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DIELECTRIC RELAXATION MECHANISM FOR PROTON GLASS

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Abstract Dielectric relaxation of proton glasses is controlled by O-H...O proton intrabond hopping responsible for ''Takagi'' HPO_4 and H_3PO_4 intrinsic defect diffusion. The diffusion path has a one-dimensional fractal topology. The defects diffuse in a potential which also has a fractal nature, giving a barrier height distribution leading to a wide spread in dielectric relaxation times at low temperature. Expressions for dielectric relaxation and ac susceptibility are derived, and their fit to experimental results is briefly discussed.

The proton glass[1] $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP) is a mixed crystal of RbH_2PO_4 (RDP) and $NH_4H_2PO_4$ (ADP). Its constituents, RDP and ADP, have the same tetragonal paraelectric (PE) phase structure. They undergo ferroelectric (FE) and antiferroelectric (AFE) order-disorder transitions at 146 and 148 K respectively which order the ''acid'' O-H...O protons differently. The mixed crystal RADP has no transitions for $0.22<x<0.74$, but proton glass (PG) behavior exhibiting a wide spread in dielectric and nuclear magnetic resonance (NMR) relaxation times sets in near 75 K.

The dielectric behavior is described accurately by a phenomenological model[1] with 7 adjustable parameters based on the Vogel-Fulcher law. Presented here is a microscopic model which explains some features of the dielectric relaxation.

This model has no adjustable parameters. It is based on three short-range interactions. The first is the Slater interaction which gives the nonpolar H_2PO_4 groups found in the AFE phase of ADP an energy ε_0 higher than the polar groups constituting the FE phase of RDP. It is assumed[2] that ε_0/k retains for all x the value 74.5 K reported[3] for pure RDP. The second (cross-cation) interaction ε_a links two acid protons via an NH_4^+ (but not Rb^+) cation.[2] Its definition in Ref. 2 is correct, but its strength is $\varepsilon_a=\varepsilon_0$ and not $\varepsilon_a=2\varepsilon_a$ as stated in Refs. 2 and 4. The third interaction is ε_1, half the creation energy for a Takagi HPO_4-H_3PO_4 defect pair.[4] Its value for all x is assumed to be $\varepsilon_1/k=647$ K as reported[3] for pure RDP. All these proton-proton interactions can be represented by pseudospin interactions.[4]

To summarize a review[4] of effects of these interactions, the Slater interaction ε_0 alone gives the FE transition in RDP but cannot explain dynamic behavior. Adding the cross-cation ε_a interaction predicts[2] static behavior of RADP including the x-T phase diagram if ε_0 is kept independent of x and ε_a is proportional to x in that mean-field model. Explanation of dynamic behavior requires consideration also of Takagi pairs and their creation energy $2\varepsilon_1$ in Monte Carlo simulations [5,6] and dielectric and NMR relaxation studies.[7,8]

The chart below outlines the steps in the model calculation.

$$\begin{tikzcd}
& \tau_0 \arrow[dr] & & & \\
& & R(t) \arrow[dr] & & \\
\varepsilon_d \arrow[r] & U(r) \arrow[ur] \arrow[dr] & & P(t) \arrow[r] & (\varepsilon',\varepsilon'') \\
& & (R_0, n) \arrow[ur] & & \\
& (D,\varepsilon_1) \arrow[ur] & & &
\end{tikzcd}$$

Following the flow chart from left to right, ε_d is the *rms defect diffusion energy* per diffusion step. Its mean square value is given by

$$\varepsilon_d2=\langle\ \varepsilon^2\ \rangle=2x\varepsilon_a2+2f_g(1-f_g)\varepsilon_02. \tag{1}$$

Here $x=0.35$ is the ammonium fraction in crystals used by Courtens *et al*. in dielectric[1] and Brillouin scattering[9] studies whose results are compared with predictions of this model. The factor $f_g=0.77291$ is the limiting fraction[2] of zero-energy Slater groups in the PG regime. In pure ADP a proton transfer has probability 1/2 each of changing U by $\pm2\varepsilon_a$ and of leaving U unchanged, giving the first term in Eq. (1). The second term assumes that the probability of creating or annihilating a Slater group of energy 0 or ε_0 is proportional to the respective fractions f_g and $1-f_g$ of those groups already present. Because $\varepsilon_a=\varepsilon_0=74.5$ K in our model as discussed above, we obtain the value $\varepsilon_d=76.4$ K.

The ε distribution leading to Eq. (1) is discrete but nearly equivalent to the normalized gaussian form

$$w(\varepsilon)=(2\pi)^{-1/2}\varepsilon_d^{-1}\exp[-(\varepsilon-\varepsilon_b)^2/2\varepsilon_d^2]. \tag{2}$$

The bias energy ε_b in thermal equilibrium must be such that defect diffusion on the average does not change the internal energy U.

The distribution $W(\varepsilon)$ of internal energy change ε per step along defect diffusion paths actually taken is found by assuming

$$W(\varepsilon)=w(\varepsilon)\exp(-\varepsilon/kT). \tag{3}$$

The assumption that U is unbiased along paths actually taken then determines the value of ε_b and gives $W(\varepsilon)$ the form

$$W(\varepsilon)=(2\pi)^{-1/2}\varepsilon_d^{-1}\exp(-\varepsilon^2/2\varepsilon_d^2)\ \text{if}\ \varepsilon_b=\varepsilon_d^2/kT. \tag{4}$$

If motion of other Takagi defects is neglected, we can equate U to an *internal energy potential* U(r) of a defect r steps along its diffusion path away from its original site. Although U(r) defined in this way is single-valued, U for a given defect at a given site can be multivalued because the change in U in going to a new site depends on the path. The 2-d analog of this potential is a depression with caves in the surrounding slopes, so that though an outward path (A in Fig. 1) chosen randomly using w(ε) is uphill, a typical actual outward path (B in Fig. 1) using W(ε) is level on the average.

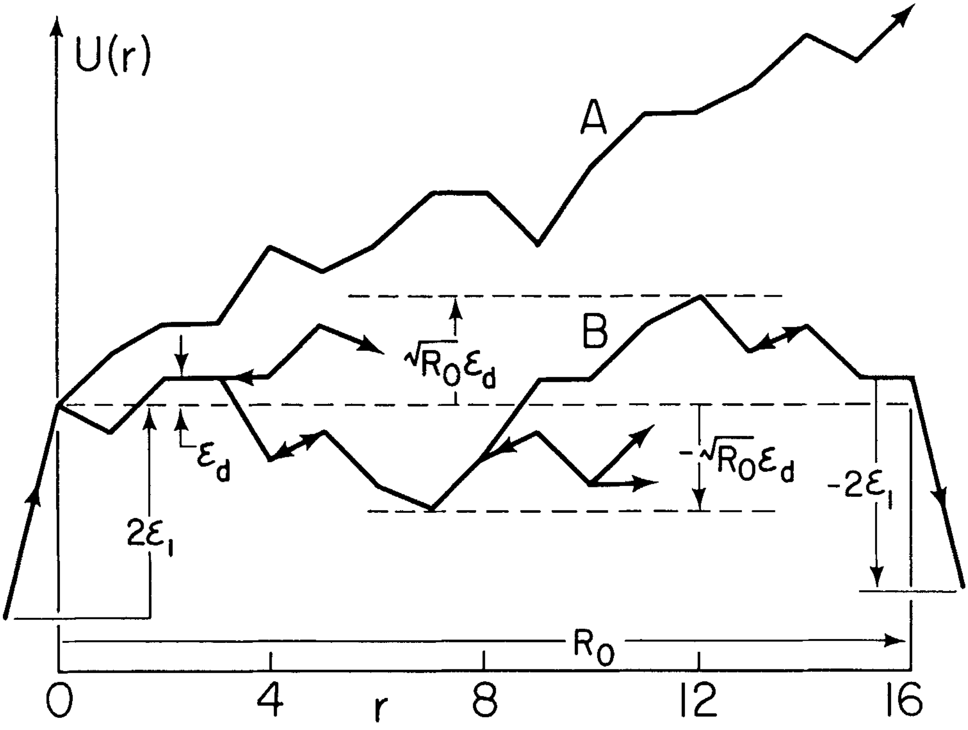

FIGURE 1 Typical Takagi defect diffusion path showing creation, diffusion and annihilation and illustrating parameters discussed in text.

The diffusion paths available to a defect locally have the topology of a double-branching Cayley tree (Bethe lattice) because a defect can move to two new positions or return to its former site. We made a Monte Carlo study of diffusion on such a Cayley tree for a number of paths of maximum length $r=13$ steps from the origin. These simulations indicate that the number N_s of new sites visited obeys the fractal relation $N_s=r^D$, with *Hausdorff dimensionality*[10] $D=1.15\pm0.05$. A value 1 for D would correspond to one-dimensional (1-d) diffusion with no side trips.

A defect can take a branch path as shown in Fig. 1, but retracing the path cancels the polarization changes made while taking that branch. Accordingly the net path causing polarization change is at any instant strictly 1-d. Because $U(r)$ along such 1-d paths obeys the unbiased ε distribution of Eq. (4), $U(r)$ is a fractal potential of a type considered by Dotsenko.[11]

The defect diffusion rate depends on the Boltzmann factors found from $U(r)$ for the defect's three possible new sites, and on the *attempt time* τ_0. Brillouin scattering studies by Courtens *et al.*[9] fix τ_0 at 5×10^{-14} s.

Because defect diffusion has the net effect for purposes of dielectric relaxation of reversing the dipoles along a 1-d path, we define a *diffusion path length* $R(t)$ of number of steps taken in time interval t. The maximum barrier encountered in R steps, a parameter important for dielectric relaxation, is about $\varepsilon_d R^{1/2}$ as shown in Fig. 1 for the $W(\varepsilon)$ distribution of Eq. (4).

These barriers are negligible at high temperature, so the defect jump time is simply τ_0 and it requires a time near $\tau_0 R^2$ to diffuse R steps, thus giving the usual diffusion relation. But in the PG regime the largest barrier dominates the diffusion time, so the factor R^2 should be omitted, giving diffusion time $t(R)$ and diffusion rate $R(t)$ shown below:

$$t(R)=\tau_0\exp(\varepsilon_d R^{1/2}/kT),\quad R(t)=\langle R^2\rangle^{1/2}=[(kT/\varepsilon_d)\ln(t/\tau_0)]^2. \qquad (5)$$

These equations are strictly valid only for 1-d systems,[11] but apply here because the defect diffusion path is almost 1-d so that the maximum barrier is unlikely to be in a branch path.

The *fractional Takagi defect density* n is found from the Boltzmann factor for such groups, using the fact that $n<<1$:

$$n=\exp[-(\varepsilon_1-R_0^{1/2}\varepsilon_d)/kT], \qquad (6)$$

For the *Takagi defect creation energy* ε_1 we choose 647 K as discussed above. The average *defect annihilation path length* R_0 shown in Fig. 1 is the path length in number of steps from creation to annihilation with a new partner. This path length determines the size of the mean trapping energy $-R_0^{1/2}\varepsilon_d$ also shown in Fig. 1, by the same argument used above to find the maximum barrier height $+R^{1/2}\varepsilon_d$.

The second relation needed to solve for R_0 and n comes from the above relation between N_s and r. We set $r=R_0$ and find N_s by noting that the defect has probability near n of annihilating with a new partner at each new site visited, so on the average it will visit $N_s=n^{-1}$ sites, giving the relation

$$n^{-1}=R_0^D. \qquad (7)$$

Both n and R_0 are found from Eqs. (6) and (7), and n is

$$n=\{[\varepsilon_1+kT\ln(n)]/\varepsilon_d\}^{-2D}. \qquad (8)$$

The *polarization relaxation* P(t) following step removal at t=0 of a small dc electric field is found by integrating the fractional polarization change dP/P which equals ndR(dt) if the defect wanders randomly, as at high temperature. Here dR(dt) is the mean number of dipoles reversed by a defect during time dt.

Near the FE transition temperature T_c for Rb-rich crystals the defect path is nonrandom and because RDP-type crystals generally exhibit mean-field behavior, the relaxation is expected[12] to show Curie-Weiss behavior:

$$dP/P=-[(T-T_c)/T]n\,dR. \qquad (9)$$

Such slowing down of polarization decay near T_c was seen in Monte Carlo simulations on the Rb-rich side of the phase diagram.[6]

For mixed crystals in the PG concentration range, T_c can be approximated by 0. Integration of Eq. (9) then yields $\ln(P)+\mathrm{const}=-nR$. Substitution of $R(t)$ from Eq. (5) and taking the exponent provides the following expression for polarization decay from an initial value P_i:

$$P/P_i=\exp\{-n[(kT/\varepsilon_d)\ln(1+t/\tau_0)]^2\}. \qquad (10)$$

This decay has $\ln^2(t)$ in the exponent. A form with arbitrary power of $\ln(t)$ was derived by Dotsenko,[11] and by Palmer *et al*. using two models employing hierarchically constrained dynamics[13] and relaxation of isolated clusters of unfrustrated spins.[14]

The ac response is found from Eq. (10) by integrating the responses at time t to an ac electric field of angular frequency ω made up of differential steps beginning at times $t'<t$. The *complex dielectric susceptibility* $\varepsilon=\varepsilon'-j\varepsilon''$ found in this way is

$$\varepsilon=\varepsilon_\infty+(\varepsilon_{dc}-\varepsilon_\infty)\{1-\int_0^\infty (\sin u+j\cos u)\exp[-a^2\ln^2(1+u/f)]du\}, \qquad (11)$$

where $u=\omega(t-t')$, $a=kTn^{1/2}/\varepsilon_d$, $f=\omega\tau_0$, and ε_{dc} and ε_∞ are the ε' values at temperatures just above and below the dispersion region.

We compared predictions of this model with audio frequency dielectric results[1] and with the relaxation time range found[9] by a Brillouin scattering study at GHz frequencies. We used $\tau_0=5\times10^{-14}$ s, D=1.15, $\varepsilon_d/k=76.4$ K and $\varepsilon_1=647$ K as discussed above. The fit was qualitatively correct, but was improved considerably by reducing the latter two parameters to 50 K and 400 K respectively. A graphical comparison has been submitted for publication elsewhere. The overall fit is quite satisfying, because only two of the four model parameters had to be changed somewhat. Most important, this fit was made with a realistic microscopic model.

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