Structural glasses and Rb_1-x(NH_4)_xH_2PO_4

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Structural glasses and Rb$_{1-x}$(NH$_4$)$_x$H$_2$PO$_4$

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Abstract. Disordered or frustrated cooperative systems pose some major unsolved problems in solid-state physics. In magnetism, frustration can lead to condensation into spin glasses. In this paper, structurally frustrated systems are discussed, which lead to what we call by analogy "structural glasses". After a brief review of previous work, the attention concentrates on the mixed system Rb$_{1-x}$(NH$_4$)$_x$H$_2$PO$_4$ in which ferroelectric and antiferroelectric tendencies compete. Dielectric, optical, structural, NMR, and thermal data are summarized which indicate a great resemblance to the spin glasses. A new aspect of the structural glasses are the large strictive effects which might help in producing and detecting *real* glass transitions.

I. Introduction

Following the considerable success in the understanding of phase changes in structurally ordered systems, there has been a great revival of interest in disordered or random systems [1]. The basic questions of the existence of real transitions and of the nature of the order parameter remain challenging [2]. By far the main effort concentrated on dilute magnetic alloys, the old Kondo systems, and more recently on other magnetic crystals including insulating ones. The existence of a cooperatively frozen spin state at low temperatures has now been well established in many cases [3]. However, the central question of the occurrence of a true thermodynamic transition into this *spin-glass* state remains open to a great extent [4], at least experimentally. Investigations of disordered or mixed structural systems are certainly just as old [5,6], and the analogy with the spin-glass problem was recognized quite early [7]. The present paper discusses these structural analogs of spin glasses, concentrating on a new system with considerable promise [8], namely, mixed salts of RbH$_2$PO$_4$ (RDP) and NH$_4$H$_2$PO$_4$ (ADP) that will be abbreviated

$R_{1-x}A_xDP$, or simply RADP-100x. The system is called a *structural glass*, as it turns out that in the field of structural phase transitions it is an analog of the magnetic case. Confusion with amorphous or "window" glasses should be avoided. The latter relate to the liquid-solid transformation and their detailed understanding therefore is likely to be much more difficult [2].

The plan of the paper is as follows. In Section II, some previous work is reviewed, quite briefly unfortunately. In Section III, the motivation for studying RADP glasses, and the main results obtained so far are described, with emphasis on the static, dynamic, and microscopic transformations that have been found. Theoretical aspects and directions for future work are evoked.

II. Brief review of dipole, orientational, and other structural glasses

A. *Dipole glasses*

The model systems are alkali halides with substitutional polar molecules, such as KCl:OH [6]. On cooling, and at sufficient OH^- concentration, these crystals exhibit a susceptibility maximum associated with $OH^- - OH^-$ interactions. More generally, not only OH^- or CN^-, but also small ionized atoms taking off-center positions in their cage, such as Li^+ or F^-, can be used as local dipoles [9]. Within the molecular-field approximation, and taking into account tunneling between the various equilibrium positions, a transition to glass is predicted for these systems, and the measured susceptibility maximum can be derived [10]. It has been shown quite generally that random dipolar interactions cannot lead to an ordered state in an *isotropic* matrix [11]. The situation is different for dipoles embedded in an almost unstable lattice. The impurities can then destabilize the lattice, producing a new ordered phase [12]. An example could be $KTaO_3$:Li [13]. Making estimates following [12], one finds that this system, at typical Li^+ concentration (~ 1%), might become destabilized. Conflicting reports have appeared [14] but results seem to converge towards the existence of a domain state [15] possibly complicated by the very slow single Li^+ dynamics [16]. Further work on the halide glasses would be most useful, in particular to search for static changes associated with freezing.

B. *Mixed perovskites and related high-temperature oxides*

This is by far the richest family. Landolt-Börnstein [5] lists over 100 complexes of either the perovskite or tungsten-bronze families, and over 200 solid solutions, many of which with properties very suggestive of glass transitions. In an early review, Smolensky interpreted the observations as "diffused transitions" [17]. His main example is the disordered complex $PbMg_{1/3}Nb_{2/3}O_3$ which exhibits remarkable properties, such as a very broad dielectric relaxation peak that occurs much above the onset of birefringence, and a peculiar field-dependent polarization. More recent studies have been performed by Burns [18] who gave the somewhat aversive name of "dirty" displacive ferroelectrics to these systems. He interprets the observed birefringence as being due to a random distribution of frozen polarization, truly a glass. The great variety of effects obtainable by mixing continuously attracted interest for those solid solutions. The search for better growing procedures is of current concern, as witnessed by recent work on $(Sr,Ca)TiO_3$ and $(Sr,Ba)TiO_3$ [19]. There is no doubt that with suitable growth methods, this rich family will provide some of the best examples for structural glasses.

C. *Orientational or quadrupolar glasses*

So far, there are two main representatives of this category: solid H_2 in which the ortho-concentration has been reduced below 55% [20], and solid solutions of KCN with either KBr or KCl [21]. It is the diluted quadrupolar interactions, between ortho-hydrogen molecules in the first case, or between dumbbell-shaped CN^- ions in the other, which lead to a random orientational freezing. The possibilities of diluting a constituent having orientational degeneracies are presumably numerous [22]. This can also be achieved in two-dimensional systems, such as adsorbates on graphite [23]. Our brief comments will concentrate on $(KCN)_x(KBr)_{1-x}$. In pure KCN, the CN^- are disordered and directed along cube diagonals in the high-temperature cubic phase. On cooling, an ordering occurs with the CN^- directors along one of the former cubic [110] directions; they keep head-to-tail disorder. On reducing the CN^- concentraton below $x_c \sim 0.58$, this structural transition to an orthorhombic phase ceases, and strong indications for the condensation of frozen CN^- clusters on cooling is obtained, in particular from the appearance of a neutron-scattering

central peak [24]. Other studies have considered the modifications of the
elastic anomaly [25], or of the dielectric response [26]. On the basis of
those latter results, it was suggested that the glass would be of *relaxational*
type, meaning by this that there is no *real static* freezing. In this respect,
it should be noted that an electric field does not couple linearly to the
proper tensor component of the $\overline{CN}$ ordering. It is well possible that in spite
of a really frozen "director" network, the response to the field would appear
relaxational. To clarify this question, either high-resolution neutron scatter-
ing on the central peak, or a very careful search for static changes, such as
an anomaly in the static volume, are needed.

D. *Jahn-Teller glasses*

It was suggested very recently that in suitably diluted Jahn-Teller
(J-T) systems, both positive and negative effective Ising interactions between
the ions can be achieved [27]. Hence, glasses could be formed provided the
strains associated with dilution can be smaller than the J-T strains, as seems
to be the case for $Tm_x Y_{1-x} VO_4$ [28]. Another possibility of obtaining a glass
would be to populate higher levels which do show J-T coupling, although the
ground state is non J-T [29]. More work along these lines will be needed.

III. Structural glasses of RADP

A. *Motivations*

Why investigate structural glasses and, given the large number of
examples cited above, why a new one? The elusive nature of the freezing in
spin glasses stimulates a search for other than magnetic systems in which
couplings might occur that could reveal aspects remaining hidden in the spin
case. If something like an Edwards-Anderson order parameter [30] develops,
by symmetry it can couple linearly to all scalars, in particular to density.
This could be observable if the coupling strength were sufficient, as can be
the case for electrostriction as opposed to magnetostriction. Furthermore,
strictive effects are long-range. In favorable cases, they might justify a
mean-field approach, and might produce *real* transitions. With this in mind,
we searched for a random structural system with *large* striction. Hence, it

should be a concentrated solid solution rather than a dilute impurity system. Furthermore, the crystals should be obtainable with high structural perfection, as it is well-known that structural transitions can be strongly affected by defects that lead to quasi-static central peaks [31]. There is now growing evidence that the latter might be associated with randomly oriented frozen clusters, also a sort of "glass", that would form within a small temperature interval about T_c [32]. Structural systems in which these disturbing effects can be reduced to a negligible proportion seem to be the exception rather than the rule [33]. If such effects were enhanced by imperfect mixing and/or built-in strains, they might lead to transition rounding-off which, in many measurements, could be mistaken for a genuine glass manifestation. This ought to be avoided. Furthermore, "good" crystals, with little strain, will allow certain measurements which otherwise might become difficult or meaningless. Hence, the crystals should be easy to grow, preferably from water solutions as that method can yield material of exceptional quality [33]. The crystals should preferably be transparent, to allow optical measurements. More important, the solid solution should be stable over the entire concentration range (x = 0 to 1), there should be no chemical clustering, and it should be easy to check for this. Preferably, both extreme compositions should already be fairly well-known systems, and the nature of the frustration should be reasonably understood to allow modeling. Finally, it should be possible to apply the field conjugated to the order parameter of at least one of the pure systems, if not of both.

　　　None of the examples of Section II seemed able to satisfy completely at present this demanding list of requirements. However, at room temperature, the hydrogen-bonded phosphates form a large isostructural family of tetragonal crystals, rather easy to grow, and already extensively studied [34]. Considering KDP, RDP, and ADP, the room-temperature unit-cell volumes are 387.4, 422.3, and 424.7 $\overset{\circ}{A}^3$, while the c/a ratios are 0.936, 0.959, and 1.0067, respectively. The closeness of volume of RDP and ADP, and the fact that RDP has a continuous ferroelectric (FE) transition near 145 K [35], while ADP becomes antiferroelectric (AFE) near 148 K, gave strong hopes that continuous mixing and a genuine glass state could be achieved. So far, this is fully borne out by experiments, as will be summarized presently.

B. *Growth and phase diagram*

RADP is easy to grow by slow evaporation of water solutions. The only delicate point is that the distribution coefficient of NH_4^+ favors its incorporation in the solid [36]. For example, RADP-35 will grow from a solution with x ~ 30%. Hence, special measures are needed to obtain large homogeneous crystals, and their NH_4^+ content should be determined after growth. For this, chemical analysis, picnometry, or also x-ray determination of the lattice constants can be used as will be explained in detail elsewhere [36]. Using diffuse x-ray scattering on RADP-35, it was also found that there is no detectable tendency to chemical clustering [37]. No hint of any superstructure, or of a non-uniform diffuse background was seen at high temperatures, this in spite of the very different x-ray structure factors of Rb^+ and NH_4^+.

The phase diagram was obtained from a series of crystals by combination of optical and electrical means [Fig. 1(a)]. The birefringence of thin plates cut perpendicular to the FE axis [001], and provided with semitransparent electrodes was observed using a low-power He-Ne laser. On entering either the FE or AFE orthorhombic phases, near forward scattering from domain walls is readily observed. The direction of the scattering cross indicates the preferred domain-wall orientation, different in RDP and ADP [Fig. 1(b)]. The heavy lines of Fig. 1(a) correspond to the appearance of the scattering cross on cooling. For $0 < x \lesssim 0.20$, it is possible to pole the samples by cooling under an applied field. The birefringence $\Delta n_{12} = n_o^3 \rho_{63} P_3$ can then be measured meaningfully [38]. The electrooptic coefficient ρ_{63} was also determined for the PE phase. To this effect, the ac-electrooptic constant r_{63} was obtained as well as the dielectric constant ϵ_{33}'; ρ_{63} follows from $\rho_{63} = r_{63}/\epsilon_o (\epsilon_{33}' - 1)$. The result is almost temperature-independent and decreases slowly with increasing x. Extrapolating ρ_{63} to the FE phase, the birefringence data is expressed in terms of P_3, as shown in Fig. 2. It is remarkable that the saturation value of P_3 does not decrease on increasing x, and that strong metastability effects are observed at x = 0.17, with P_3 discontinuous on cooling but continuous on heating. For $0.20 \lesssim x < x_{cl} \sim 0.22$, we were not able to pole the samples, but the scattering cross sharply appeared on cooling.
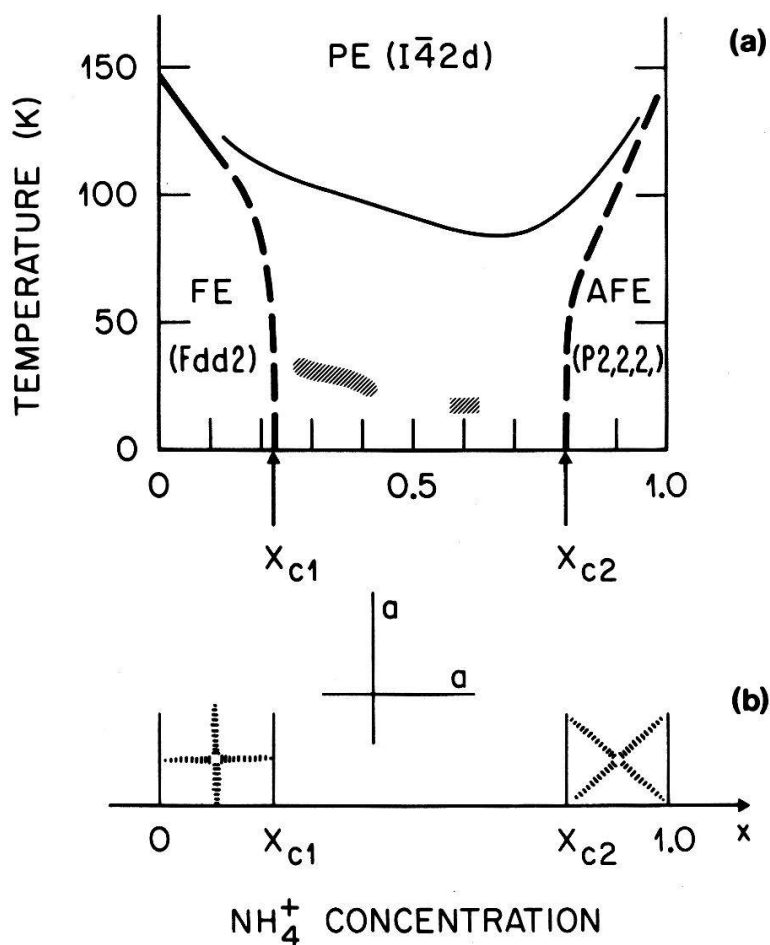
Figure 1.
(a) Phase diagram of RADP. Heavy solid line: apparently continuous transition;
dashed line: apparently first-order transition on cooling; thin solid line:
first appearance of anomalies at T_M; shaded region: second appearance of
anomalies at T_g.   (b) Near forward scattering patterns of the FE ($0 \leq x \leq x_{c1}$)
and AFE ($x_{c2} \leq x \leq 1$) domains when the a axes of the BCT unit cell are ori-
ented as shown.

For $x_{c1} < x < x_{c2}$ (see Fig. 1), *no cross is seen* down to $\sim$ 8 K. This, plus

detailed x-ray diffraction investigations on RADP-35 [37], indicate that the

symmetry most probably remains that of the PE tetragonal phase. Above x_{c2}, an

apparently first-order transition to the AFE phase occurs. The value $x_{c2} \sim$

0.80 in only indicative, as both the quality and the number of crystals avail-
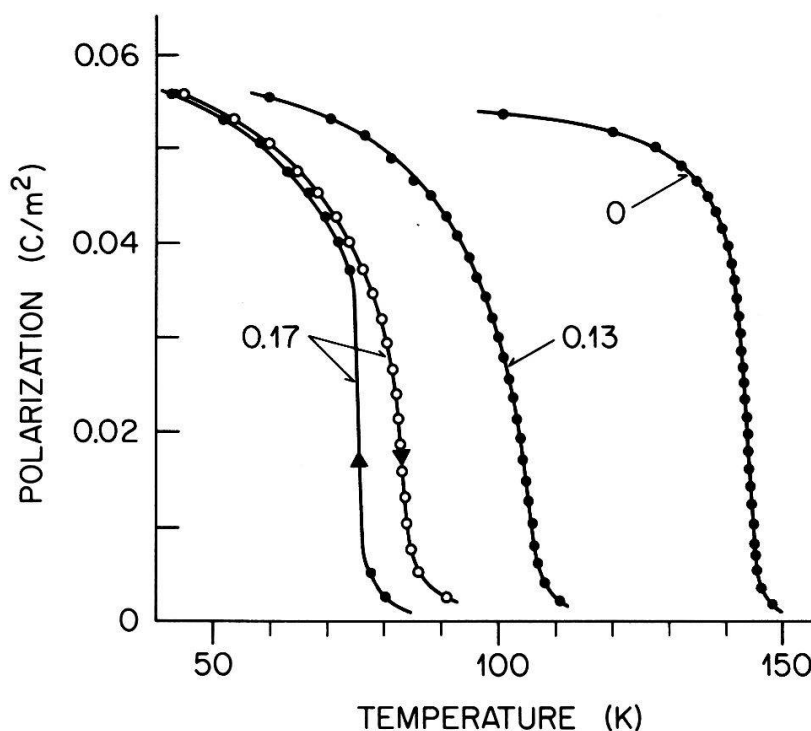
able in that region were somewhat insufficient.

Figure 2.
Polarization at typical concentrations $x < x_{cl}$, measured under moderate poling
fields E_3 of 1 to 2 kV/cm.

C. *The high-temperature anomalies*

In the intermediate composition range, two regions of anomalies are
seen, as described here and in the following subsection. The high-temperature
anomaly at $T_M \sim 100$ K is shown by a thin line in Fig. 1(a). It is character-
ized for $x = 0.35$ by the following three dielectric features [8]:

i) The low-frequency longitudinal dielectric constant ϵ'_{33}, which
obeys a Curie-Weiss law from room temperature down to T_M, starts departing
from that law near T_M. On cooling, ϵ'_{33} increases slower than the law predicts.

ii) Around T_M, an inflection point occurs on the low-frequency
transverse dielectric constant $\epsilon'_{11}(T)$. Above T_M, $d^2\epsilon'_{11}/dT^2$ is positive, where-
as it becomes negative below T_M.

iii) The natural birefringence of the sample, $(n_o - n_e)$, has a tem-
perature dependence above T_M which can be accounted for simply by lattice-
anharmonic effects. This is illustrated in Fig. 3, both for pure RDP and for
RADP-35. The measurements are obtained by counting extinction fringes as a
function of temperature; hence, they present birefringence changes $\Delta(n_o - n_e)$,
with an arbitrary origin. The solid lines in Fig. 3(a) are fits to the points

T > 110 K for RADP-35, or T > 146 K for RDP, using the following Debye expression:

$$\Delta(n_o - n_e) = n_1 - n_2 \frac{T}{\Theta} F(\frac{\Theta}{T}) , \qquad (1.a)$$

$$F(u) = \frac{3}{u^3} \int_0^u \frac{x^3 dx}{e^x - 1} . \qquad (1.b)$$

Here, n_1 and n_2 are constants and Θ is a Debye temperature determined by the fits. $F(u)$ is the appropriate Debye function for the internal energy [39]. Equation (1) results from the approximation that both n_o and n_e are proportional to the density. With $d\rho/dT = \gamma C_v/B$, where both the Grüneisen constant γ and the compressibility B are approximately constant, (1) follows. For pure RDP, below T_c the measured points depart suddenly from the extrapolated fit [Fig. 3(a)] due to the quadratic electrooptic effect [40]. The difference between the fit and the measurement [Fig. 3(b)] is proportional to P_3^2. A similar anomaly remains for RADP, although the departure from the fit is then progressive. All the above results are compatible with a gradual condensation and the development of a *local* polarization. In view of the sign of the effect on ϵ'_{33}, it is reasonable to presume that the condensation is mostly connected with lateral Slater configurations [41] favored by the nearby presence of several NH_4^+, although short-range AFE order does not develop, as demonstrated by diffuse x-ray scattering [37].

Is this condensation static or dynamic? There is good indication that there could be a partial freeze-out of these lateral Slater configurations. In particular, the curve x = 0.17 of Fig. 2 strongly suggests that on cooling, a long-range condensation that competes with FE ordering first occurs, in spite of the poling field of ~ 2 kV/cm. When the FE order finally prevails, then it also remains upon heating, and decreases gradually like at the lower concentration x = 0.13. Effects on the volume and on the lattice parameters, for example, on *c* which shows an anomalous decrease, are fully consistent with the above interpretation [37].
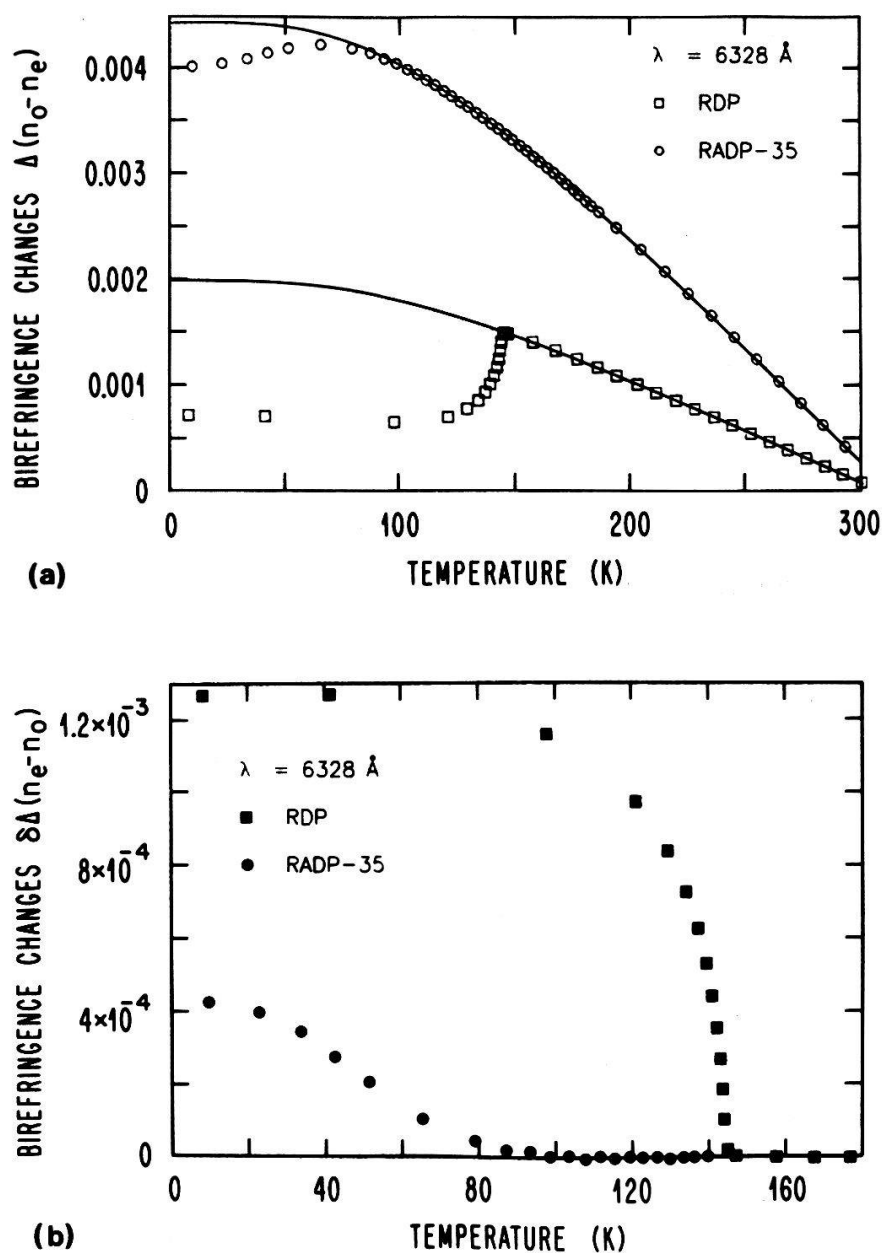
(a)

(b)

Figure 3.
Examples of the birefringence anomaly $\Delta(n_o - n_e)$ at $x = 0$ and $x = 0.34$. In
(a), the solid line is a fit to the high-temperature points that gave Debye
temperatures of 424 K for RDP and 415 K for RADP-35, respectively. In (b),
the difference between the low-temperature extrapolation of the anharmonic
behavior and the measured data is shown.

D. *The low-temperature anomalies*

The low-temperature anomalies, in the region $T_g \sim 40 \ldots 20$ K, occur approximately in the shaded regions of Fig. 1. They might also occur in other regions of x, for example, between 0.5 and 0.7, but so far measurements are insufficient to determine this with certainty. The best results have been obtained on RADP-35, and these anomalies will be described presently:

i) Dispersion of the longitudinal dielectric constant: $\epsilon_{33}(\omega,T)$ in this region develops a strong dispersion, measured from 30 Hz to 100 kHz [42]. The value of ϵ'_{33} drops from $\sim$ 140 at 35 K to $\sim$ 15 below 4 K, while the dielectric loss $\epsilon''_{33}(\omega,T)$ develops. Remarkably, a simple relation is found between ϵ' and ϵ'', indicating a distribution of relaxation times τ which is broad in ln τ [43]. Furthermore, this distribution cuts off towards long times with a cut-off frequency f_c that obeys a Vogel-Fulcher law [44]

$$f_c = f_o \exp [-T_E/(T - T_o)] , \qquad (2)$$

with physically meaningful values of f_o and T_E. For RADP-35, one finds $T_o \sim$ 11 K. Finally, the entire data for $\epsilon''_{33}(\omega,T)$ can then be collapsed to a single curve by suitable scaling [42]. NMR T_1 measurements performed at 30 MHz also support the above description [45]. However, if the sample is compressed along the *c*-axis, a direction that favors the freezing of lateral Slater configurations [46], the behavior can be changed to the extent that appreciable loss does not develop, and that $\epsilon'_{33}(\omega,T)$ maintains its high value down to at least 8 K. I shall return to a possible interpretation of this observation below.

ii) Dispersion of the transverse dielectric constant: in the same region, $\epsilon_{11}(\omega,T)$ exhibits effects that are similar in many ways, although the scaling to a Vogel-Fulcher law does not follow as simply as for ϵ_{33}. It appears that other relaxation components are still effective below T_o. This should be related to the fact that ϵ_{33} is properly the susceptibility corresponding to the order parameter P_3 of the frustrated FE phase, whereas ϵ_{11} bears a more complicated relation to that ordering. It suggests that the electric susceptibility of $(KCN)_x(KBr)_{1-x}$ might suffer from complications similar to the ϵ_{11} measurements here [26]. It cannot be ruled out that a

Vogel-Fulcher law would also be found if the response to the proper field
(a director rather than a vector) could be measured in the KCN-KBr system.

iii) Static anomalies, which can be seen on the electrooptic coef-
ficient r_{63} [8], or by measuring polarization currents upon "step" cooling
under an applied electric field. Figure 4 shows typical time dependences ob-
tained on a sample with free boundaries. The onset of "noise" around 50 K
(curve 2) is associated with a reduction of the "static" $|d\epsilon_c/dT|$. Curve 3
demonstrates a change of sign at "short" times, although ϵ_c still increases
at "long" times. Near 32 K, the negative sign persists to "long" times, so
that ϵ_c goes through a weak maximum. More anomalies in $d\epsilon_c/dT$ are seen at
lower temperatures around T_o. Around 50 K, diffuse satellites appear near
some Bragg reflections in x-ray scattering [37]. They are always very weak
and broad, but they grow on cooling, and indicate a very short-range order
with a periodicity of $4a$, although the structure always remains the tetrago-
nal structure of KDP. These results strongly suggest an elastic instability
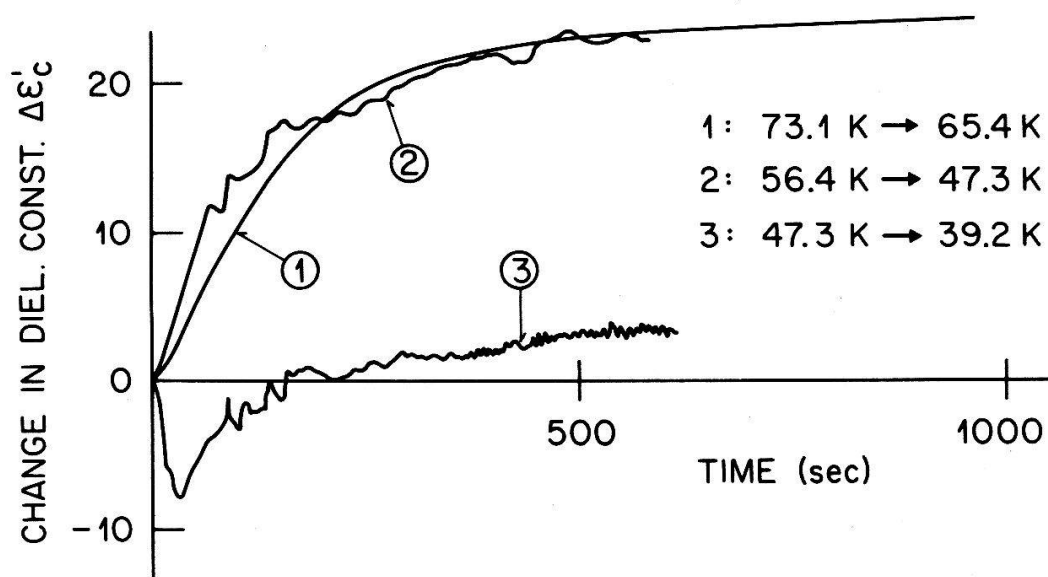
Figure 4.
Time development of the polarization current obtained by "step" cooling
RADP-35 under a constant static field of 117 V/cm. The cooling has approxi-
mately the shape of curve 1. It is slow due to the poor thermal contact (He
exchange gas). The starting and final temperatures are given for each step.
The vertical axis is in units of effective changes of the "static" dielectric
constant. A positive sign means that ϵ_c increases on cooling.

of Type-0, for which there is no symmetry-breaking, no microscopic soft mode, but just an unstable singular point in reciprocal space (q = 0) [47]. Such transitions are highly sensitive to the sample boundaries, and can produce the type of "noise" observed, as well as the pressure effects. Development of the Bragg satellites could then be understood in terms of local compensation for polarization-associated shears, whereas the compressibility anomaly would be related to quadratic electrostrictive effects unable to compensate locally.

E. *Theoretical aspects and summary*

A complete discussion of the system will clearly require consideration of percolation effects, strictive effects, and competing lateral and up-down Slater configuration. Furthermore, as already pointed out by Slater himself [41], configurations with an odd number of protons (1 or 3) on a PO_4 have to be allowed to be able to produce perturbations in the proton arrangement which do not immediately extend to infinity. Hence, these Takagi configurations [48], are likely to play a very important role in the glass. A simplified approach, based on an effective-crystal approximation and on a molecular-field theory of the glass [49], has been proposed [50]. It predicts a glass phase, but in view of the approximations involved (neglect of percolation, of Takagi configurations, and of strictive effects) it cannot pretend to describe the experimental results. Indeed, for example, it is not able to obtain the observed inflection point in ϵ'_{11}. Furthermore, it is based on a description of ADP which predicts only two low-temperature domains [51] instead of the four that should be obtained correctly.

To summarize, the structural glass proposed has a great resemblance to spin glasses. Preliminary results [52] on the specific heat show no discontinuity but a broad maximum in the region 40 ... 80 K, just as in spin glasses [1]. The dispersion of the susceptibility resembles the spin-glass case and, in one instance, magnetic satellites have also been seen far above T_g in Cu:Mn [53]. At this stage, there is good indication that the sequence of phenomena observed will find its explanation in the long-range condensation of at least two competing disordered structures, the first mostly based on lateral Slater configurations, the second on up-down configurations.

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