MODELING OF POLAR CLUSTERS IN DISORDERED PEROVSKITES: THE S-K MODEL WITH TUNNELING

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Abstract: The polar clusters generated by random non-central impurities in quantum paraelectrics determine to a great extent the complex dielectric behaviour observed in systems like SCT, KTN or KTL. The competition between a quantum paraelectric phase and an impurity-driven ferroelectric or glass phase depends on the concentration and on the nature of the interaction between clusters. This work presents a simple model in which each cluster is represented by a quantum two level system involving an effective Ising dipolar moment η and a tunneling energy A. The interactions between clusters are taken into account by following the guide-lines of the Sherrington-Kirkpatrick model for spin glasses. General expressions for the polarization (P) and the Edwards-Anderson order parameter (q) are given and the phase diagram involving temperature, the normalized mean interaction energy J_0/J and tunneling energy A/J_0 is built.

Keywords: Solid-solid transitions; domains; glass phase; ferroelectricity.

INTRODUCTION

Quantum paraelectric with non-central impurities like KTL ($Li_xK_{1-x}TaO_3$), KTN ($KTa_{1-x}Nb_xO_3$) or SCT ($Sr_{1-x}Ca_xToO_3$) display interesting and complex dielectric properties at low temperatures[1,2]. In the pure compounds (x=0), the ferroelectric order is suppressed by quantum fluctuations and the material remains in a paraelectric phase. The linear electric susceptibility χ_l increases

to very high values as the temperature decreases, and saturates at very low temperatures. The general temperature dependence of $\chi_1(T)$ is well described by the Barrett law [3].

The presence of dopants induces electric dipoles that are randomly distributed in the host lattice and are capable of being reoriented between several directions dictated by the symmetry of the lattice [4,5]. Due to the high susceptibility of the system, the local dipole field polarizes the lattice and originates the rise of local and highly correlated polar domains, with dimensions of the order of 1-100 nm [6]. Within a certain approximation, each polar domain can be described by its effective or dressed dipolar moment η.

At very low dopant concentrations, the nano-domains interact very weakly and the system behaves like a quantum super-paraelectric. As x is increased, dielectric peaks arise at finite temperatures, non-linear susceptibilities become more intense, dielectric dispersion and relaxation become more complex and aging and ergodicity breaking is observed [6-10]

The nature of dipolar order stabilized at low temperatures depends on the nature of the cluster interaction, as well as on their concentration. For high enough concentrations ($x>X_c$) an impurity-driven transition to a more or less disordered ferroelectric phase is observed. At intermediate concentrations ($x>X_g$), random-site electric dipoles may freeze into a glass like polar phase.

Mean-field models were used to describe the contributions of the random polar clusters to linear and non-linear susceptibilities. The conventional series expansion and a classic Langevin-type approximation were used to describe the contributions of the host lattice and the clusters respectively [6]. This classical approach is at variance with the importance of quantum fluctuations and, moreover, implicitly assumes that the host lattice and of the polarized clusters produce independent contributions to χ(T,E). More recently, the transverse Ising model was used to interpret both the linear and the non-linear electric susceptibility in pure strontium titanate [11]. Along the same lines, the same model was adapted to KTL by considering two sets of interacting pseudo-spins, describing the host lattice and the dopants, respectively [12]. These models have the drawback of neglecting the effects of disorder and the possible freezing of dipoles or the onset of a glass phase.

In a recent work we discussed the linear and non-linear susceptibilities in low doped SCT by using a model where the dipolar moments within each cluster were represented by an equivalent quantum two-level system [13]. Effects of disorder were taken into account and the competition between ferro and glass phases were discussed by using appropriate analytic solutions.

The idea of considering a finite tunneling between up and down states of an effective pseudo-spin to describe the dielectric properties of some disordered dielectrics is not new. In fact, the simplest prototype model for a proton glass such as RADP ($Rb_{1-x}(NH_4)_xH_2PO_4$), as an example, is the random-exchange version of the Ising model with a transverse field representing the tunneling of protons [14,15]. This model has been previously applied to describe random-fields tend to smear out the dielectric cusp observed at the glass transition or to discuss the dynamics of the freezing transition in a deuteron glass. However, the idea of representing the polar clusters in systems like SCT or KTL as random interacting quantum two level systems is simple and stresses the importance of the quantum fluctuations induced by the host lattice.
In this work, we report general expressions for the temperature and field dependence of the Edward-Anderson [16] order parameter (q) and of the electric polarization (P) of interacting two level systems with an effective dipolar moment $\pm\eta$. Following the guidelines of the Sherrington-Kirkpatrick model [17], the interaction is considered to be random by assuming that the coupling constants follow a Gaussian distribution with a mean energy J_0 and width J. The equations for q and P are numerically solved and the phase diagram involving the temperature, the normalized mean energy J_0/J and the tunneling energy A/J_0 is constructed.

RESULTS

As referred to above, each polar cluster is represented by a quantum two level system involving an Ising dipolar moment and a tunnelling energy A. The hamiltonian of a single cluster in the presence of an applied field can therefore be represented by the matrix:

$$\hat{h} = \begin{bmatrix} \eta E & -A \\ -A & -\eta E \end{bmatrix} \qquad (1),$$

where E, η and A are the applied field, the effective dipolar moment of the cluster and the tunneling energy, respectively. Referred to the eigenstates of (1), the dipolar moment of each cluster is:

$$\overline{\eta} = \left\langle \psi_+ \middle| \hat{D} \middle| \psi_+ \right\rangle = -\left\langle \psi_- \middle| \hat{D} \middle| \psi_- \right\rangle = \eta \frac{\eta E}{\sqrt{A^2 + (\eta E)^2}} = \eta \cos(\theta) \qquad (2)$$

where $|\psi_\pm\rangle = \cos(\frac{\theta}{2})|+\rangle \mp \sin(\frac{\theta}{2})|-\rangle$ are the eigenvectors of (1) with energies $e_\pm = \pm(A^2 + \eta^2 E^2)^{\frac{1}{2}}$ and $\theta = \tan^{-1}(-\frac{A}{\eta E})$.

A tunneling energy $A \neq 0$ has therefore the two-fold effect of reducing the effective dipolar moment of the cluster ($\eta \to \overline{\eta}$) and modify the Zeeman energy ($\mp\eta E \to e_\pm$).

The inter-cluster interactions can now be included, by considering the coupling $\hat{H}_{\text{int}} = \sum_{\langle i,j \rangle} J_{ij} \overline{\eta}_i \overline{\eta}_j$, where $\langle \text{i,j} \rangle$ means that each distinct pair is counted once.

For simplicity we can assume now the general framework of the mean-field model of Sherrington and Kirkpatrick for spin glasses. Due to the random distribution of the clusters, one considers that J_{ij} follows a Gaussian distribution with average interaction energy J_0 and standard deviation J. The general results of the S-K model [17] for the local electric field E(z), the electric polarization P and the Edwards-Anderson order parameter q can therefore be used with the necessary modifications:

$$E(z) = E_0 + \frac{J_0}{\eta} P + \frac{J}{\eta} \sqrt{q}\, z \qquad (3)$$

$$P = \frac{\eta N}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{-\frac{z^2}{2}} \frac{\eta E}{\sqrt{A^2 + (\eta E)^2}} \tanh\left(\frac{\sqrt{A^2 + (\eta E)^2}}{k_B T} \right) dz \qquad (4)$$

$$q = \frac{\eta^2}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{-\frac{z^2}{2}} \frac{(\eta E)^2}{A^2 + (\eta E)^2} \tanh^2\left(\frac{\sqrt{A^2 + (\eta E)^2}}{k_B T} \right) dz \qquad (5)$$

These set of equations must be solve numerically in order to obtain the temperature dependence of P(T) and q(T). We used Simpson rule to integrate and a self-consistent iterative method to solve equations 3-5. The calculations

were performed assuming no external applied electric field. The temperature dependencies of P and q, as well as critical temperatures, were obtained as functions of the normalized mean interaction energy J_0/J and tunneling energy A/J_0. The observed phases are paraelectric when P=0 and q=0, ferroelectric when P≠0 and q≠0, and glass when P=0 and q≠0.

Figure 1 shows the corresponding phase diagram, involving the critical temperatures, the normalized mean interaction energy J_0/J and tunneling energy A/J_0. For A=0 (no tunneling energy) the model exactly reduces to the mean-field theory of Sherrington and Kirkpatrick for spin glasses as shown in the inset of fig. 1. Accordingly, ferroelectric order is found for $J_0/J>1.25$ and $T<T_c= J_0\eta^2/k_B$ (T_c being the Curie Temperature), and a glass phase is obtained for $J_0/J<1$ and $T<T_f= J\eta^2/k_B$ (T_f being the freezing temperature).

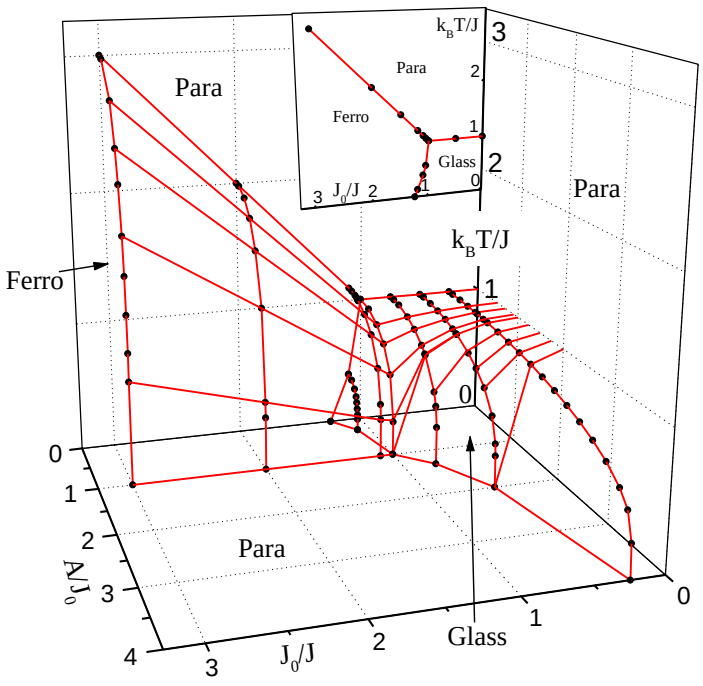

FIGURE 1: Phase diagram involving temperature, the normalized tunneling energy A/J_0 and the normalized mean interaction energy J_0/J (for $\eta=1$). The inset shows the results for A=0 (J_0/J-k_BT/J plane).

In the intermediate region ($1<J_0/J<1.25$), the glass phase is stable at low temperatures and a ferroelectric phase appears, sandwiched between this phase and the paraelectric phase. This behaviour, known from the S-K model, can be clearly seen in the temperature dependence of the polarization, as shown in figure 2a). In fact, $P = 0$ and $q \neq 0$ at low temperatures (fig. 2b), which is characteristic of the glass phase. This stability of the glass phase at low temperatures has been considered a consequence of the mean field approach.
However, a finite tunneling energy tends to decrease T_f and suppresses the glass phase, as can be observed in figures 2a) and 2b). In fact, for high enough tunneling energies, the system becomes ferroelectric below T_c and the P *versus* T curves do not present the characteristic maximum at intermediate temperatures.
Figures 2c) and 2d) show the temperature dependencies of the polarization P and order parameter q for J_0/J in the ferroelectric region ($J_0/J>1.25$). As the tunneling energy A is increased, the Curie temperature T_c progressively

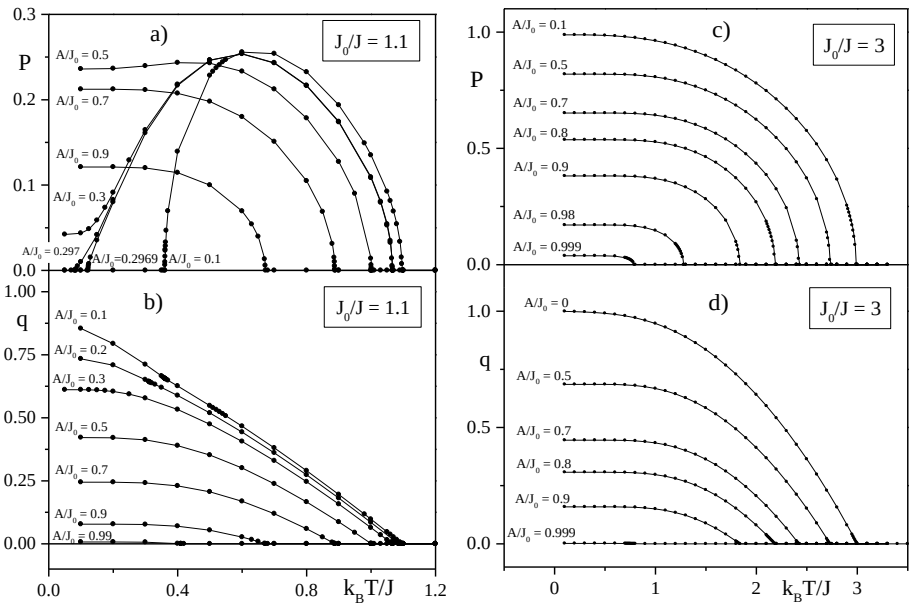

FIGURE 2: Temperature dependencies of the electrical polarization P and order parameter q in the phase diagram regions: a) and b) $1<J_0/J<1.25$; c) and d) $J_0/J>1.25$.

decreases towards zero, so that for $A \geq J_0$ the ferroelectric phase is not stable. In the glass region ($J_0/J<1$), the tunneling energy reduces the freezing temperature T_f and, for $A \geq J$, the system remains paraelectric.

The previous analysis shows that the stabilization of the glass phase depends essentially on the relative values of the tunneling energy A and the parameter J, while the stabilization of the ferroelectric phases results from the balance between the tunneling energy A and the intensity of the ferroelectric coupling J_0. This can be clearly seen in figure 3, where A/J_0 is plotted as a function of J_0/J: the line representing the transition from paraelectric to glass corresponds to the condition A=J, while the line corresponding to the transition from ferroelectric to paraelectric corresponds to the condition $A=J_0$

In conclusion, the model reported incorporates a non-zero tunneling in the S-K model and allows an analysis of the competition between different phases found in some disordered quantum paraelectrics. It may provide a simple framework for an analysis of phase diagrams and temperature dependencies of the linear and non-linear susceptibilities, in systems like SCT and KTL. This analysis of the susceptibilities in these systems is presently under course.

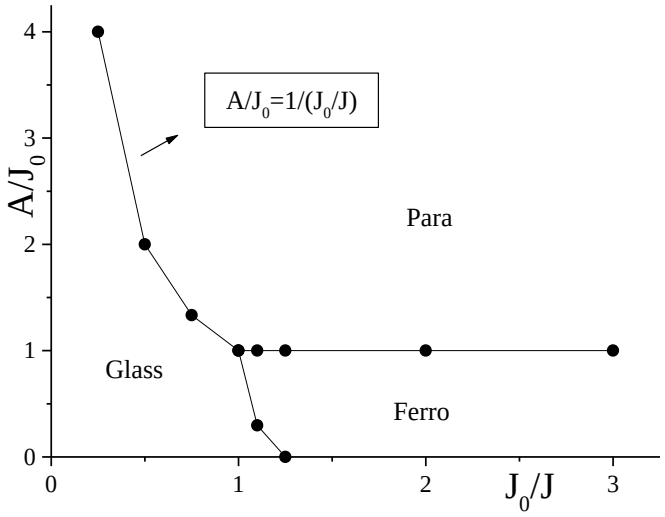

FIGURE 3: Projection of the phase diagram on the T=0 plane, showing the stability ranges of the different phases

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