon_\infty)=\omega\tau_0/(1+\omega^2\tau_0^2)=1/\cosh(s)=D(s),$$

plotted in Fig. 2 vs $s=\ln(f)$, where f is in units of $f_0=1/2\pi\tau_0$. The broadening observed is attributed to a distribution of relaxation times $g(\tau_0)$, according to one of four models. Back in 1913, Wagner[12] assumed a Gaussian distribution $G(u)$ reflecting a Gaussian for the barrier heights, $u=\ln(\tau/\tau_0)=v_B/kT$.

A numerical fit to the data of the Wagner function

$$W(s)=A\int du\,\exp(-u^2/\Delta u^2)/\Delta u\,(\sqrt{\pi})^{1/2}\cosh(s+u),$$

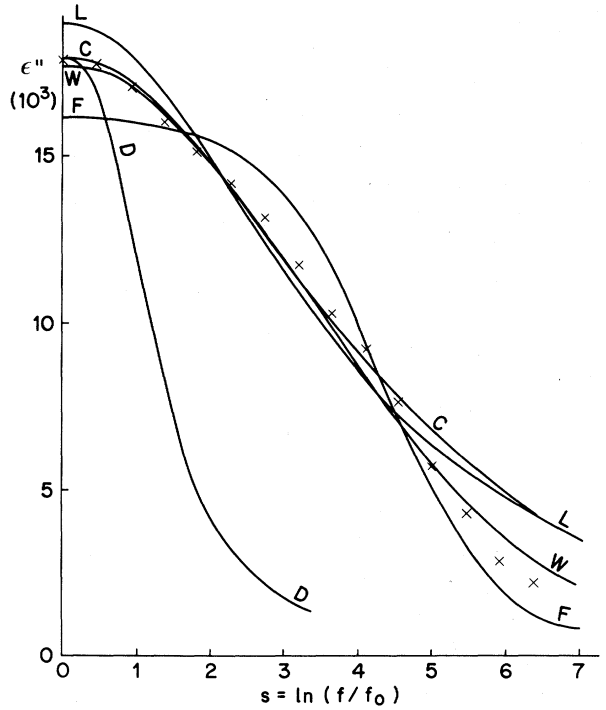

FIG. 2. Imaginary part of the dielectric susceptibility as a function of frequency at T = 57.2 K. Theoretical curves are from the convolution of the Debye relaxation formula $\omega\tau/(1+\omega^2\tau^2)$ with relaxation distributions, C: Cole, L: Lorentz, W: Wagner, F: Fröhlich, and D: Debye.

whose parameters are the amplitude of the relaxation step A, its width Δu, and center $\ln f_0$ (f_0 in hertz), yields $A=0.94$, $\Delta u=4.55$, and $\ln(f_0)=9.3$. The difference $1-A=0.06$ reflects the relative error of the estimate of $\epsilon_0-\epsilon_\infty$ from a Cole-Cole plot,[13] and $f_0\approx 10$ kHz is the frequency at which ϵ'' is maximum. The most probable effective relaxation time and its width of distribution is thus $\tau_0=1.5\times10^{-5\pm2.5}$ sec.

Fröhlich[14] avoided numerical analysis by assuming $G_F(u)=g_0$ for $|u-u_0|<\Delta u$ and 0 outside. The best fits of

$$F(s)=A_F\int du\,G_F(u)/\cosh(s+u),$$

as well as the Lorentz fit

$$L(s)=A_L\int\pi[\Delta u_L/(\Delta u_L{}^2+u^2)]\cosh^{-1}(s+u)$$

and the time-honored Cole-Cole fit[13] $C(s)=A_C\cosh^{-1}(as)$, are all shown in Fig. 2. Inspection of Fig. 2 shows, and the error analysis confirms, that Wagner-Gauss distribution fits the data better than any other distribution. Its parameter f_0 is transformed into a single-channel relaxation rate $\tau^{-1}=\tau_{s.c.}{}^{-1}=\tau_0{}^{-1}/4=\pi f_0/2$, where one takes into account that the dipole may convert its orientation from z to $-z$ by four channels, via x, $-x$, y, $-y$. τ^{-1} is given in Fig. 3 for several temperatures in the freezing range. A heuristic fit to the data of $\ln[\tau^{-1}(0)]-v_BT^{-1}+DT^{-2}$ yields $\ln[\tau^{-1}(0)]=31$, $v_B=1100$ K, and $D=-0.0132$ K^2, i.e., an Arrhenius function with an attempt frequency of $e^{31}\sim10^{13}$ Hz and a barrier of 1100 K just as was found for small Li concentrations, $x=0.006$. The slight curvature found

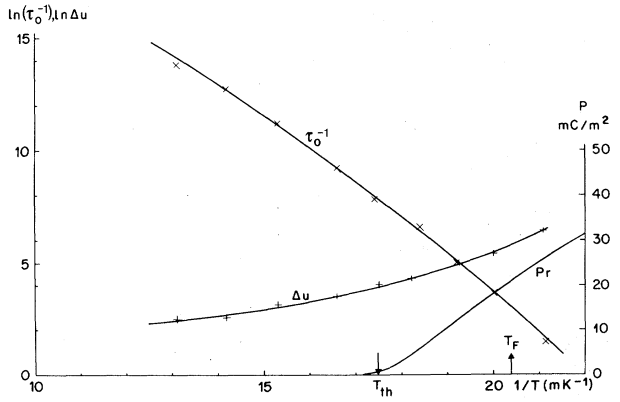

FIG. 3. Most probable relaxation rate $\tau_0{}^{-1}$, and width of distribution (Δu) as a function of $1/T$. Parameters for best-fit curves are given in the text. To the right: remanant polarization P_r from pyroelectric effect below the thawing temperature T taken on the same sample; Li concentration is 0.026.

here for $x = 0.026$ is characteristic for all $x \gtrsim 0.015$ and T close to the freezing temperature T_f. This temperature may be defined as that of maximum dielectric dispersion,[11] $T_f = 49$ K, but it is also close to the temperature of maximum $|\epsilon|$, at the lowest accessible frequency $T_\epsilon \sim 52$ K (Fig. 2) and the thawing temperature of the remanent polarization $T_{th} = 57$ K (Fig. 3). There is no sign of discontinuity of $\ln\tau_0$ vs T^{-1} at either of those temperatures marked by arrows in Fig. 3. Accordingly, an attempt to fit the data by the Fulcher law,[15] $s = -v_B/(T - T_f)$, fails.

The width of this distribution appears to be constant far away from T_f, and to increase as $\Delta u = 2.2 + 0.044(T^{-1} - 0.012)^2$, i.e., continuously from 80 to 47 K. Expressed in units of k_B, the most probable barrier height and its true standard deviation (not the experimental uncertainty) are (1100 ± 160) K far away from T_f, and rise continuously to (1400 ± 300) K at T_f. These distributions are related to field distribution by a crude estimate of the shift δs_0 of the relaxation distribution in an electric field δE. At 70 K, this method (which is not trivial since it implies sorting out piezoelectric resonances) yields $\delta s = 0.2 \pm 0.1$ for $\delta E = 0.5$ MV/m, and thus a width $\Delta E = 10 \pm 5$ MV/m. Inspection of data on KCl:OH[16] suggests that the phenomenon of broadening E distributions is widespread among glasses[17] but absent in ferroelectrics.[18]

Fisher and Klein[7] predict that the electrical field distribution at the impurity site is Lorentzian below and Gaussian above a crossover field $|E_c| = |P|/3\epsilon\epsilon_0$, and that its width increases upon lowering T. Since $E_c \sim 1$ MV/m, and the experimental $\Delta E \sim 10$ MV/m, the distribution predicted should be dominantly Gaussian. Both predictions are clearly borne out by the experiment (Figs. 2 and 3).

At sufficiently low temperatures, according to Fischer and Klein, the dipolar system should be described by a new thermodynamic phase. On the basis of the experimental evidence presented, this assertion cannot be upheld: Both the characteristic time scale and the width of the distribution are continuous and monotonous functions of temperature. Of the two assumptions made by Fischer and Klein, it is probably the mean-field hypothesis which leads to this spurious phase transition, and not the particular form of the distribution to which the system's response is only moderately sensitive (Fig. 2).

How to explain the apparently critical behavior of the susceptibility in the presence of uncritical relaxation dynamics? Assume a distribution of clusters, each of which has its own effective dipole-lattice interaction, v_{cl}, feeding back on the susceptibility as

$$\chi = \chi_{bare}/(1 - v_{cl}\chi_{bare}).$$

In this simplified picture,[19] a small change of either $\langle v_{cl}\rangle$ or the width of its distribution will enhance χ drastically, with large slow clusters playing the dominant role. This feedback is absent for nuclear spin-lattice relaxation, governed by fast-relaxing small clusters. This explains the observation of fast spin relaxation under conditions where the polar configuration appears macroscopically frozen.[11] Thus, I conclude that in $KTaO_3$:Li, in KCl:OH, and presumably in spin-glasses and orientational glasses, breakdown of translational symmetry leads to a distribution of the conjugate field. On cooling, these distributed fields force the disordered system into a glass-like state and are presumably responsible for the specific-heat anomaly.[20] They feed back on the susceptibility leading to a precipitously fast change of macroscopic properties which simulates the presence of a thermodynamic phase transition. Its existence is, however, disproved by the continuity of local order and the continuity of dynamical time scales in glasses.

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Upper Critical Field of a Percolating Superconductor

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The upper critical field H_{c2} of the random percolating superconductor InGe has been measured as a function of the metal volume fraction x. Near the percolation threshold x_c, H_{c2} diverges with a critical exponent which is significantly smaller than that of the normal-state resistivity. An interpretation of this behavior is proposed in terms of the properties of the infinite cluster.

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It has long been recognized that the high upper critical field H_{c2} of dirty superconducting alloys is due to the existence of a short impurity-limited mean free path[1] rather than to macroscopic inhomogeneities.[2] Early work on solid-solution alloys[3] demonstrated that, in agreement with theoretical predictions, H_{c2} increases linearly with the normal-state resistivity ρ_n of the alloy (itself proportional to the impurity concentration). In this Letter, we wish to report on the critical behavior of a different class of superconducting alloys, consisting of unmiscible metal and insulator distributed at random.[4] In contrast with the case of solid solutions, we find that the inhomogeneity of these alloys has a determining influence on their upper critical field.

We find that near the percolation threshold[5] where ρ_n becomes much larger than the values typical of solid solutions (i.e., $\rho_n \gtrsim 50\ \mu\Omega$ cm), $H_{c2} \propto \rho_n{}^{\omega}$ with $\omega = 0.5 \pm 0.05$, in contrast with the behavior of solid solutions. We interpret this result as due to the diffusion process on a percolating network, for the case where the percolation correlation length ξ_p is of the order of or larger than the effective superconducting coherence length $\bar{\xi}_s$. We propose that the value of $\omega < 1$ results from the fact that in this limit the dead ends of the infinite cluster contribute very little to its superconducting properties. The experimental data suggest that the effective superconducting density of the infinite cluster is close to that of its backbone.

Samples were prepared by coevaporation of indium and germanium from two distinct electron beam guns, spaced apart, onto a room-temperature glass substrate. Nine samples, about 2000 Å in thickness, were simultaneously evaporated onto one glass substrate, their metal concentrations varying by about 2% between neighboring samples.[5] The pressure during the evaporation was held at approximately 1×10^{-6} Torr and never exceeded 5×10^{-6} Torr. In-Ge films pre-

