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PHASE COEXISTENCE IN PROTON GLASS

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Abstract - Proton glasses are crystals of composition $M_{1-x}(NW_4)_x W_2AO_4$, where $M=K,Rb$, $W=H,D$, $A=P,As$. For $x=0$ there is a ferroelectric (FE) transition, while for $x=1$ there is an antiferroelectric (AFE) transition. In both cases, the transition is from a paraelectric (PE) state of tetragonal structure with dynamically disordered hydrogen bonds to an ordered state of orthorhombic structure. For an intermediate x range there is no transition, but the hydrogen rearrangements slow down, and eventually display nonergodic behavior characteristic of glasses. We and others have shown from spontaneous polarization, dielectric permittivity, nuclear magnetic resonance, and neutron diffraction experiments that for smaller x there is coexistence of ferroelectric and paraelectric phases, and for larger x there is coexistence of antiferroelectric and paraelectric phases. We present a method for analytically describing this coexistence, and the degree to which this coexistence is spatial or temporal.

Keywords - Phase transition, Ferroelectric, Antiferroelectric, Glass

INTRODUCTION

A proton glass is a crystal in which the protons dynamically occupy disordered positions in hydrogen bonds, and freeze into these disordered positions as temperature decreases. The prototypical proton glass, discovered by Courtens (1982), is $Rb_{1-x}(NH_4)_x H_2PO_4$ (RADP). We briefly review some structural features of proton glass and its parent crystals.

Proton glass retains its room temperature body-centered tetragonal structure down to the lowest temperatures. The dielectric permittivity increases with decreasing temperature according to a Curie-Weiss law, but then decreases to a small temperature-independent value with considerable frequency dispersion as temperature decreases further. The dielectric loss shows a corresponding dispersion. There is no thermodynamic phase transition from the paraelectric (PE) to the proton glass (PG) phase, but we and others refer to these as separate phases for reasons which are discussed later.

One parent crystal of proton glass is RbH_2PO_4 (RDP), which undergoes a weakly first-order ferroelectric (FE) phase transition at $T_c=123$ K in which the hydrogens in the O-H...O bonds arrange themselves into ordered off-center positions in these bonds (Jona and Shirane, 1962). The transition is accompanied by a structural change from a body-centered tetragonal unit cell with c the preferred axis, to a double-sized face-centered orthorhombic unit cell with the a and b axes rotated 45° about c . The spontaneous polarization P_s which develops along c rises sharply below T_c and soon

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levels off to a saturation value. The permittivity along \underline{a} , which is unaffected by domain wall displacement, obeys a Curie-Weiss law down to T_c and then drops rapidly to a low temperature-independent value.

The other parent crystal is $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP), which undergoes a strongly first-order antiferroelectric (AFE) transition at 122 K in which the hydrogens order in a different manner (Känzig, 1957). The unit cell keeps nearly the same size and orientation, but becomes orthorhombic and loses the body center Bravais lattice point. Both the \underline{a} and \underline{c} axis permittivities behave similarly to the \underline{a} axis permittivity for RDP.

Two reviews of proton glass behavior provide the phase diagram for RADP (Schmidt, 1987) shown in Fig. 1, and the specific range over which RADP crystals exhibit proton glass behavior without coexistence, namely $x=0.22$ to $x=0.74$ (Courten, 1987). For x values outside this range, it is possible to observe effects of phase coexistence of the PE or PG phase with the FE phase (for small x) or with the AFE phase (for large x). The purpose of this paper is to examine this coexistence. First we describe the evidence for coexistence. Then we present a method for describing the temporal and spatial nature of this coexistence. We conclude with a discussion of unsolved problems regarding coexistence.

EXPERIMENTAL EVIDENCE FOR COEXISTENCE

For mixed crystals of $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{AsO}_4$ (RADA) and its deuterated analog $\text{Rb}_{1-x}(\text{ND}_4)_x\text{D}_2\text{AsO}_4$ (DRADA) with x below the range where no FE behavior appears, we have found that the spontaneous polarization does not rise sharply at a well-defined Curie temperature T_c (Pinto and Schmidt, 1993). Instead, it rises gradually with decreasing temperature. One could consider the ratio $P_s(T)/P_{\text{sat}}$ as the fraction f of FE material coexisting with the remaining PE material. However, more evidence for coexistence is needed, because one could argue that the crystal is entirely FE, but that the atomic displacements and corresponding polarization are temperature-dependent.

Some of this additional evidence comes from dielectric measurements for crystals in this x range (Pinto and Schmidt, 1993). If we look at the permittivity vs. temperature curves for various frequencies for $x=0.12$ RADA shown in Fig. 2, we can describe three envelopes. The " ϵ_{dc} " envelope followed by the lowest frequency curves as temperature decreases approximately obeys a Curie-Weiss law at higher temperature, then reaches a somewhat rounded cusp, drops more or less rapidly, and then tends to flatten out. The " ϵ_{∞} " envelope followed by the highest frequency curves as temperature increases is a temperature-independent line representing the electronic and fast ionic contributions. The difference $\epsilon_{\text{dc}}(T) - \epsilon_{\infty}(T)$ represents the response resulting from hydrogen rearrangements. The " ϵ_{pg} " envelope is the extrapolated Curie-Weiss-like curve that would be followed if no FE ordering occurred. It is obtained from the permittivity curve for a crystal with x just large enough so no FE ordering occurs, by multiplying that curve by a constant which provides a good fit to the ϵ_{dc} envelope in the temperature region above the cusp. The difference $\epsilon_{\text{pg}}(T) - \epsilon_{\infty}(T)$ represents the response that would have resulted from hydrogen rearrangements if none of the crystal were in the FE phase. Then the fraction f of FE material is assumed to be given by the fraction of "missing" dielectric response, namely

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$$f = (\epsilon_{pg} - \epsilon_{dc}) / (\epsilon_{pg} - \epsilon_{\infty}). \quad (1)$$

We found that for both RADA and DRADA, the f values found from this permittivity method agree well at all temperatures with the f values found from the spontaneous polarization method, as shown in Fig. 3. This provides strong evidence that both the dielectric and spontaneous polarization phenomena for crystals in this low x range can be explained by coexistence of the FE and PE phases. Additional dielectric evidence for coexistence, in this case for AFE/PE coexistence in $x=0.75$ RADP, comes from measurements by Takeshige, Terauchi, Miura, Hoshino, and Nakamura (1985), who at that time attributed the behavior to a reentrant phase diagram, going from PE to AFE to PG with decreasing temperature. The first mention of phase coexistence as the origin of such behavior (first a permittivity cusp, then dispersion at lower temperature) was by Trybula, Schmidt, and Drumheller (1991), in connection with FE/PE phase coexistence in RADA.

Nuclear magnetic resonance (NMR) provides additional evidence for coexistence. Kind, Liechti, Brüscheweiler, Dolinšek, and Blinc (1987) reported that in $x=0.78$ DRADP the ^{87}Rb NMR spectra of the PE and AFE phases overlap from 150 to 140 K. This to us implies phase coexistence, though they did not use this term. Later, Korner, Pfammatter, and Kind (1993) presented a phase diagram for DRADP over the whole x range based on NMR results. This diagram shows a FE/PG phase segregation region, but they remarked that it is not clear whether such segregation is intrinsic or induced by defects. They also showed a region labeled AFE relaxor, which in our opinion could be a PE/AFE coexistence region. In $x=0.10$ DRADA, our deuteron NMR spin-lattice relaxation time T_1 measurements show that as temperature decreases through the temperature of onset of the FE phase, T_1 increases because only the moving deuterons remaining in the PE phase contribute to spin-lattice relaxation (Pinto, Howell, and Schmidt (1993). However, these deuterons are coupled by spin diffusion to the stationary deuterons in the FE phase, so their common T_1 increases. The fact that they are coupled by spin diffusion indicates that the correlation lengths for the FE and PE phases must be short, because otherwise spin diffusion could not achieve a common spin temperature for deuterons in the two phases. This T_1 increase, which is superimposed on a downward T_1 trend with decreasing temperature because of the slowing down of the fast intrabond deuteron motion, occurs in the range 138 to 125 K. Evidence for coexistence is also seen in the ND_4^+ rotationally-narrowed deuteron spectrum, in which a broad peak characteristic of the FE phase starts to appear near 138 K, while the two sharp peaks characteristic of the PE phase disappear near 131 K, as shown in Fig. 4.

Finally, neutron diffraction provides clear evidence for coexistence, because the Bragg reflections for both the PE and FE (or AFE, depending on x) phases are seen over a temperature range of width of order 10 K (Schmidt, Brandt, and Shapiro, 1996). Each $(hk0)$ Bragg spot divides into four FE-phase spots (corresponding to the four types of FE domains) arranged around the original PE-phase spot if h and k are both nonzero, so it is easy to note the coexistence of both types of spots. In the transition to the AFE phase, half the Bravais lattice points are lost, so a new set of Bragg spots appears. Also, each original Bragg spot divides into two spots on either side of the original spot, because the

four types of AFE domains exist in pairs whose members cannot be distinguished by diffraction spot locations.

ANALYTICAL DESCRIPTION OF COEXISTENCE

In systems without quenched spatial disorder, phase coexistence usually occurs only in connection with critical fluctuations at a second-order phase transition temperature. An exception is semicrystalline polymers, because it is easy for the long molecules to align locally into crystals, but practically impossible for all the remaining amorphous material to align in this manner.

For crystals with quenched disorder, such as relaxor ferroelectrics and proton glasses, phase coexistence over an extended temperature range is possible in principle. Consider proton glasses, where the quenched disorder consists in random quenched placement of the ammonium and alkali cations. By chance, some regions will have higher concentrations of ammonium ions than adjacent regions. For small- x crystals, these regions will resist transformation to the FE phase as temperature decreases, remaining in the PE phase. For large- x crystals, such regions will transform first into the AFE phase, while other regions remain in the PE phase. Elastic forces will tend to counteract this tendency to separate into two phases having different unit cell shapes and sizes.

Is the resulting FE/PE or AFE/PE coexistence itself describable as quenched disorder? This question cannot be settled directly from experiments performed thus far. However, the answer can be found by considering, for example, the FE transition of RDA (RADA in the $x=0$ limit). Some description of microscopic models for this transition is needed as background for answering the question. Slater (1941) developed the first explanation of the FE transition in KH_2PO_4 (KDP) which is isomorphous to RDA. He postulated random off-center H positions above T_c , which order into a FE arrangement below T_c . This model predicted a step function change in polarization at T_c , from zero to a maximum value consistent with complete proton order.

A defect of the Slater model is that he allowed only six proton configurations around each phosphate ion, two protons close and two far, in the four H-bonds attached to the phosphate ion. Two of these H_2PO_4 "Slater groups" are zero-energy polar groups corresponding to the two directions of FE polarization, while the other four are nonpolar and have higher energy ϵ_0 . This model leads to an order-disorder transition involving motion of hydrogens. The problem is that if a hydrogen moves within its bond, it creates a pair of HPO_4 and H_3PO_4 groups not allowed by the Slater model. Takagi (1947) remedied this problem by allowing such "Takagi groups" whose creation requires an energy ϵ_1 , typically about 5 times ϵ_0 . His model for the FE transition, including such groups, gave a second-order transition with P_s rising initially with infinite slope at T_c , then curving gradually toward P_{sat} as temperature decreases further. This result fit experiment much better than the Slater prediction of a P_s step function.

On the microscopic level, the "missing" polarization $P_{\text{sat}} - P_s$ can be attributed to thermally generated HPO_4 - H_3PO_4 Takagi pairs which then in effect diffuse apart within the FE domain by means of successive proton intrabond transfers. This diffusion leaves a chain of nonpolar Slater groups connecting the Takagi pair, thus lowering the

polarization. At temperatures low enough so that these chains rarely cross, a model based on such chains reproduces the $P_s(T)$ curve predicted by the Takagi model (Schmidt, 1961).

This dynamic process of pair creation, chain growth and decay, and pair recombination, first at one location and then another, is generally considered as part of the nature of the FE phase. For purposes of describing coexistence, it is preferable to consider these chains as part of the PE phase. From this viewpoint, we say that the PE and FE phases coexist, but that this coexistence is "temporal" because the PE chains are as likely to be at one location as another.

At the other extreme, if we consider a crystal with small or large x such that some ordered phase coexists with the PG phase, upon approaching zero temperature this coexistence will be quenched and we can call it "spatial." In general, for finite temperature and for x not equal to 0 or 1, the coexistence will be some combination of temporal and spatial.

It is desirable to describe the degree of coexistence, and the extent of its temporal and spatial natures, mathematically so that these parameters can be determined experimentally. For guidance, we consider the concept that a material must exist in some phase. For proton glass crystals, the fractions f , a , p , g of material in the FE, AFE, PE, and PG phases respectively must obey

$$f+a+p+g=1. \quad (2)$$

To generalize this concept, we square both sides of the equation, giving

$$(f+a+p+g)^2=1. \quad (3)$$

Then we call terms such as f^2 the FE autocorrelation parameter, and terms such as $2fg$ the FE/PG coexistence parameter. In principle, proton glass crystals can exhibit six kinds of coexistence, but so far it appears that the FE/AFE parameter $2fa$ is zero under all conditions.

Each type of coexistence for a given x and T can have different fractions s of spatial nature of coexistence. To discuss these, we need first to examine characteristics of the four phases. The FE and AFE phase regions are characterized by ordered hydrogen arrangements in the O-H...O or O-D...O bonds. The PG phase is characterized by a fixed (on some time scale) disordered hydrogen arrangement in these bonds. The PE phase is characterized by dynamic (on that time scale) disorder of hydrogens in these bonds. Accordingly, FE/PG or AFE/PG coexistence is completely spatial in nature, as would be FE/AFE coexistence if it were found to occur. Evidently, the PE phase is the vehicle for any hydrogen rearrangements. In order for boundaries between phases to shift, the PE phase must be involved, by means of temporal PE/FE, PE/AFE, or PE/PG coexistence.

Whether coexistence is spatial or temporal depends on the time scale over which the system is observed. Let us consider the example of FE/PE coexistence within a FE domain in $x=0$ RDA. The simplest way to determine the fraction f of ferroelectric phase

is to assign a pseudospin value $S=1$ to each hydrogen whose position is consistent with that phase, and $S=-1$ to each hydrogen whose position is inconsistent with that phase. Then $f=\langle S \rangle$, where $\langle S \rangle$ is the spatial average over all pseudospins. The degree $s(t)$ to which coexistence is spatial over a time interval t is then expressed by

$$s(t)=[\langle S(0)S(t) \rangle - f^2]/[1-f^2]. \quad (4)$$

To derive Eq. (4), we note that the probability that $S=\pm 1$ for a given pseudospin is $(1\pm f)/2$. Because there is no spatial inhomogeneity (no quenched disorder),

$$\langle S(0)S(\infty) \rangle = [(1+f)/2 - (1-f)/2]^2 = f^2. \quad (5)$$

Accordingly, Eq. (4) predicts that $s(0)=1$ and $s(\infty)=0$, as it should for this system which has no long-term correlations. For a crystal with nonzero x , we expect that $s(t)$ would decay from unity to some value greater than zero as time increases.

The above apply equally well to AFE/PE coexistence, if f is replaced by the AFE fraction a . This fraction can be determined by dielectric and neutron diffraction methods, but of course there is no spontaneous polarization which can be determined from hysteresis loops.

In considering PE/PG coexistence, there is no ordered phase, so in Eq. (4) f must be replaced by zero, giving the familiar Edwards-Anderson order parameter form for $s(t)$:

$$s(t) = \langle S(0)S(t) \rangle. \quad (6)$$

Because of the effective local bias "field" resulting from some H-bonds being asymmetric, having one oxygen also H-bonded to an ammonium ion and the other oxygen close to an alkali ion, $s(\infty)$ will be nonzero at all temperatures, going from a small value at room temperature to unity as temperature approaches zero. This bias smears out the pseudo-spin-glass transition that would otherwise be observed. Such a transition would be characterized by the Edwards-Anderson order parameter suddenly rising from zero to a value near unity. This behavior is analogous to that of a second-order FE transition, which is smeared out by a dc electric field applied along the spontaneous polarization axis. Just as in this situation we still talk about the PE and FE phases, so with proton glass we talk about the PE and PG phases.

To summarize, there are several parameters associated with coexistence. First, there are the fractions f , a , p , g of the FE, AFE, PE, PG phases respectively, which sum to unity. Next, there are the autocorrelation parameters f^2 etc. and the coexistence parameters $2fp$ etc. which together also sum to unity. Finally, there is the spatial correlation parameter $s(t)$, which for long times has the limiting values $s(\infty)=0$ for crystals with $x=0$ or $x=1$, and $s(\infty)=1$ for $T=0$.

DETERMINATION OF COEXISTENCE PARAMETERS

First, for determination of the fractions of the various phases, the most direct way to find the FE fraction f is from the height of the hysteresis loop compared to its height for the parent ferroelectric crystal well below T_c , where $P_s = P_{sat}$. As

mentioned above, f can also be found from dielectric measurements using Eq. (1), from NMR measurements, and (with some care) from neutron diffraction integrated intensities. To find the AFE fraction a , all of the above methods except hysteresis loops can be employed.

The PE and PG phases cannot be distinguished by an instantaneous view of the structure, even if it could be seen on the atomic scale. There is, however, a method called zero-field heating after field cooling, which provides this information. Upon removing a dc field after cooling to helium temperature, there is a remanent polarization P_{r0} . It decays first slowly, and then quickly to zero, upon heating the crystal slowly through the temperature at which it becomes ergodic. The fraction $g(T)$ of PG phase is given by

$$g(T) = P_r(T) / P_{r0}, \quad (7)$$

where $P_r(T)$ is the remanent polarization at a given temperature T .

This experiment was first performed by Levstik, Filipič, Kutnjak, Levstik, Pirc, Tadić, and Blinc (1991) on $x=0.60$ DRADP. Later it was done for $x=0.28$ DRADA by Pinto, Ravindran, and Schmidt (1993), who in addition performed a field heating after zero-field cooling experiment. In this case, application of a dc electric field at helium temperature produces a polarization P_i from the electrons and the ions in the absence of hydrogen rearrangement. With slowly increasing temperature, $P_r(T)$ increases slowly at first, then rapidly to a maximum value P_f , after which it decreases slowly according to a modified Curie-Weiss law. In this case, the fraction g of PG material is given by

$$g(T) = [P_f P_r(T)] / [P_f P_i]. \quad (8)$$

Both Eqs. (7) and (8) agreed on the temperature evolution of g as the respective experiments were performed for DRADA, as can be seen by examining Fig. 5.

Because these experiments were performed for x values between the two coexistence ranges, the paraelectric fraction was simply $p=1-g$. Similar cooling/heating experiments could be performed in the coexistence ranges of x . Then f or a would first be determined by one of the methods given above. The g values from Eqs. (7) or (8) would have to be multiplied by $1-f$ or $1-a$ to give the correct g values. This approach assumes that f and a no longer depend on T as the crystal approaches the ergodic limit temperature. Whether this assumption is correct can be determined by whether the lowest-frequency permittivity curves flatten out above this temperature. (There is still controversy on whether there is a real ergodic limit, or only a practical one based on time which can be devoted to the experiment.)

For determination of the Edwards-Anderson order parameter of Eq. (6), 2d NMR is an ideal technique and has been employed by Blinc, Dolinšek, Zalar, and Milia (1994) in DRADP. This technique directly determines what fraction of deuterons in a given type of site at $t=0$ are still in that site at a later time t , thus providing $s(t)$. In actuality, the technique will observe some subset of the deuterons at $t=0$, but all subsets are equivalent if there is no coexistence with FE or AFE phases.

If there is, say, coexistence of FE and PE phases, then it would be possible to choose a subset of FE phase deuterons with a certain electric field gradient tensor orientation to observe at $t=0$. In determining the spatial coexistence parameter $s(t)$ in Eq. (4), these deuterons would be given a weight factor f . One could then choose a nonequivalent set of PE phase deuterons and then give them a weight factor $p=1-f$, in determining the spatial average $\langle S(0)S(t) \rangle$ in Eq. (4). Similar experiments could determine $s(t)$ for AFE/PE coexistence.

Another approach to examine questions of ergodicity, phase coexistence, and response rate which we have used is Monte Carlo stochastic-dynamics simulations (Sinitski and Schmidt, 1996). These have yielded results, for instance, in good accord with the field cooling and field heating experiments.

CONCLUSIONS

We have proposed nomenclature and expressions for representing analytically the fractions of coexisting phases, and the degree to which their coexistence is spatial or temporal. Our example system is proton glass, but the ideas can be extended to other systems with quenched structural features which give rise to phase coexistence. We have shown how some of these coexistence parameters have already been measured, and have indicated how other ones could be determined.

For systems with coexistence, typical phase diagrams such as in Fig. 1 are inadequate. One could show contours on such diagrams of constant fractions such as $f=0.9$, etc. for the various phases. Contours of constant spatial coexistence parameter $s(x,T)$ could also be shown.

Numerous problems remain, such as determination of the spatial nature (correlation length, shape) of coexisting phases. Also, existing data should be plotted on contour-map-type phase diagrams as suggested above, and additional data should be accumulated to fill in what would presently be the mostly blank spaces on such diagrams.

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FIGURE CAPTIONS

Fig. 1. Phase diagram for RADP (Schmidt, 1987) showing boundaries determined by experiment, by theory, and by Monte Carlo heating (crosses) and cooling (circles) runs.

Fig. 2. Temperature dependence of the real part of the \underline{a} axis dielectric permittivity for RDA and three RADA crystals (Trybula *et al.*, 1991).

Fig. 3. Spontaneous polarization (Pinto and Schmidt, 1993) obtained from hysteresis loops in RDA (solid circles) and $x=0.08$ RADA (solid triangles) and from dielectric permittivity measurements using Eq. (1).

Fig. 4. Temperature dependence of the ND_4^+ deuteron NMR line shape (Pinto, Howell, and Schmidt, 1993) in $x=0.10$ DRADA for $\text{H}_0 \parallel \underline{a}$ at 28 MHz.

Fig. 5. Temperature dependence of the field-heated (open circles), field-cooled (solid circles), and zero-field-heated (open diamonds) polarization (Pinto, Ravindran, and Schmidt, 1993) in $x=0.28$ DRADA. A field of 500 V/cm was applied along the \underline{a} axis, and the heating and cooling rates were 1 K/min. The \underline{a} axis permittivity scale has meaning in the ergodic region above 50 K. Solid lines represent fits to a theory described in the above reference.

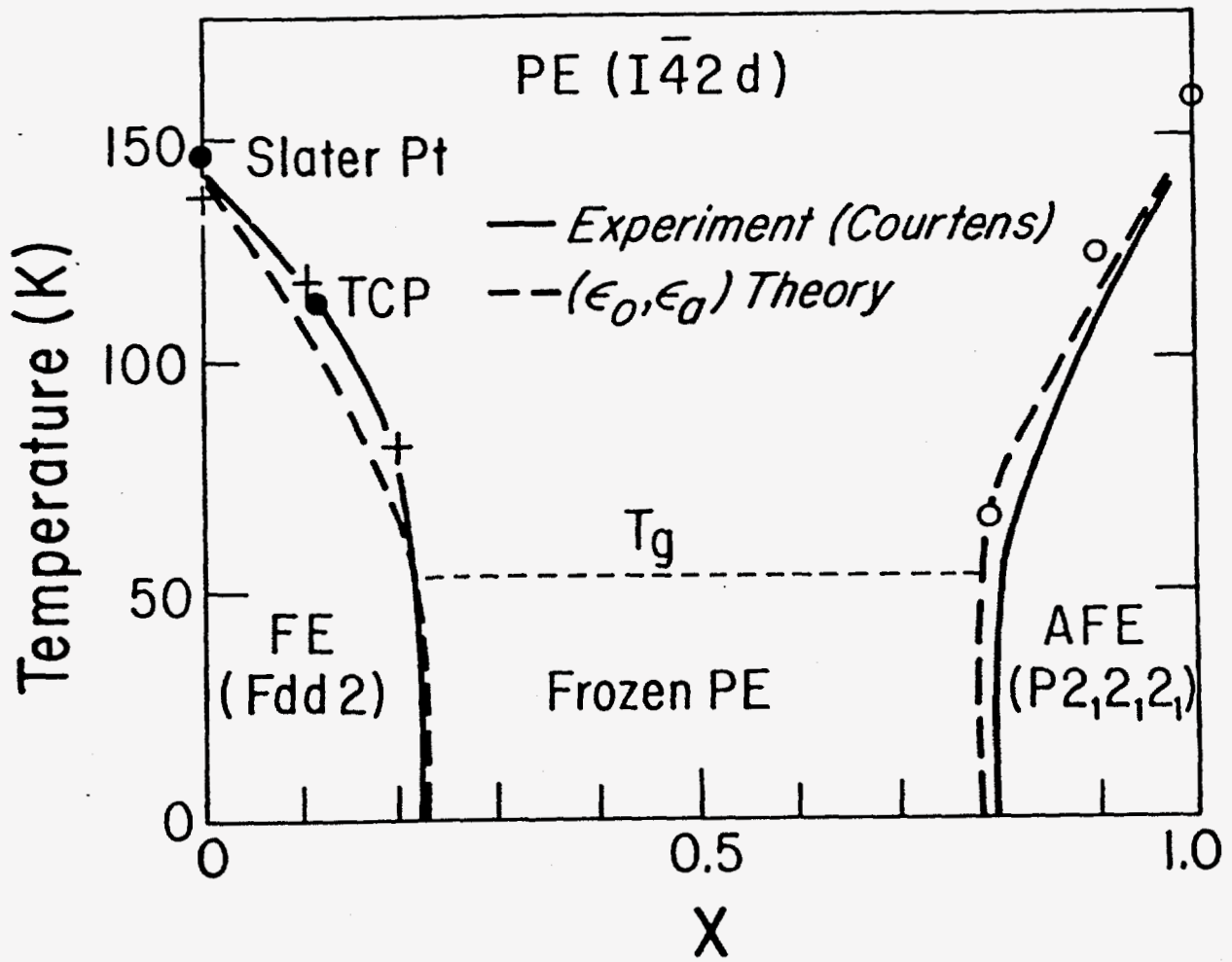


Fig. 1.

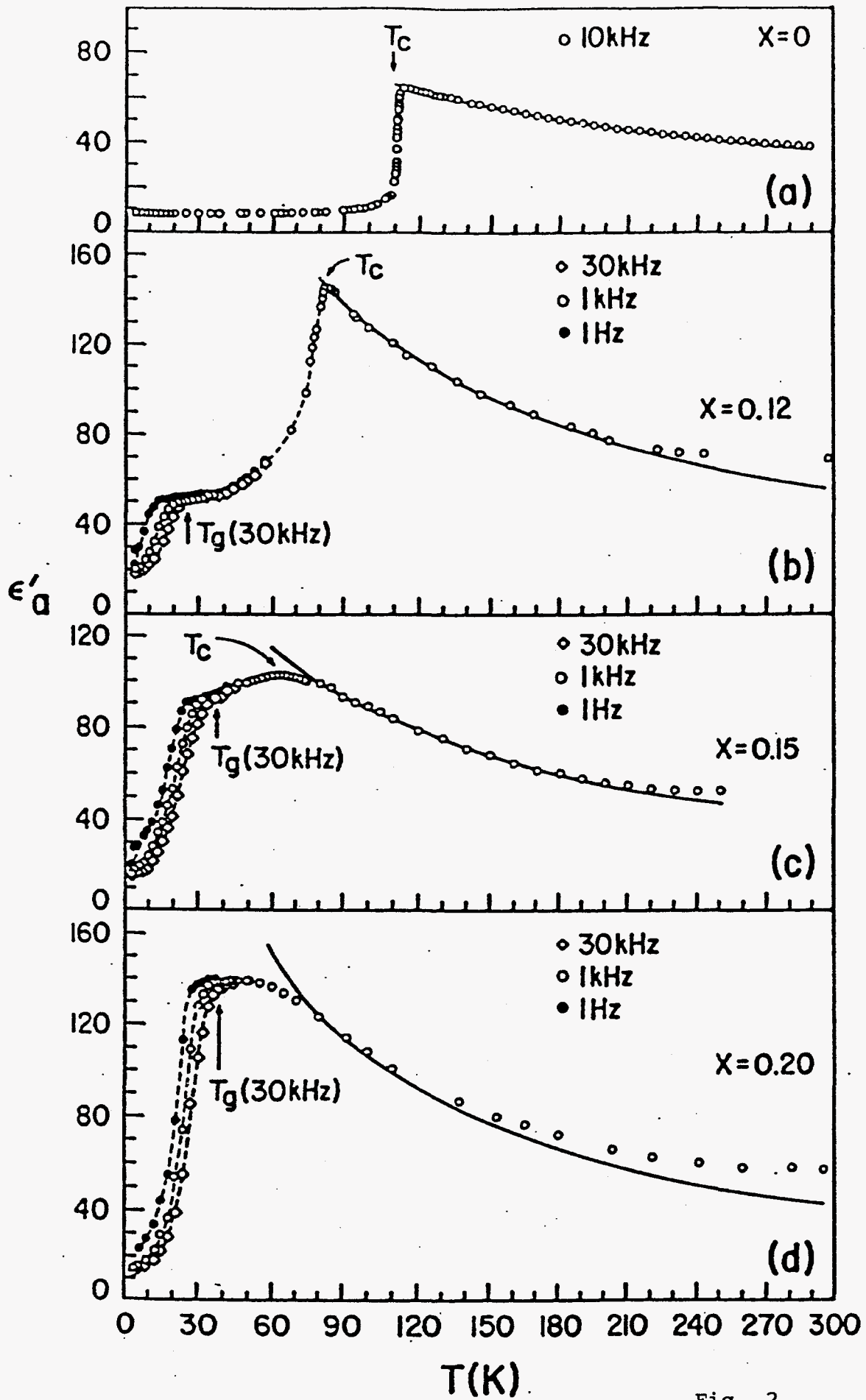


Fig. 2.

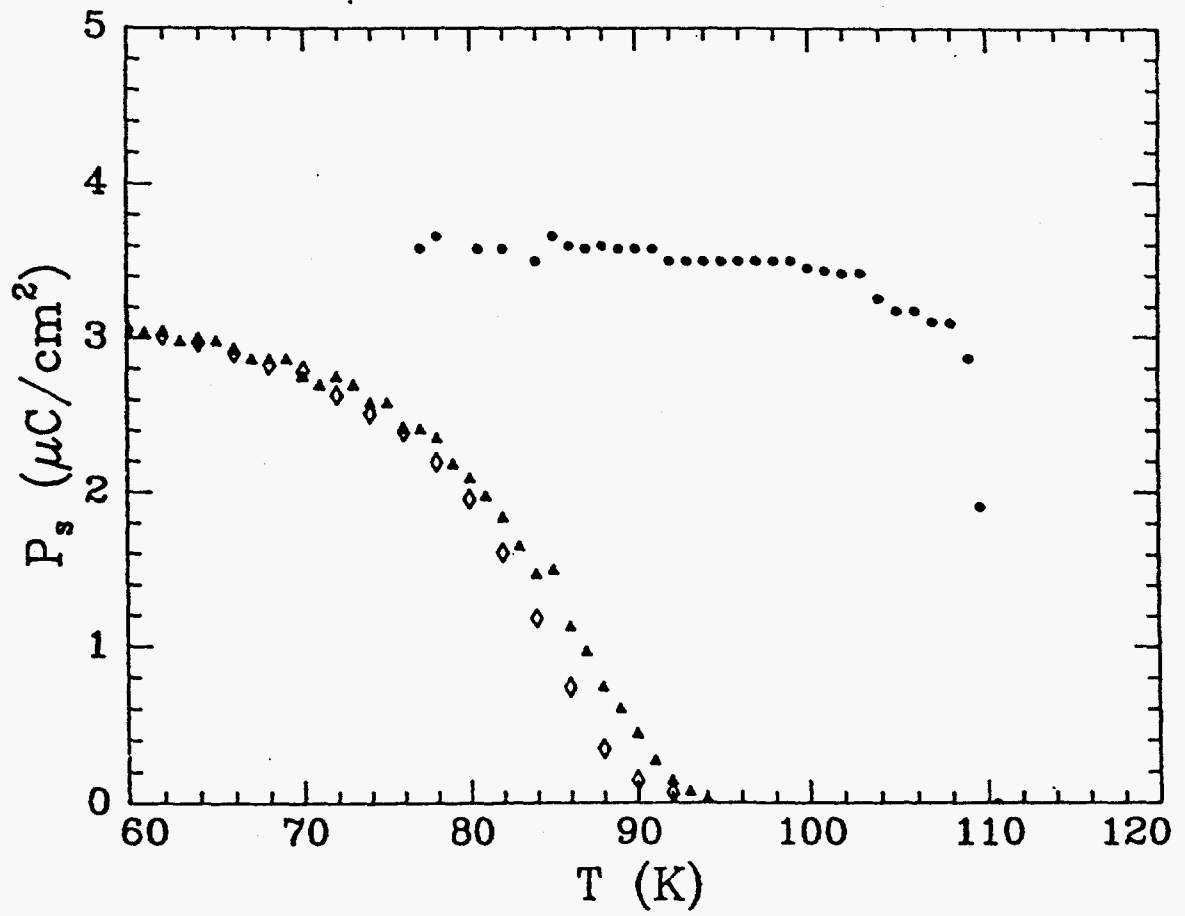


Fig. 3.

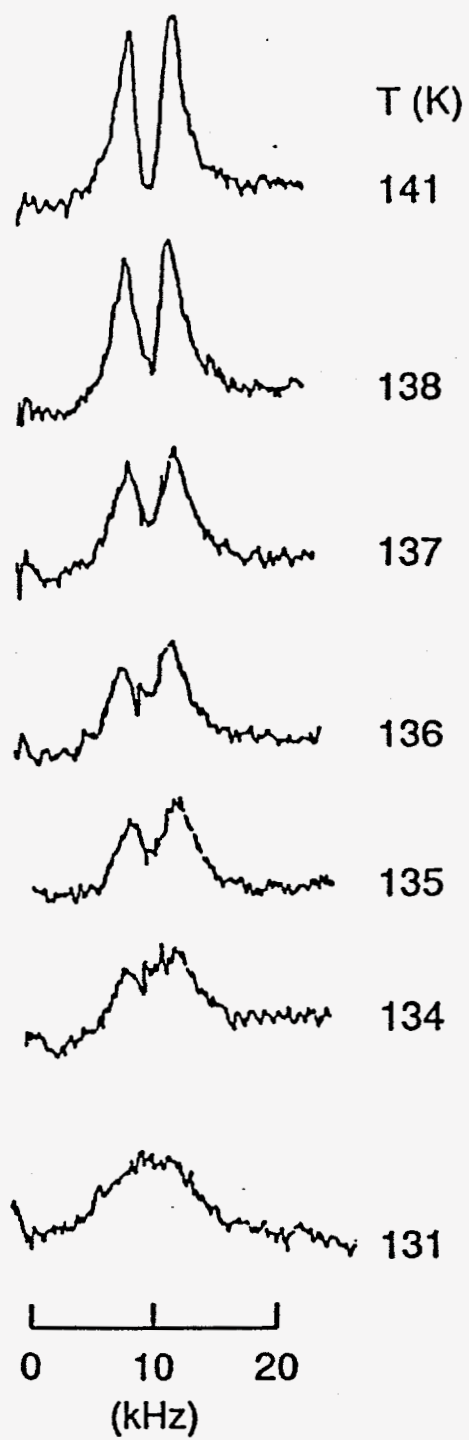


Fig. 4.

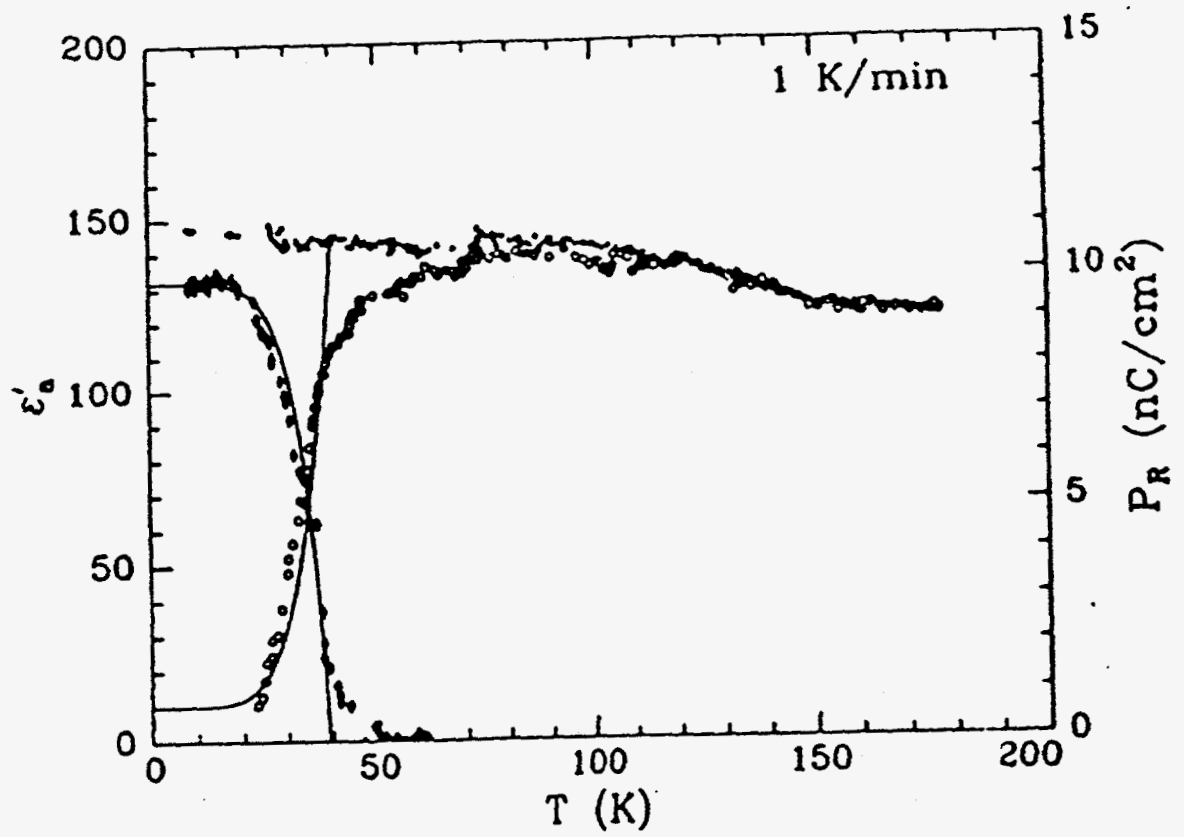


Fig. 5.