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Phase Coexistence in Proton Glass

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Phase coexistence results from quenched structural randomness and frustrated interactions. The nature of this randomness and the frustrated interactions in proton glass are explained. The six types of ordered domains and corresponding ferroelectric and antiferroelectric phases are described, as well as the disordered paraelectric and proton glass phases. Experimental evidence for phase coexistence is presented. Parameters are introduced which describe the volume fractions of phases, and the overall amount of coexistence. This last parameter provides the basis for locating the nominal phase boundaries, and for an expression which describes the sharpness of any of the five smeared-out phase transitions which occur in proton glass crystals.

I. INTRODUCTION

A glass by definition possesses quenched (frozen) structural randomness and frustrated ordering tendencies. The randomness can be the chemical bonding configuration in an ordinary glass, the magnetic ion locations in a spin glass crystal, or the Rb^+ and NH_4^+ cation placement in a proton glass crystal such as $Rb_{1-x}(NH_4)_xH_2AsO_4$ (RADA). The frustration in proton glass results from the ferroelectric (FE) and antiferroelectric (AFE) ordering tendencies caused by the Rb^+ and NH_4^+ ions, respectively.

If a crystal without quenched structural randomness has a solid-solid phase transition, according to the Landau theory it must be mathematically sharp, with no coexistence temperature range, whether it is a first- or second-order transition. Renormalization group theory predicts a narrow temperature range over which fluctuations on wide length and time scales can occur for a second-order transition. If a suitably ordered region above a given minimum size is defined to be FE, then FE and PE (paraelectric) phases can coexist over this narrow range in an appropriate crystal. This coexistence can be called temporal or dynamic, because over time the regions which are FE vary randomly.

A proton glass crystal has frustrated interactions, so its Landau free energy expansion will have coefficients of different powers of the polarization P which depend on x. Hence its FE transition temperature T_c will depend on x. If x is averaged locally, random variations in cation placement will give random variations in local x and corresponding variations in local T_c. This will lead to PE/FE phase coexistence over some temperature range.

To examine the nature of phase coexistence in proton glass, we first describe the chemical and structural nature of proton glass and its parent crystals [1,2]. Then we discuss the phases present in these crystals. Finally, we discuss the temporal and spatial nature of coexistence of these phases, and how this coexistence depends on temperature.

II. PHASES PRESENT IN PROTON GLASS CRYSTALS

The word “proton” signifies that the hydrogen-bonded protons order in different ways in the parent phases, leading to the frustration in the mixed crystals. The parent crystals both exhibit a room-temperature PE phase having the same tetragonal space group. These parent crystals undergo phase transitions to a FE phase for RbH_2AsO_4 (RDA) and an AFE phase for $NH_4H_2AsO_4$ (ADA), both orthorhombic but with different space groups. Mixed crystals in an intermediate composition range show a gradual onset of a spread in relaxation times with decreasing temperature, and finally become nonergodic. This behavior is considered here as a transition from the tetragonal PE phase to a nonergodic proton glass (PG) phase of the same space group. Accordingly, this proton glass system exhibits 4 phases, the ordered FE and AFE phases, the statically disordered PG phase, and the dynamically disordered PE phase.

Phase coexistence, according to our definition of phases, occurs even in the parent crystals. Below their transition temperatures but above 0 K they exhibit temporal coexistence of the PE phase with the FE and AFE phases respectively. Only mixed crystals can exhibit spatial coexistence, which results from the quenched randomness of the structure of the mixed crystals. This coexistence also has a temporal nature, except at 0 K.

We now discuss the above ideas and phenomena in more detail.

From the foregoing discussion, it is evident that there

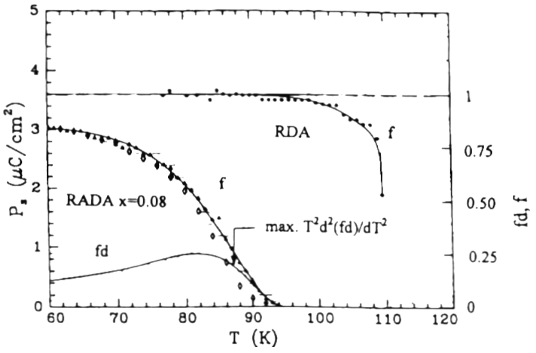

Fig. 1. (Adapted from Ref. [5]) Solid circles and solid triangles are spontaneous polarization data for RDA and RADA $x = 0.08$ respectively. Open diamonds are the **a** axis dielectric permittivity for RADA $x = 0.08$, subtracted from the permittivity for RADA $x = 0.28$, and scaled to meet the P_s curve at 60 K; this represents the decrease in permittivity caused by the coexistence with the ferroelectric phase. The fraction of the crystal volume in the ferroelectric phase is represented by f. The coexistence parameter c, divided by 2, is indicated by fd. The nominal phase transition temperature, where c has its maximum negative curvature, is indicated by an arrow.

are at least three phases present in the proton glass system. The PE phase exists for all x in a wide range above and below room temperature. It is characterized by dynamic disorder of the acid hydrogens and also, probably, of the ammonium positions. For low x, the FE phase exists with two possible domain structures below a temperature $T_c(x)$, where T_c decreases monotonically to zero as x increases. Similarly, for high x, the AFE phase exists with four possible domain structures below a temperature $T_N(x)$, where T_N decreases monotonically to zero as 1-x increases. Each of these six domain structures corresponds to one of the six ways that two hydrogens can be located close to an arsenate ion in its four hydrogen bonds to its arsenate neighbors. Experimentally, there is always an intermediate x range separating the FE and AFE phases even at low temperature, although in Monte Carlo simulations it is possible to have these phases be contiguous in the x-T plane by proper choice of model parameters.

Accordingly, there are at least two experimentally observed phase transitions, from the dynamically disordered PE phase to the statically ordered FE and AFE phases. The important remaining question concerns the existence of a fourth, statically disordered, proton glass (PG) phase.

The occurrence of static disorder as temperature approaches zero is no guarantee of the existence of the PG phase. A system of noninteracting two-orientational-state dipoles, with barriers hindering change of dipole orientation, and with or without random fields, would achieve static disorder as temperature approaches zero. This behavior would not be called a phase transition, but rather a manifestation of the properties of a PE phase.

If the system has random interactions but no random bias, as for many spin glass systems, it can show susceptibility cusps which have been considered indicative of a transition to a spin glass phase. This transition is a cooperative phenomenon; as one dipole or group of dipoles settles into a low-energy configuration, it encourages its neighbors to do likewise. It seems probable that proton glass crystals in the intermediate x range (where no FE or AFE transitions occur) would similarly undergo a transition to a statically ordered PG phase. A complicating factor is the random bias field caused by the difference in environment seen by the oxygens on the two ends of each hydrogen bond. This bias field would smear out the transition, just as a uniform externally applied bias field smears out a second-order PE-FE transition.

Presently, neither experimental results nor Monte Carlo simulations offer evidence concerning whether proton glass crystals exhibit a smeared-out spin-glass-type transition, or merely undergo noncritical slowing down as temperature decreases. In this paper, we adopt the view that there is a PG phase, without being dogmatic about its existence. Having adopted this view, we now consider the nature of coexistence involving these four phases.

III. EXPERIMENTAL EVIDENCE FOR COEXISTENCE

There is now considerable evidence for phase coexistence in proton glass. Neutron diffraction shows overlap over temperature ranges of tens of degrees, of the PE phase diffraction pattern with the FE phase pattern in the deuterated crystal DRADA $x = 0.10$, and with the AFE phase pattern in DRADA $x = 0.50$ [3]. Permittivity measurements along the crystalline **a** axis in RADA and DRADA show a more or less sharp drop of permittivity with decreasing temperature characteristic of the transition to the FE phase, followed by dispersion of the real and imaginary parts of the permittivity characteristic of proton glass [4]. The amount of permittivity decrease, relative to that exhibited by a higher-x crystal which remains in the PE phase, is proportional to the spontaneous polarization, as shown in Fig. 1. Accordingly, both methods agree on the gradual rise of the FE order parameter, and gradual decay of the PE phase, in the coexistence region which extends down toward 0 K [5]. Takeshige *et al.* [6] observed similar dispersion curves following a permittivity drop, in RADP. There is evidence from nuclear magnetic resonance for coexistence, based on overlap of PE with FE- or AFE-phase quadrupole-perturbed NMR spectra [7–9], and also from deuteron spin-lattice relaxation time in DRADA [9]. Brillouin scattering in $x = 0.10$ DRADA also shows overlap of FE and PE phase spectra over some temperature range [10].

If nonergodic regions of a crystal are interpreted as being in the PG phase, then the gradual decrease in "frozen-in" polarization as a crystal is heated in zero field (after being cooled to 4 K in an electric field), is evidence for coexistence of PG and PE phases [11,12].

IV. PHASE FRACTION AND COEXISTENCE PARAMETERS

For phase fraction parameters we choose f, a, g, and d for the FE, AFE, PG, and (dynamically disordered) PE phases, to represent the volume fractions that each phase occupies in the crystal.

$$(f + a + g + d)^2 = f^2 + a^2 + g^2 + d^2 + c = 1, \quad (1)$$

$$c = 2(fa + fg + fd + ag + ad + gd). \quad (2)$$

Here, c is a coexistence parameter, whose utility will be explained later. First, we discuss how material in the crystal is assigned to the four phases. To assign arsenate groups to a phase, we divide the crystal into clusters composed mostly of groups of the same type. There are 8 types of clusters, 6 of them corresponding to the 6 types of Slater groups which form the 6 types of FE and AFE domains. (Domains in this context are large clusters with well-defined walls.) The other two types are PG (frozen) and PE (dynamic) disordered clusters. We then require that each group be consistent with the cluster in which it is embedded, noting that all types of H_xAsO_4 ($x = 1$ to 4) groups are consistent with PE clusters. Thus, the FE fraction f is the sum of the products of each volume fraction V_{pi} of the ith up- or down-polarized FE cluster, multiplied by the magnitude $|p_i| = | <S_{pj}S_{ij}> |$ of the FE order parameter p for that cluster. The pseudospin S_{ij} is 1 (-1) for the jth hydrogen if its off-center position corresponds to an up (down) polarized FE domain. The reference pseudospin S_{pj} is 1 for all sites j for FE clusters. An AFE cluster has q or r as an order parameter. In either case, there are equal numbers of 1 and 1 reference pseudospins. For PG clusters, the reference pseudospin is the S value at a much earlier time, leading to the long-time limit of the Edwards-Anderson order parameter, q_{EA} (not to be confused with the AFE q).

These requirements lead to the mathematical definitions

$$\begin{aligned} f =& \quad V_{pi}|p_i|, \\ a =& \quad V_{qi}|q_i| + V_{ri}|r_i|, \\ g =& \quad V_{EAi}q_{EAi} + (V_{pi}q_{EAi} - f) + (V_{qi}q_{EAi} + V_{ri}q_{EAi} - a) \\ & \quad \text{if} > 0, \quad \text{otherwise} \quad g = 0, \\ d =& \quad 1 - f - a - g. \end{aligned} \quad (3)$$

Accordingly, f includes only FE groups of the right polarity in FE clusters, a includes only AFE groups of the right type in AFE clusters, and d includes the entire contents of PE clusters plus PE inclusions in other clusters. An example of such a PE inclusion is a chain of nonpolar groups within a FE domain, which must have a head and tail consisting of an H_3AsO_4 and $HAsO_4$ group, respectively.

The PG fraction g includes the frozen groups in PG clusters (1st term), and frozen inclusions of inconsistent groups in FE (2nd term) and AFE (3rd term) clusters. (An arsenate group is frozen if $S_j(-)S_j(0) = 1$ for each of its 4 H-bond pseudospins.) The need to require nonnegative g arises because near a 2nd-order transition, fluctuating FE or AFE clusters can occur for which q_{EA}. Simpler definitions, $g = q_{EA} - f - a$ and $d = 1 - q_{EA}$, are not used because random Rb^+ and NH_4^+ ion placement biases the H-bonds and causes q_{EA} to be nonzero at all temperatures. Our definition yields the correct $g = 0$, $d = 1$ result at room temperature.

To qualify as a cluster, a collection of arsenate groups must be sufficiently compact and large. Any definition is arbitrary, but common sense must lead to a minimum size of 1 to 2 nm. To address the compactness issue, we say that a group (of any type) cannot be part of a FE or AFE cluster unless it is at the center of a compact "seed" for which over half of the groups correspond to that type of cluster. We define this seed as the 13 arsenates at the center or on the corners and sides of the tetragonal unit cell, plus the 6 which provide "end caps" along the **c** axis, so that the seed contains the central arsenate and the two immediately above and below it along **c**. This basic cluster consists of 8 interlocking rings, each containing 6 arsenates H-bonded together in a loop. This seed is about 1 nm on a side and contains 19 arsenate groups. We further require, to address the size issue, that a cluster consist of 19 contiguous groups (not necessarily arranged in the shape of this "seed") which meet this definition. This definition allows clusters large enough to be detected experimentally, but disallows smaller regions which are ordered merely by chance.

After groups are assigned to FE and AFE clusters by this definition, the remaining groups are checked to see if they belong to "frozen" PG clusters, using the same compactness and size rules. Any material still remaining is in PE clusters, for which no compactness or size rules apply because the PE phase is characterized by its dynamic nature.

Now the utility of the coexistence parameter of Eq. (2) for locating phase boundaries and describing their sharpness will be explained. Even though phase boundaries are spread out for proton glasses, it is desirable for some purposes to locate nominal phase boundaries on a composition-temperature phase diagram. The rules for locating such boundaries should be symmetric in the various phases, and should go over to the usual definition in the case of the sharp phase boundaries exhibited by the parent FE and AFE crystals. A symmetric expression which is associated with the transition is the coexistence parameter c, which in the case of a PE-FE transition is simply $2fd$. A symmetric way of defining the transition would be the location where c has its maximum value of

0.5, which occurs where $f = d = 0.5$. However, this definition puts the transition temperature lower than T_c for a second-order FE transition, which occurs where $d = 1$, $f = 0$, and df/dT has its maximum value of negative infinity. Definitions such as maximum slope of f, extrapolation of maximum slope to zero f, or actual location of zero f, put f on an unequal footing with d, and have other difficulties. The location of the maximum negative curvature of c is a symmetric definition, because the negative curvature region is sandwiched between two regions of positive curvature, as seen in Fig. 1. Also, the maximum negative curvature temperature coincides with the usual definition of T_c in the case of a second order phase transition. To make this definition dimensionless, one can multiply by T^2. Then, to put x and T on an equal footing in the definition, one can say that the transition occurs where the "transition sharpness parameter" σ, given by

$$\sigma = -(\partial^2 c/\partial x^2 + T^2 \partial^2 c/\partial T^2), \tag{4}$$

has its maximum value. On a contour plot of $-\sigma$ on the x-T phase diagram, the various valleys locate the FE-PE, FE-PG, PG-PE, AFE-PG, and AFE-PE phase boundaries.

V. CONCLUSIONS

Experimental evidence for phase coexistence in proton glass has been summarized. Parameters are introduced for describing the volume fractions of the various phases. From these volume fractions, a coexistence parameter is developed to describe the degree of coexistence in different parts of the composition-temperature phase diagram. The "Laplacian" of this coexistence parameter is defined as a transition sharpness parameter. This parameter is useful in describing the location and sharpness of phase transitions in proton glass, in which these transitions are spread out because of phase coexistence.

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