Vogel-Fulcher Scaling of the Susceptibility in a Mixed-Crystal Proton Glass

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Low-temperature dispersion of the electric susceptibilities in a mixed crystal of $Rb_{1-x}(NH_4)_xH_2PO_4$ ($x=0.35$) is reported. The frustrated proton ordering of this system relates it to spin-glasses. The measurements reveal a broad distribution of relaxation times. The data scale using a temperature-independent distribution of activation energies linked to the relaxation times by a Vogel-Fulcher law with a freezing temperature of 10 K.

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It becomes increasingly apparent that a better grasp of the peculiar dynamics of spin-glasses will be essential to their understanding.[1] Broad distributions of relaxation times are experimentally observed,[2] and near or below the glass transition magnetic viscosity produces long-time tails.[3] Theoretically, the most recent approach[4] relates to a hierarchy of characteristic times, each of them tending to infinity.[5] The imaginary part of the susceptibility, a quantity resulting from response-time delays, is hard to obtain in conducting glasses,[6] and few measurements exist for insulating magnets as well.[7] On the other hand, $\epsilon''(\omega, T)$, the frequency- and temperature-dependent imaginary part of the complex dielectric constant, is a readily measurable quantity for dielectric analogs to spin-glasses, making their study potentially rewarding.[8] Recent dielectric results on reorientational glasses suggested an Arrhenius relaxational behavior.[9] The apparent absence of freezing in that case might however be due to the lack of linear coupling between the electric field and the frustrated ordering parameter in KBr-KCN.

The present Letter reports the dielectric-constant dispersion obtained on mixed crystals of the KH_2PO_4 (KDP) family. These polar materials are characterized by a high-T disordered network of O-H--O bonds. At low T, the ordering of these H bonds corresponds with the onset of a ferroelectric polarization parallel to the tetragonal c axis in KDP or RDP (RbH_2PO_4), while antiferroelectric moments parallel to the a-a planes develop in ADP ($NH_4H_2PO_4$).[10] In the present system, crystals of $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP), those transitions are suppressed by random NH_4 substitution. The NH_4^+ ions form themselves H bonds with nearby PO_4 tetrahedra, occupying O sites and frustrating the low-T acid-proton ordering. A glass at the level of the acid-proton sublattice results,[11] and this for a broad range of concentrations x.[8] The present data, obtained with $x=0.35$, reveal below ~30 K an extremely wide distribution of relaxation times. The *entire* ϵ'' data (and not only the peak positions) can be scaled onto a single curve with the assumption that the relaxation times are related to a distribution of activation energies by a Vogel-Fulcher (VF) law[12] of finite freezing temperature T_0. The parameters characterizing the relaxation-time distribution agree remarkably with other knowledge that we have on this system. This establishes irrefutably for the first time that a freezing temperature $T_0 \neq 0$ can exist in dielectric analogs to spin-glasses.

Small RADP platelets of approximate size $3\times9\times0.8$ mm^3 were cut from a large homogeneous single crystal. They were oriented with a major axis perpendicular to the main faces and electroded with gold after a chromium flash. The longitudinal (ϵ_c) and transverse (ϵ_a) complex dielectric constants were obtained with a GR1621 bridge.[13] Care was taken to select frequencies sufficiently distant from disturbing piezoelectric resonances. Results extrapolating the data of Fig. 1 were observed both at higher (~100 kHz) and lower (down to 10 Hz) frequencies, although with reduced accuracy. At high frequency the increased relative density of resonances is perturbing. At low frequency, the combined effects of reduced bridge sensitivity and smaller equivalent sample conductance $G\propto\omega\epsilon''$ adversely affect the ϵ'' measurements.

The real part of the dielectric constant, Fig. 1(a), decreases below ~30 K, and peaks in the loss appear [Figs. 1(b) and 1(c)] which vary slowly in $\ln\omega$. This indicates, like in spin-glasses, a distribution $g(\tau, T)$ of relaxation times broad in $\ln\tau$.[6] Representing phenomenologically the dielectric response by a sum of Debye relaxators, one writes

$$\epsilon(\omega, T)=\int_{\tau_0}^{\infty} g(\tau, T)\,\frac{\epsilon_0(T)}{1-i\omega\tau}\,d\ln\tau, \qquad (1)$$

where $\epsilon_0(T)$ is the very-low-frequency limit of ϵ,

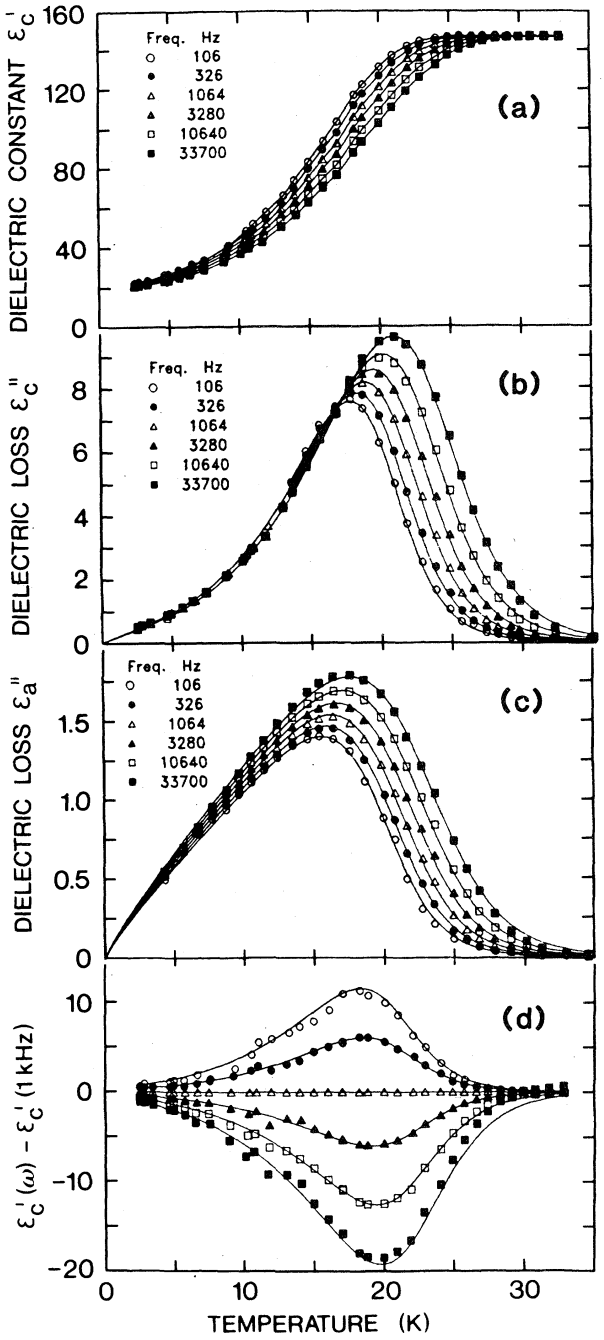

FIG. 1. (a) The real part of the dielectric constant ϵ_c'. The lines are guides to the eye. (b), (c) The imaginary part of the dielectric constants ϵ_c'' and ϵ_a'', respectively, fitted with Eq. (5). (d) The differences $\epsilon_c'(\omega) - \epsilon_c'(1\text{ kHz})$, where the lines are calculated from Eq. (6) without any adjustable parameter.

and $\tau_0 = \omega_0^{-1}$ is the inverse of the attempt frequency ω_0. If $g(\tau)$ is much broader in $\ln\tau$ than $\omega\tau/(1+\omega^2\tau^2)$, one can approximately integrate (1)

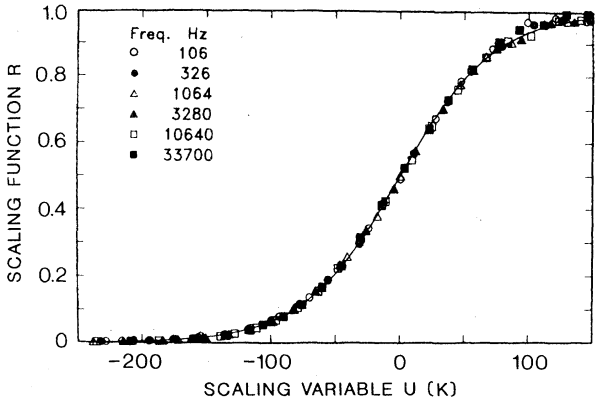

FIG. 2. The scaling of the entire ϵ_c'' data where the solid line is a fit by a hyperbolic tangent function.

for ϵ'', which for $\omega\tau_0 \ll 1$ gives[6]

$$\epsilon''(\omega, T) \simeq (\pi/2)\epsilon_0(T)g(1/\omega, T). \quad (2)$$

The dielectric loss is thus an important quantity as it relates directly to g in this model.

The above considerations, and a close inspection of Fig. 1(b), suggest scaling the data with $\epsilon'' = h(T)R(u)$, where $u(\omega, T)$ is a scaling variable. At low temperatures, $R(u) \simeq 1$ and ϵ'' simply equals $h(T)$ which is well approximated by a power law. In the relaxation region ($15 \lesssim T \lesssim 35$ K), this power law is relaxed by $R(u)$ which tends progressively to zero. One finds that the entire data scale (Fig. 2) with

$$u = E_c - E, \quad (3)$$

where E_c is a constant cutoff energy (in units of T) and E is a variable related to $\tau = 1/\omega$ [Eq. (2)] by the VF law

$$\tau = \tau_0 \exp[E/(T - T_0)]. \quad (4)$$

In the range of the measurements, the scaling function is well represented by $R(u) = 0.5(1 + \tanh du)$, where d is constant.

To optimize all parameters, ϵ_c'' and ϵ_a'' [Figs. 1(b) and 1(c)] were fitted. At low temperatures, a weak $\ln\omega$ dependence is evident in ϵ_a'' and was also found in ϵ_c''. Hence, the function

$$\epsilon_i'' = h_i(T)R_i(u)(1 - x_i \ln\omega\tau_0) \quad (5)$$

($i = a, c$) was used. The details on $h_i(T)$ and the resulting fit parameters are explained in Ref. 14. The solid curves in Figs. 1(b) and 1(c) and in Fig. 2 illustrate the quality of the fits. From ϵ_c'' the freezing temperature $T_0 = 10$ K is obtained, and this value also agrees with the ϵ_a'' data. As the parametrization was empirical, its physical sig-

nificance must be checked carefully. To assess the reliability of the freezing temperature, fits to the ϵ_c'' data were repeated with forced T_0 values and all other parameters varying. Results are shown in Fig. 3. The cutoff energy E_c [Fig. 3(a)] and the attempt frequency ω_0 [Fig. 3(b)] are strongly correlated with T_0. At the variance minimum ($T_0 = 10$ K), they take the values 228 K and 40 cm^{-1}, respectively, in remarkable agreement with NMR and Raman data as will be discussed presently.

The NMR spin-lattice relaxation time T_1 of ^{87}Rb was recently measured at $\omega_L \sim 2\pi \times 30$ MHz.[15] The region from 100 K to ~40 K is governed by polarization relaxation in the fast-motion regime. The relaxation rate agrees perfectly with a BPP expression[16] adapted to the present distribution, $T_1^{-1} \propto (T - T_0)\arctan 2\omega_L \tau_c$, where τ_c corresponds to E_c in (4), and with use of the above values for E_c, ω_0, and T_0.[15] This is a sensitive test of E_c giving much confidence in the significance of the scaling. Furthermore, the attempt frequency of 40 cm^{-1} should correspond to the width of the overdamped ferroelectric B_2 mode, which is the frequency at which polarization reversals are attempted. Raman measurements on RADP have not yet been performed, but our own Brillouin results on the xy-shear mode already indicate that the Raman B_2 mode does not soften much. Hence, the mode width can be estimated from the room-temperature value for RDP (58 cm^{-1}),[17] or from ADP close to its antiferroelectric transition (~70 cm^{-1}),[18] giving a remarkable agreement with ω_0 since the ordinate in Fig. 3(b) is logarithmic. In comparison, the values $E = 600$ K and $\omega_0 > 10^4$ cm^{-1} which are found with $T_0 = 0$ (Fig. 3) are totally unrealistic. A statistical significance test on the fits gives $T_0 = 10 \pm 0.35$ K, and the above considerations confirm that the actual freezing temperature has been determined to better than ± 2 K.

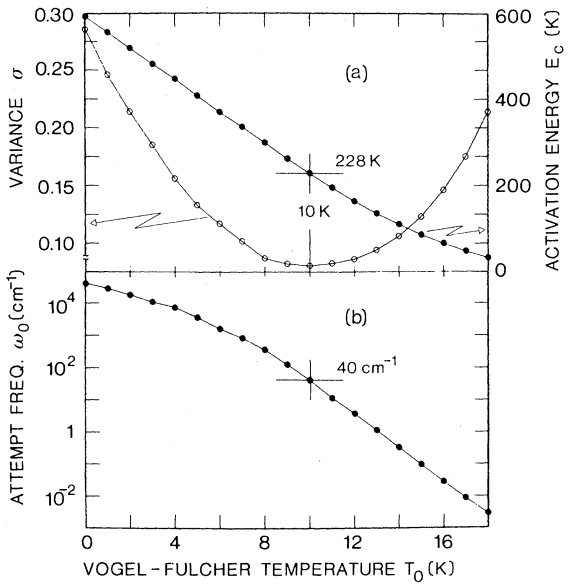

FIG. 3. Results of fits with fixed T: (a) the variance (left scale) and the corresponding cutoff energy E_c (right scale); (b) the associated attempt frequency.

Having achieved a good parametrization of the dielectric loss, it is meaningful to return to the real part ϵ_c'. With a broad distribution of relaxations, causality leads to[6]

$$\epsilon'' = -(\pi/2)\partial\epsilon'/\partial \ln\omega. \quad (6)$$

Integrating (5) to obtain $\epsilon_c'(\omega) - \epsilon_c'(1\text{ kHz})$ without any adjustable parameter, the gratifying agreement of Fig. 1(d) results. Although this is mainly a consequency of causality, it confirms that the initial assumption of a broad relaxation-time distribution is fully consistent with our data.

The scaling variable u implies that $g(\tau, T)$ derives from a *temperature-independent* energy distribution $f(E)$ related to $R(u)$ by normalization. From $f(E)dE = g(\tau, T)d\ln\tau$ one finds $g(\tau, T) = (T - T_0)f(E)$. This result seems irreconcilable with smoothly *growing* glass clusters which should have a strongly T-dependent activation energy.[19] A progressive freeze-out of *localized normal modes*[20] is more likely. Those modes could be rearrangements along correlated strings of mostly ice-rule acid-proton configurations H_2PO_4.[21] The number of possible configurations is restricted randomly by NH_4 condensation at higher T, the NH_4 protons binding to PO_4 groups,[22] excluding acid protons from the corresponding O sites. There are good indications that below ~100 K, NH_4 groups start to condense.[11,15]

Another interesting implication of these results is that $\epsilon_0(T) \simeq h(T)/(T - T_0)$. The divergence at T_0 is unobservable as it relates to an infinite spread of relaxation frequencies requiring an infinite observation time. For long-time measurements, the effective dielectric constant upon application of a voltage step at time $t = 0$ is

$$\epsilon_{\text{eff}}(t) = \int_{\tau_0}^{\infty} \epsilon_0(T)(1 - e^{-t/\tau})g(\tau)d\ln\tau. \quad (7)$$

This gives $\epsilon_{\text{eff}}(t) \cong \ln t$ up to $\ln t \simeq E_c/(T - T_0)$. For $T - T_0 = 1$ K, the limit is ~10^{91} yr, beyond the age of the universe. In practice we were able to observe logarithmic long-time tails up to ~10^4 sec, the limit being set by the input current of the electrometer. This confirmed qualitatively the be-

havior (7) and the resemblance with spin-glasses.[3] For $T < T_0$, the VF law loses its meaning but the fits to (5) remain applicable since $R(u) \simeq 1$.

In conclusion, convincing evidence for a finite freezing temperature in RADP has been obtained, and the distribution of relaxation times derives from a remarkably simple distribution of Vogel-Fulcher activation energies. It is hoped that the present work will stimulate further theoretical investigations of glass dynamics, in particular for these interesting proton glasses.

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[14]Fits to ϵ_a'' were performed with $h_a(T) = c_1 T^{c_2}$ and with $T_0 = 10$ K. They gave $c_1 = 0.227$, $c_2 = 0.892$, $d = 0.0106$, $E_c = 240$ K, $x_a = -0.016$, and $\ln\nu_0 = 29.6$, where $\nu_0 \equiv \omega_0/2\pi$ in hertz. For ϵ_c'', $h_c = c_1 T^{0.89} + c_2 T^{c_3}$ was used. The c_1 term with the exponent of h_a helps in fitting the very-low-temperature behavior. However, forcing $c_1 = 0$ does not dramatically affect the final value of T_0. One finds $c_1 = 0.1217$, $c_2 = 6.31 \times 10^{-4}$, $c_3 = 3.054$, $d = 0.0134$, $E_c = 228$ K, $x_c = 0.0296$, and $\ln\nu_0 = 27.83$.

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