

Critical behavior of long-term dielectric relaxation in a new class of proton glasses

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Transitions to a proton-glass phase have been observed in $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot \text{H}_2\text{O}$ crystals and also in previously annealed $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot \text{H}_2\text{O}$ crystals. The transitions result from a “freezing” of a dynamically disordered network of hydrogen bonds. The anomalous behavior observed for the long-term dielectric relaxation, which reflects a change in the proton dynamics near the glass transition point, can be described by the dynamic theory of Ising spin glasses.

Disordered systems in which a frustration of the interaction suppresses phase transitions to an ordered state, giving rise to a glassy state—a spin glass, an orientation glass, or a dipole glass—have recently attracted much interest.^{1–4}

In this letter we report a study of dielectric relaxation in $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot \text{H}_2\text{O}$ (CTSM) crystals and in previously annealed $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot \text{H}_2\text{O}$ (CTSeM) crystals. The results indicate a “freezing” of the orientational and positional disorder of a network of hydrogen bonds. It was shown in Refs. 5–7 that a state with disordered network of H bonds results from a specific proton disorder which can arise in crystals with hydrogen bonds if their symmetry group includes threefold, fourfold, and sixfold rotation axes. A dynamic disordering of a network of hydrogen bonds implies their delocalization and correspondingly leads to a high proton conductivity (up to 10^{-1} S/cm) in the crystalline state.^{5–7} The “freezing” of this proton disorder should thus also be manifested in the diffusion of protons.

The CTSM crystal at $T < 413$ K is in a hexagonal phase⁷ (space group $P6_3/mmc$). The acid protons are disordered in the (001) plane, forming 2D networks of orientationally and positionally disordered hydrogen bonds. This circumstance is seen, in particular, in the quasi-2D nature of the proton conductivity ($10 < \sigma_a/\sigma_c < 10^3$). It was shown in Ref. 7 that in CTSM, in contrast with other crystals with this type of proton disorder, a transition to an ordered phase does not occur. Near $T_g = 240$ K, however, this crystal exhibits dielectric anomalies which are characteristic of transitions to a state of a structural glass.^{3,4}

The CTSeM crystals grown at room temperature differ from the CTSM crystals in that they are in the orthorhombic phase (space group $Pbcn$). This phase is characterized by an ordered network of hydrogen bonds and thus a low proton conductivity⁶ ($< 10^{-8}$ S/cm). During a first cycle of heating of CTSeM at $T_{si} = 346$ K the crystal undergoes a transition to a superprotonic phase which is isostructural with the hexagonal phase of CTSM. However, the results of the present study show that after prolonged annealing the inverse transition to the ordered state is

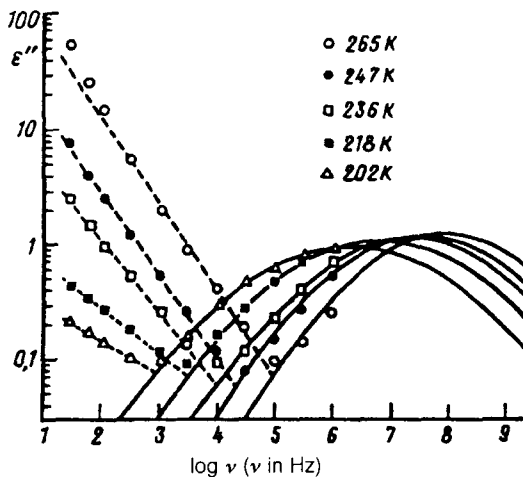


FIG. 1. Dielectric spectra of CTSM at various temperatures. Points—Experimental; solid and dashed lines—calculated from Eqs. (2), (3), and (5), respectively.

suppressed in this phase, and during cooling some anomalies are observed in the dielectric spectrum near $T_g = 273$ K. These anomalies are similar to those observed in CTSM.

The complex dielectric constant $\epsilon^* = \epsilon' + i\epsilon''$ was measured over the frequency range $10\text{--}10^6$ Hz by a bridge method. At lower frequencies, $10^{-3}\text{--}1$ Hz, the dielectric relaxation was studied on the basis of the time dependence of the discharge current. Figure 1 shows some typical curves of $\epsilon''(\nu)$ for a CTSM crystal near T_g , measured in the plane of disordering of the H bonds, i.e., the (001) plane. These curves are determined by the sum of three components:

$$\epsilon''(\nu) = 2\pi\sigma_0/\nu + \epsilon''_\alpha(\nu) + \epsilon''_\beta(\nu), \quad (1)$$

where σ_0 is the static proton conductivity, and $\epsilon''_\alpha(\nu)$ and $\epsilon''_\beta(\nu)$ are the contributions from two well-distinguished relaxation mechanisms.

It was shown in Ref. 7 that the dielectric dispersion in CTSM is determined by a high-frequency β -relaxation which can be described quite accurately by

$$\epsilon^*_\beta(\nu, T) = \epsilon'_\beta(\nu, T) + i\epsilon''_\beta(\nu, T) = \epsilon_{\infty\beta} + [\epsilon_0(T)_\beta - \epsilon_{\infty\beta}] \frac{g_\beta(\tau, T)}{1 + i2\pi\nu\tau} d\ln(\tau) \quad (2)$$

with a Gaussian distribution of relaxation times,

$$g_\beta(\tau, T) = \frac{kT}{\sqrt{2\pi\sigma}} \exp\left[-\frac{(kT)^2}{2\sigma^2} \left[\ln\frac{\tau}{\tau_m}\right]^2\right]. \quad (3)$$

Here σ and τ_m are the half-width of the distribution and the most probable relaxation time, respectively. Over the temperature range studied, τ_m increases exponentially with decreasing temperature:

$$\tau_m = \tau_0 \exp(-H/kT), \quad (4)$$

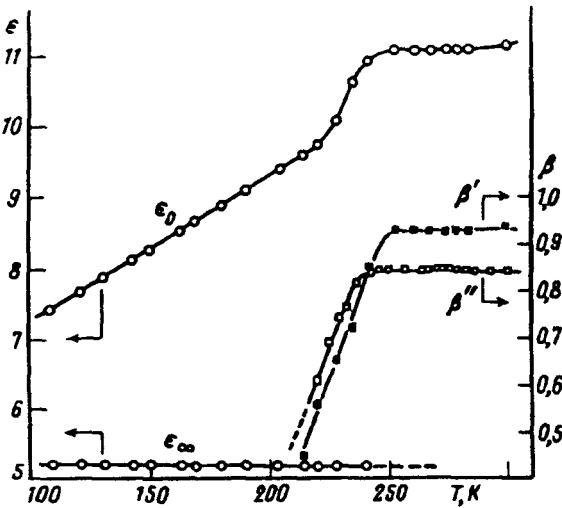


FIG. 2. Temperature dependence of the parameters $\epsilon_{0\beta}$ and $\epsilon_{\infty\beta}$ in Eq. (2) and of the parameters β' and β'' in CTSM.

where $\tau_0 = 0.8 \times 10^{-14}$ s and $H = 0.27$ eV. Note that the dielectric frequency dispersion governed by the β -relaxation is essentially isotropic, in contrast with the static conductivity σ_0 . As can be seen from Fig. 1, the curves of $\epsilon_{\beta''}(\nu)$ calculated from Eqs. (2)–(4) agree quite well with the experimental results. Figure 2 shows corresponding curves of the adjustable parameters ϵ_0 and ϵ_{∞} versus the temperature for the direction perpendicular to the c axis.

The low-frequency α -relaxation differs from the β -relaxation in that it is characterized by an asymmetric distribution of relaxation times, $g_{\alpha}(\tau, T)$, and by a strong anisotropy of the relaxation force, which is similar to the anisotropy of static proton conductivity.⁷ The latter circumstance means that α -relaxation can be interpreted as a frequency-dependent conductivity. This conductivity reflects the diffusion dynamics of the acid protons which are disordered in the hexagonal plane.

In the frequency range corresponding to the high-frequency tail, the curve of $\epsilon''_{\alpha}(\nu)$ can be approximated by a power law

$$\epsilon''_{\alpha}(\nu, T) \sim \nu^{\beta'(T)} \quad (5)$$

(see the dashed line in Fig. 1). It is important to note that the exponent β' is temperature-dependent near T_g , falling off from ~ 0.93 at $T > 290$ K to zero at $T \sim 200$ K (Fig. 2). For times in the vicinity of the α -relaxation times, a more accurate and more informative method is to measure the discharge current $I(t) = -dP(t)/dt$. This method can be used to study the behavior of the polarization $P(t)$ (the decay function) after the application of a polarizing pulse in real time. This method is more sensitive. Figure 3 shows some typical curves of $I(t)$ for a CTSM crystal measured after the application to the sample of a polarizing electric-field pulse with the optimum height of 1 V and the optimum length of 50 s. Analysis of these results shows that at $T > T_g$ the best approximation of the experimental $I(t)$ dependence is given by the derivative of the Kohlrausch decay function:^{4,8}

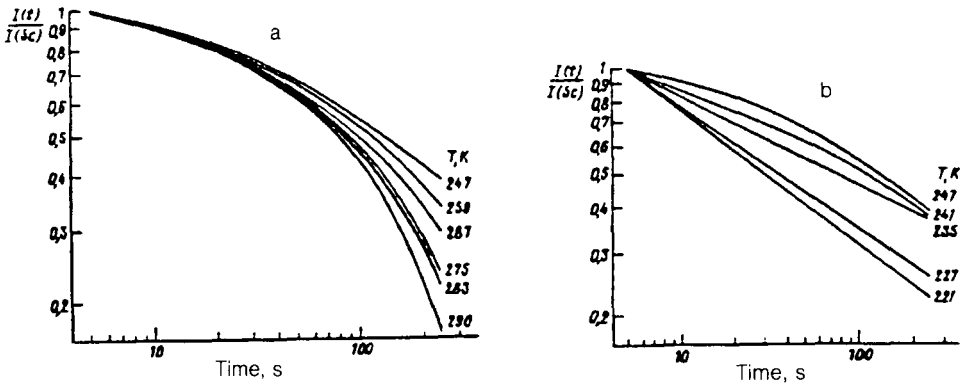


FIG. 3. Time evolution of the discharge currents in CTSM at various temperatures, normalized to their values at $t=5$ s. a) $T > T_g$; b) $T < T_g$.

$$I(t) = \frac{dP(t)}{dt} = \frac{d}{dt} \left[P_0 \exp \left(-\frac{t}{\tau} \right)^{\beta''} \right], \quad (6)$$

where P_0 is the value of the polarization at $t=0$, β'' is a temperature-dependent parameter, and τ is a characteristic relaxation time.

At $T = T_g$ the shape of the $I(t)$ curves changes; these curves become power laws below T_g (Fig. 3b). This change is reflected in an anomalous behavior of the parameters β'' and τ near T_g . As can be seen from Fig. 2, the plot of $\beta''(T)$ is similar to that of $\beta'(T)$. The relaxation time τ increases sharply below T_g and reaches values $\sim 10^5$ s at $T = T_g - 20$ K. The time interval studied is thus much shorter than τ , and the $I(t)$ curve can be described exclusively by the first term of a series expansion of function (6):

$$I(t) \sim t^{-(\beta-1)}. \quad (7)$$

This expression corresponds to the power law observed experimentally.

From the anomalous behavior of the parameters β' , β'' , and τ we can draw the unambiguous conclusion that there is a pronounced slowing of the α relaxation below T_g , as is characteristic of a transition to a glass state.^{1,2,9,10} In addition, the tendency of β' and β'' toward zero at $T \approx 220$ K (Fig. 2) indicates a logarithmic decay function $P(t)$ below this temperature:

$$P(t) = P_0 - \ln(t). \quad (8)$$

This behavior is an important indication that the system is not ergodic.^{2-4,9}

In annealed CTSeM, the critical behavior of the α -relaxation near $T_g = 273$ K is similar to that described above for CTSM.

Generalizing these results, we can draw the following conclusions. The essentially isotropic high-frequency β -relaxation, which is characterized by a symmetric distri-

bution of relaxation times, (3), and thus by a temperature-independent Gaussian distribution of activation barriers, is associated with a continuous freezing of noninteracting constant dipoles (probably dipoles with the structure of water). On the other hand, the long-term α -relaxation, which reflects the diffusion dynamics of the acid protons, can also be described by Eq. (2), with the axisymmetric distribution of relaxation times $g_\alpha(\tau, T)$ characteristic of a glassy state.^{4,8} The anomalies in the temperature dependence of the parameters describing the change in the spectrum of α -relaxation indicate that the freezing of the disordered network of acid hydrogen bonds is of a cooperative nature. This conclusion supports theoretical results regarding a change in the dynamics of correlation functions near the glass transition temperature.^{1-4,9,10} In addition, the experimental curves of $I(t)$ (Fig. 3) and also $\beta'(T)$ and $\beta''(T)$ (Fig. 2) are in fairly good quantitative agreement with theoretical curves of the corresponding parameters found by Monte Carlo calculations for 3D Ising spin glasses in Ref. 10.

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