The Spherical Random Bond - Random Field Model and the Relaxor to Ferroelectric Transition

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Abstract. To check whether the recently proposed SRBRF model also adequately describes the relaxor to ferroelectric transition the temperature dependence of the static dielectric constant of PMN has been fitted to the SRBRF model. The results show that in contrast to dipolar glasses the mean coupling constant $J_0$ is here indeed close to the root mean square variance $J$. For $E \geq E_C$ $J_0$ can therefore become bigger than $J$ resulting in a transition from a relaxor to a ferroelectric state. The relaxor to ferroelectric cross-over in the non-linear dielectric response $a_3 = \chi_3 / \chi_1^4$ in the form predicted by the SRBRF model for $E \geq E_C$ has been observed in PLZT ceramics. The temperature dependence of the Edward-Anderson order parameter $q$ has been determined via NMR in PSN in the region of the ferroelectric transition and as well shows the $T$-dependence predicted for $J_0 > J$. The relaxor to ferroelectric transition can be thus well described by the SRBRF model.

INTRODUCTION

The relaxor transition [1,2] in substitutionally disordered perovskites is characterized by the appearance of nanosized polar clusters embedded in a non-polar matrix. [1,2,3] The disorder induced polar regions form far above the relaxor transition $[3] T_r$. The polar clusters in e.g. lead magnesium niobate (PMN), are formed when two or more Nb ions moving in a multi-site potential around the cubic perovskite sites begin to respond along with their surroundings as a single reorientable polar unit. The polarizations of the polar clusters are randomly oriented and the crystal remains macroscopically cubic both above and below the relaxor transition which is characterized by a giant frequency dependent dielectric anomaly. Compositional fluctuations will also induce randomly oriented pinned “chemical” clusters which act as sources of random fields. It should be also noticed that the off-center displacement of the ions are such that we have competing ferroelectric (FE) and anti-ferroelectric (AFE) interactions.

The above behavior can be described by the recently proposed spherical random bond - random field (SRBRF) model. [4,5,6] The model describes the randomly competing FE and AFE coupling between the reorientable polar clusters in the presence of random fields. Since the polar clusters - which are the basic reorientable dipoles in the structure - vary not only in their orientation but also in their size, the system can not be described by an ordering field of fixed length as in e.g. Ising type
systems. The dimensionless order parameter field $\tilde{S}_i$ which is related to the dipole moment of the $i$-th polar cluster is of variable length

$$\begin{array}{c}
-\infty \leq S_{i\mu} \leq \infty, \quad \mu = x, y, z
\end{array}$$

subject only to the closure relation

$$\sum_{i=1}^{N} \tilde{S}_i^2 = 3N$$

where $N$ is the total number of reorientable clusters. This and the existence of randomly competing FE and AFE interactions leads to the SRBRF Hamiltonian \[4,5,6\]

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} \tilde{S}_i \tilde{S}_j - \sum_i h_i \cdot \tilde{S}_i - g\vec{E} \cdot \sum_i \tilde{S}_i$$

where $g$ is an effective dipole moment corrected by the appropriate local field factor. The randomly frustrated bond couplings are characterized by the mean value

$$[J_{y}]_{AV}^c = \frac{J_o}{N}$$

and the variance

$$[J_{y}^2]_{AV}^c = \frac{J_o^2}{N}$$

whereas the random fields are characterized by the variance

$$[h_{ij}]_{AV}^c = \delta_{ij} \delta_{\mu\nu} \frac{\Delta}{J^2}$$

We further assume that the randomly frustrated interactions are infinitely ranged in view of the long range nature of the phonon mediated strain - polarization inter-cluster interactions. \[4,5,6\]

The evaluation of the average free energy now yields two limiting cases:

i.) For

$$J_o < \sqrt{J^2 + \Delta^2}$$

we get below
\[ T_f \approx \frac{J}{k} \]  

(5b)

a spherical glass without long range order.

ii.) For

\[ J_0 > \sqrt{J^2 + \Delta} \]  

(6a)

we get, on the other hand, a ferroelectric state below

\[ T_c \approx \frac{J_0}{k}. \]  

(6b)

It should be noted that a critical value \( \Delta_c = J_0^2 - J^2 \) exists so that for \( \Delta > \Delta_c \) there can be no long range order at any temperature. The corresponding phase diagram is shown in Fig. 1.

![Phase diagram of a relaxor according to the SRBRF model.](image)

**FIGURE 1.** \( T - J_0 / J \) phase diagram of a relaxor according to the SRBRF model.

The spontaneous polarization is here for \( J_0 > \sqrt{J^2 + \Delta} \) given by

\[ P^2 = \left[ 1 - \left( \frac{J}{J_0} \right)^2 \right] \left[ 1 - \left( \frac{T}{J_0} \right)^2 \right] - \frac{\Delta}{J^2}, \quad T < T_c \]  

(7a)

and the Edwards-Anderson glass order parameter \( q \) as [6]
\[ q = 1 - T / J_0, \quad T < T_c. \quad (7b) \]

In the presence of an external electric field \( J_0 \) is expected to vary as

\[ J_0(E) = J_0(E = 0) + \alpha E^2. \quad (8) \]

For \( J_0^2(E) > J^2 + \Delta \) a relaxor to ferroelectric transition takes place as indeed observed. [7,8]

Previous studies [4,5,6] have shown that the SRBRF model adequately describes the paraelectric to relaxor transition. Here we wished to check whether the SRBRF model is also capable of properly describing the relaxor to ferroelectric transition. First we wished to see why the ferroelectric state in relaxors can be established so much more easily than in dipolar glasses. For this purpose we decided to determine the mean coupling constant \( J_0 \) and the root mean square variance \( J \) in PMN from the temperature dependence of the static linear susceptibility of PMN. If the SRBRF model is correct \( J_0 \) must be smaller but close to \( J \) so that with a relatively small electric field the condition \( J_0^2(E) > J^2 + \Delta \) can be met. Secondly we wished to see whether the relaxor to ferroelectric cross-over in the dielectric non-linearity \( a_3 = \chi_3 / \chi_1^4 \) follows the prediction of the SRBRF model. Last but not least we wanted to see whether the \( T \)-dependence of the glass order parameter \( q \) in a ferroelectric relaxor follows the predictions of the model for \( T < T_C \).

**THE STATIC DIELECTRIC SUSCEPTIBILITY**

The temperature dependence of the field cooled static dielectric susceptibility of PMN [9] is shown in Fig. 2 together with the fit to the SRBRF model. The linear susceptibility is here given by [3,4]

\[ \chi_1 = \frac{\beta(1-q)}{1-\beta J_0(1-q)}, \quad \beta = \frac{1}{kT} \quad (9a) \]

whereas \( q \) is determined from [2,3,4]

\[ q = \beta^2 J^2 \left( q + \frac{\Delta}{J^2} \right)(1-q)^2 \quad (9b) \]

The fit is rather good and shows that in zero bias field \( J_0 \approx 193 \text{ K} \) is indeed smaller but rather close to \( J \approx 219 \text{ K} \).
FIGURE 2. Temperature dependence of the static dielectric constant of a PMN crystal. The solid line is the fit to the SRBRF model with $J_0 = 193$ K and $J = 219$ K.

FIGURE 3. Temperature dependence of $a_3 = \chi_3 / \chi_1^4$ according to the SRBRF model for i) $E = 0$ and ii) $E \gg E_c$. 
The Relaxor to Ferroelectric Cross-Over in $a_3$

As discussed previously [4,5,6] the SRBRF model predicts that the static dielectric non-linearity $a_3 = \chi_3 / \chi_1^4$ shows in zero bias d. c. field a sharp peak at the freezing temperature

$$T_f = \sqrt{J^2 + \Delta / k}$$

(10)

$\chi_3$ is here the third order dielectric susceptibility. This has been indeed observed. [5] The SRBRF model also predicts for $E > E_C$ a cross-over from the increasing temperature behavior of $a_3$ to the monotonously decreasing $T$-dependence of $a_3$ in the whole temperature region above $T_f$ (Fig. 3). This has been observed in 9/65/35 PLZT ceramics [8] at $E = 8.5$ kV/cm > $E_c$ (Fig. 4). The obtained results are quite analogous to the ones found in ferroelectric TGS.

\[\text{FIGURE 4. Experimentally observed temperature dependence of } a_3 = \chi_3 / \chi_1^4 \text{ in PLZT ceramics for } E = 8.5 \text{ kV/cm} > E_c.\]

NMR and the $T$-Dependence of $q$ for $T < T_C$

The $T$-dependence of the $^{93}\text{Nb}$ NMR spectra of an annealed PSN single crystal exhibiting a relaxor to ferroelectric transition around $T_C \approx 300$ K has been measured [10] at a Larmor frequency $\nu_L(\text{Nb}) = 92.9$ MHz and at an orientation $B_0 || [001]$. Two components corresponding to “ordered” and “disordered” PSN were observed. The Edwards-Anderson order parameter $q$ is here related [4,5] to the second moment $M_2$ of the corresponding frequency distribution $f(\nu)$:
The observed $T$-dependence of $q$ is compared with the predictions of the SRBRF model in Fig. 5. The fit is rather good.

**FIGURE 5.** Temperature dependence of the Edwards-Anderson glass order parameter $q$ as determined by $^{93}$Nb NMR in PSN in the region of the relaxor to ferroelectric transition.

**CONCLUSIONS**

The above results show that:

i.) In contrast to dipolar glasses, $J_0$ is close to $J$ in relaxors. This explains why a ferroelectric state can be easily induced by an external electric field in relaxors but not in dipolar glasses. 

ii.) The relaxor to ferroelectric cross-over in the dielectric non-linearity $a_3$ in the form predicted by the SRBRF model has been indeed observed in PLZT ceramics.

iii.) The $T$-dependence of the Edwards-Anderson order parameter $q$ has been determined by NMR in PSN in the region of the relaxor to ferroelectric transition and agrees with the SRBRF model.

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