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PROTON TRANSFER IN PROTON GLASSES

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ABSTRACT

Proton intrabond transfer in O–H···O bonds is the mechanism for dynamic behavior of rubidium/ammonium dihydrogenphosphate mixed crystals. Because of strong proton-proton interactions, such transfer is associated with thermally activated creation of H_3PO_4–HPO_4 intrinsic defect pairs, their hindered diffusion in a random-step fractal potential, and their eventual annihilation. Predictions of a model based on this behavior are compared with determinations on a 35% ammoniated crystal by Courtens et al. of dielectric susceptibility and of relaxation time distribution limits calculated from Brillouin scattering results.

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). RDP and ADP have the same 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. RADP has no transitions for $0.22<x<0.74$, but proton glass (PG) behavior exhibiting a wide spread in relaxation times sets in near 75 K. This behavior is described accurately by a phenomenological model [1] with adjustable parameters based on the Vogel–Fulcher law.

The present work analyzes this dynamic behavior with a microscopic model having essentially no adjustable parameters. It is based on two concepts: (1) creation and annihilation of mobile intrinsic defects, and (2) hindered diffusion of these defects in a random potential.

Brawer [2] discussed similar concepts in relation to structural glasses. In the PG system the defects and their creation and diffusion energies are better understood. Spin and quadrupolar glasses, on the contrary, do not seem to exhibit relaxation caused by diffusing defects.

Static behavior of RADP including the $x-T$ phase diagram was predicted [3] by letting the Slater interaction ϵ_0 which causes the FE transition in RDP be independent of x, and letting the cross-cation interaction ϵ_a which causes the AFE transition in ADP be proportional to x in that mean-field model.

Dynamic behavior requires acid proton intrabond transfers associated with effective diffusion of thermally generated intrinsic HPO_4 and H_3PO_4 "Takagi" defects of energy ϵ_1. All these proton–proton interactions can be represented by pseudospin interactions [4].

Glassy systems have structural randomness which causes frustration and dynamic disorder. In RADP the random placement of Rb^+ and NH_4^+ cations causes competing FE and AFE interactions leading to frustration which prevents FE or AFE ordering. Instead, the acid proton system has dynamic disorder and in the PG regime develops a wide spread in relaxation times characteristic of glassy systems.

A microscopic model for proton glass dynamics thus must deal with the dynamics of the acid proton system. Presented here is the first such analytic model. Its predictions are compared with dielectric and Brillouin scattering experimental results.

The flow chart below outlines the steps in the model calculation.

$$\epsilon_d \;\left.\begin{array}{r} \tau_0 \\ \rightarrow U(r) \\ (D,\epsilon_1) \end{array}\right\} \left.\begin{array}{r} \rightarrow R(t) \\ \rightarrow (R_0,n) \end{array}\right\} \rightarrow P(t) \rightarrow (\epsilon',\epsilon'')$$

Following the flow chart from left to right, ϵ_d is the r.m.s. defect diffusion energy. These Takagi HPO_4 and H_3PO_4 defects are considered as the moving entities rather than individual protons because the strong proton–proton interactions cause proton motions to be highly correlated.

Creation and annihilation of Takagi defects involve the processes

$$H_2PO_4 + H_2PO_4 \leftrightarrow H_3PO_4 + HPO_4$$

Their effective diffusion via the processes

$$H_3PO_4 + H_2PO_4 \leftrightarrow H_2PO_4 + H_3PO_4 \text{ and } HPO_4 + H_2PO_4 \leftrightarrow H_2PO_4 + HPO_4$$

simply requires O–H···O↔O···H–O intrabond proton transfer. The importance of Takagi groups for proton glass dynamics is generally recognized [4–6].

To find ϵ_d we examine the pseudospin system Hamiltonian H. Kinetic energy terms decribing pseudospin energy exchange with the phonon bath are omitted. Hence H is equivalent to the internal energy U given by

$$H=U=N\{n(\epsilon_1 - R_0^{1/2}\epsilon_d) + (1-f)\epsilon_0\} + \textstyle\sum_i (\epsilon_a/2) S_i [S_j \delta(s_{ij} - 1) + S_k \delta(s_{ik} - 1)] \quad (1)$$

Here N is the number of molecular units. The first term will be considered later. In the second term, $(1-f)$ is the fraction of units having Slater energy

ϵ_0. In the third term, j and k indicate the protons with which proton i interacts across NH_4^+ ions only, (see ref. 4) because s_{ij} and s_{ik} are $+1$ and -1 for NH_4^+ and Rb^+ ions respectively, located between the i and j or i and k protons. The sum does not count S_iS_j or S_iS_k interactions twice. The ϵ_1 and ϵ_0 terms could also be written in terms of pseudospin interactions [4], but the above form is more useful in finding ϵ_d.

The energy change ϵ per step has contributions only from the ϵ_a and ϵ_0 interactions. The mean square change contributions per step are additive and are given by

$$\epsilon_d^2 = \langle (\epsilon)^2 \rangle = 2x\epsilon_a^2 + 2f_g(1-f_g)\epsilon_0^2 \tag{2}$$

Here $x=0.35$ is the ammonium fraction and $f_g=0.77291$ is the limiting fraction [3] of zero-energy Slater groups in the PG regime. The first term shows that in pure ADP a proton transfer has probability $\frac{1}{2}$ each of changing U by $\pm 2\epsilon_a$ and of leaving U unchanged. 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 ϵ_a as defined in eqn. (1) and ref. 3 equals ϵ_0 (and not $2\epsilon_0$ as stated in refs. 3 and 4), and because the best value known [7] for ϵ_0/k is 74.5 K which applies to pure RDP, we obtain the value $\epsilon_d = 76.4$ K.

The ϵ distribution leading to eqn. (2) is discrete but nearly equivalent to the normalized gaussian form

$$w(\epsilon) = (2\pi)^{-\frac{1}{2}}\epsilon_d^{-1}\exp[-(\epsilon-\epsilon_b)^2/2\epsilon_d^2] \tag{3}$$

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

To find the distribution $W(\epsilon)$ of internal energy change ϵ per step along the paths actually taken, we make the approximation that

$$W(\epsilon) = w(\epsilon)\exp(-\epsilon/kT) \tag{4}$$

Then the assumption that U is unbiased along paths actually taken fixes the value of ϵ_b and gives $W(\epsilon)$ the simple form

$$W(\epsilon) = (2\pi)^{-\frac{1}{2}}\epsilon_d^{-1}\exp(-\epsilon^2/2\epsilon_d^2) \text{ if } \epsilon_b = \epsilon_d^2/kT \tag{5}$$

If we ignore motion of other Takagi defects 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 sinkhole with caves in the surrounding slopes, so that though an outward path (A in Fig. 1) chosen randomly using $w(\epsilon)$ is uphill, a typical actual outward path (B in Fig. 1) using $W(\epsilon)$ is level on the average.

The crystal topology [4] is such that the defect can diffuse around a loop of

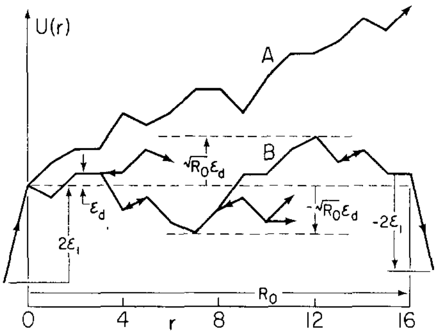


Fig. 1. Typical Takagi defect diffusion paths illustrating internal energy $U(r)$ plotted vs. number of steps r from defect creation site. Here A is a path employing the biased $w(\epsilon)$ step height distribution of eqn. (3), while B is an actual path with side branches using the unbiased $W(\epsilon)$ of eqn. (5). Also shown are the defect pair creation and annihilation energies $\pm 2\epsilon_1$, the r.m.s. diffusion step height ϵ_d, and the assumed maximum barrier and trapping energies $\pm R_0^{\frac{1}{2}}\epsilon_d$, where R_0 is the number of steps from creation to annihilation with a new partner.

6 (or 8, 10, etc.) steps back to its original position. The importance of these loops is estimated by a statistical analysis. A defect can take one of six 6-step loops or one of ten 8-step loops to return to its original site. For each step there is approximate probability 1/3 of visiting the correct new site on a given loop, giving probability 2/243 of traversing some loop 6 steps long, and 10/6561 for a loop 8 steps long, without taking side trips. Backtracking is allowed, and side trips are few because the diffusion path Hausdorff dimensionality D is near 1 as discussed below, so traversing of loops appears unimportant.

The topology of the diffusion paths available to a defect is locally equivalent to a double-branching Cayley tree because a defect can move to two new positions or return to its former site. Because looping is unimportant we studied diffusion on such a Cayley tree for a number of paths of maximum length $r = 13$ steps from the origin, using a Monte Carlo technique. These simulations indicate that the number N_s of new sites visited obeys the fractal relation $N_s = r^D$, with Hausdorff dimensionality [8] $D = 1.15 \pm 0.05$. A value 1 for D would correspond to one-dimensional $(1-d)$ diffusion with no side trips.

Although a Takagi defect occasionally takes a branch path as shown in Fig. 1, upon retracing it the polarization changes made while taking that branch are cancelled. Thus 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 eqn. (5), $U(r)$ is a fractal potential of a type considered by Dotsenko [9].

The time per diffusion step 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. [10] fix τ_0 at 5×10^{-14} s.

The net effect of diffusion over a time interval t is proton shifts only along a $1-d$ path of diffusion path length $R(t)$ steps. The maximum barrier encountered in R steps for the $W(\epsilon)$ distribution of eqn. (5) is about $\epsilon_d R^{\frac{1}{2}}$ as shown in Fig. 1, where $\frac{1}{2}$ is Dotsenko's scaling exponent ν. This maximum barrier is unlikely to occur in a branch path, because if it did, the defect would have to cross it twice.

At high temperature the barriers are negligible, so the defect jump time is simply τ_0 and it requires a time near $\tau_0 R^2$ [Dotsenko's eqn. (11)] to diffuse R steps. But in the PG regime the largest barrier dominates the diffusion time, so the factor R^2 should be omitted, giving for $\nu=\frac{1}{2}$ a diffusion time in agreement with Dotsenko's eqn. (9), which is also given below for arbitrary ν

$$\begin{aligned} t(R) &= \tau_0 \exp(\epsilon_d R^{\frac{1}{2}}/kT) \\ R(t) &= \langle R^2 \rangle^{\frac{1}{2}} = [(kT/\epsilon_d)\ln(t/\tau_0)]^{1/\nu} \end{aligned} \tag{6}$$

(Dotsenko's eqn. (9) – here $1/\nu=2$). This equation for $1-d$ systems is applicable because the Takagi defect diffusion path is close enough to being $1-d$ so that the maximum barrier is unlikely to be in a branch path.

One-dimensional discrete-time random walks with random transition probabilities p have been treated by several authors. In particular, the probability distribution

$$\rho(p) = [\delta(p-p_+) + \delta(p-p_-)]/2, p_\pm = \exp(\pm\epsilon_d/2kT)/2\cosh(\epsilon_d/2kT) \tag{7}$$

corresponding to a potential having random steps $\pm\epsilon_d$ from site to site (which gives the same results for our model as the $W(\epsilon)$ distribution in eqn. (5)) is a special case of a distribution presented by Sinai [11] and discussed by Derrida and Pomeau [12] which leads to the above $\ln^2(t)$ dependence of $\langle R^2 \rangle^{\frac{1}{2}}$, as does a more general random potential with a distribution of E_d.

The fractional defect density n for Takagi defects of energy ϵ_t is found from the Boltzmann factor for such groups, noting that the a priori (infinite T) concentration of Takagi groups is $\frac{1}{2}$, and using the fact that $n \ll 1$:

$$n = \exp(-\epsilon_t/kT)/[1+\exp(-\epsilon_t/kT)] \simeq \exp[-(\epsilon_1 - R_0^{\frac{1}{2}}\epsilon_d)/kT \tag{8}$$

Here ϵ_1 is the Takagi group creation energy for this mixed crystal, which should be close to the value $\epsilon_1/k=647$ K found [7] for pure RDP. The average defect annihilation path length R_0 is the path length in steps from creation to annihilation with a new partner. The trapping energy $-R_0^{\frac{1}{2}}\epsilon_d$ shown in Fig. 1 is found by the same argument used above to find maximum barrier height $+R^{\frac{1}{2}}\epsilon_d$.

A second relation between 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

$$n^{-1}=R_0^D \tag{9}$$

An implicit relation for n is found from eqns. (8) and (9)

$$n=\{[\epsilon_1+kT\ln(n)]/\epsilon_d\}^{-2D} \tag{10}$$

The polarization relaxation $P(t)$ following step removal at $t=0$ of a small d.c. electric field is found by integrating the fractional polarization change $\mathrm{d}P/P$ which equals $n\mathrm{d}R(\mathrm{d}t)$ if the defect wanders randomly, as at high temperature. Here $\mathrm{d}R(\mathrm{d}t)$ is the mean number of O–H····O dipoles reversed by a Takagi defect during time $\mathrm{d}t$. Near the FE transition temperature T_c for Rb-rich crystals the defect path is non-random and the relation shows critical behavior

$$\mathrm{d}P/P=-[(T-T_c)T]n\mathrm{d}R \tag{11}$$

In the PG concentration range, T_c can be approximated by 0. Then upon integration, $\ln(P)+\mathrm{const}=-nR$. Taking the exponent and substituting for R from eqn. (6) yields for decay from an initial polarization P_i the expression

$$P/P_i=\exp\{-n[(kT/\epsilon_d)\ln(1+t/\tau_0)]^2\} \tag{12}$$

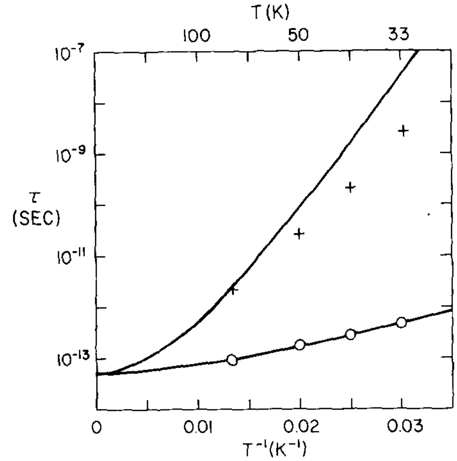
This "logarithmic gaussian" decay has $\ln^2(t)$ in the exponent. A more general form with arbitrary power of $\ln(t)$ was derived by Dotsenko [9], and by Palmer et al. using two models. The first assumes hierarchically constrained dynamics [13], but with collaboration of several pseuodspins required to advance from one level to the next, rather than surmounting of random potential barriers. The second involves relaxation of isolated clusters of unfrustrated spins [14].

The conversion from step response in eqn. (12) to a.c. response is done by integrating the responses at time t to an a.c. electric field of angular frequency ω made up of differential steps beginning at times $t'<t$. The complex dielectric susceptibility $\epsilon=\epsilon'-j\epsilon''$ determined in this way is

$$\epsilon=\epsilon_\infty+(\epsilon_{\mathrm{dc}-\epsilon_\infty})\{1-\int_0^\infty(\sin u+j\cos u)\exp[-a^2\ln^2(1+u/f)]\mathrm{d}u\} \tag{13}$$

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

We compare predictions of this model with dielectric results at 326 and 33700 Hz and with the relaxation time range found by a Brillouin scattering study at GHz frequencies. We use $\tau_0=5\times10^{-14}$ s as found by Courtens et al. [10] and $D=1.15$ as discussed above. For ϵ_d and ϵ_1 we obtained best fit by using 50 K and 400 K instead of the values 76.4 K and 647 K expected from behavior of pure RDP and ADP as discussed above. Both fitting parameters are about 36%



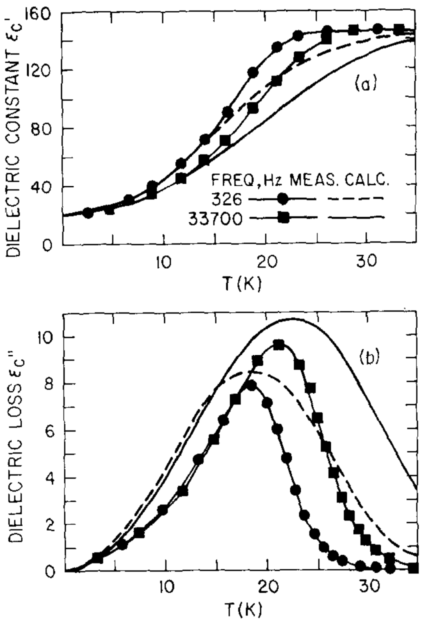


Fig. 2. Comparison of upper limits τ_2 and lower limits τ_1 of range of relaxation time τ having normalized weighting function $g(\tau)=[\tau \ln(\tau_2/\tau_1)]^{-1}$, where + and O represent τ_2 and τ_1 determined by Courtens, Vacher and Dagorn [10] from Brillouin scattering measurements on $Rb_{0.65}(NH_4)_{0.35}H_2PO_4$, and solid lines are these limits predicted from eqn. (15) using $\tau_0=5\times10^{-14}$ s, $D=1.15$, $\epsilon_1=400$ K, and $\epsilon_d=50$ K.

Fig. 3. Comparison of dielectric susceptibility measured in $Rb_{0.65}(NH_4)_{0.35}H_2PO_4$ by Courtens [1] with that calculated from eqn. (13) using parameters listed in Fig. 2.

below the expected values, so the fit for the expected parameters can be found by compressing the temperature scales in Figs. 2 and 3 by 36%.

The expression for proton glass relaxation used [10] in analyzing Brillouin scattering results assumes a spread in relaxation time τ between τ_1 and τ_2 with normalized weighting function

$$g(\tau)=[\tau \ln(\tau_2/\tau_1)]^{-1} \tag{14}$$

Fitting magnitude and slope of the step function response for this τ distribution to that of eqn. (12) at the $\frac{1}{2}$ amplitude point yields

$$\begin{aligned} \tau_1 &= \tau_0 \exp(0.232\epsilon_d/2n^{\frac{1}{2}}kT) \\ \tau_2 &= \tau_0 \exp(1.433\epsilon_d/2n^{\frac{1}{2}}kT) \end{aligned} \tag{15}$$

The relaxation time limits from eqn. (15) are compared in Fig. 2 to the values deduced by Courtens, Vacher and Dagorn [10] from Brillouin scattering experiments and shown in their Fig. 2. The model fits the lower time constant limit exactly, but somewhat overestimates the upper time constant limit.

The comparison with a.c. dielectric susceptibility results of Courtens [1] using eqn. (13) is shown in Fig. 3. The predicted loss peaks occur at the right temperatures but are too broad, and the ϵ' fits are not exact.

The overall comparison to Brillouin scattering and dielectric results covers 8 orders of magnitude in frequency and temperatures from 5 to 75 K. The overall fit is quite satisfying, because of the four parameters in the model, only two had to be changed somewhat from their expected values.

Presented here are ideas concerning hindered diffusion of intrinsic defects and the corresponding dielectric response, and examples of diffusion in a fractal potential and of hierarchically constrained dynamics. These ideas may provide hints regarding relaxation via the complex diffusion mechanisms found in structural glasses.

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