# Impurity-induced phase transition in quantum paraelectrics

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The transverse Ising model is applied to $Li_xK_{1-x}TaO_3$-like quantum paraelectrics using different kinds of pseudospins representing different perovskite unit cells. Impurity-induced paraelectric-ferroelectric phase transitions are found for appropriate parameters. The substitutional ions act as pinning centers in the system. The dependences of the Curie temperature, spontaneous polarization, and dielectric susceptibility on the concentration of the substitutional ions are calculated. The theoretical results are compared with experimental ones and good agreement is obtained. [S0163-1829(98)01521-5]

## I. INTRODUCTION

There has been great interest in quantum paraelectrics such as $SrTiO_3$ and $KTaO_3$ in recent years due to their peculiar properties at low temperature.[1–5] It has been observed that the dielectric permittivity $\epsilon_{33}$ of $SrTiO_3$ increases to a value as high as 24 000 upon cooling and remains constant below 3 K.[1] The paraelectric phase is stabilized by quantum fluctuations, i.e., by zero-point motion or tunneling excitations of the dipolar degrees of freedom.

Quantum paraelectrics containing impurities, such as $Li_xK_{1-x}TaO_3$ (KTL), $KTa_{1-x}Nb_xO_3$ (KTN), and $Sr_{1-x}Ca_xTiO_3$ (SCT) have also been studied extensively using various experimental techniques.[2–5] It is found that the dielectric permittivity at low temperature has similar features to pure quantum paraelectrics when $x$ is very small. At a critical value $x_c$, however, an impurity-induced phase transition from paraelectric to ferroelectric occurs. The spontaneous polarization at $T=0$ and the Curie temperature increase with increasing $x$. As to the theoretical aspect, much attention has been paid to the nature of the quantum paraelectric phase. As far as the impurity-induced paraelectric-ferroelectric phase transition is concerned, a local random field theory has been employed by Vugmeister and Glinchuk.[4] They demonstrated that the concentrational phase transition can occur in highly polarizable crystals, if the impurity concentration is high enough. On the other hand, in alkali halide systems, such as $K_{1-x}Li_xCl$, such a transition is impossible since the crystal is weakly polarizable. Obviously, both the nature of the quantum paraelectric and the doped impurities are responsible for the occurrence of the concentrational phase transition.

The transverse Ising model has been successful in describing the phase transitions of ferroelectrics[6] and related inhomogeneous systems.[7] Recently, it was extended to pure quantum paraelectrics.[8] Among others, the Barrett formula,[9] which depicts the temperature dependence of the dielectric permittivity of pure quantum paraelectrics at low temperature, was deduced. In the present work, doped quantum paraelectrics are studied within the framework of the transverse Ising model. In order to take the effects of different ions into account, two kinds of pseudospins are used in the system. Owing to their different interactions and tunneling frequencies, respectively, phase transitions are induced at sufficiently large concentrations. They bear many of the characteristics observed in doped quantum paraelectric systems.

## II. METHODOLOGY

For a pure quantum paraelectric, such as $SrTiO_3$ or $KTaO_3$, the onset of ferroelectric instability is hindered by quantum fluctuations. Within the framework of the transverse Ising model, this can be modeled by setting $2\Omega > ZJ$, where $\Omega$ is the tunneling frequency, $J$ is the interaction constant between pseudospins, and $Z=6$ is the coordination number of elementary cells in the cubic lattice.[6] For quantum paraelectric perovskites containing impurities, there are two kinds of atoms either at the $A$ sites (e.g., KTL) or at the $B$ sites (e.g., KTN). Therefore there should be two kinds of pseudospins in the system. One kind of pseudospin represents the pure quantum paraelectric, the other kind of pseudospin refers to the doped impurities in the system. The Hamiltonian of the system is

$$H=-\sum_i \Omega_i S_i^x-\frac{1}{2}\sum_{ij} J_{ij}S_i^zS_j^z - \sum_m \Omega'_m\sigma_m^x-\sum_{mj} J'_{mj}\sigma_m^zS_j^z, \quad (1)$$

where the interactions between dopant pseudospins are neglected. $S_i^x$ ($S_i^z$) and $\sigma_m^x$ ($\sigma_m^z$) are the $x$ ($z$) components of the host and dopant pseudospins, $\mathbf{S}_i$ and $\sigma_m$, respectively.

 

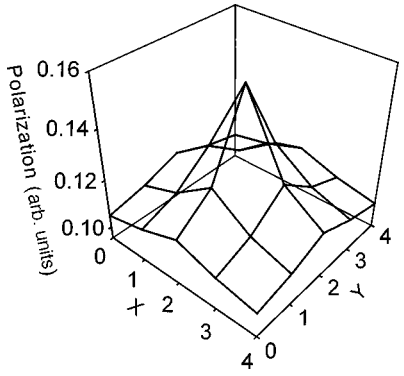


FIG. 1. Polarization profile on the (001) plane of a KTL-like crystal at $T=0$ (see text), where the units in the $x$ and $y$ directions are the lattice constants.

$\Omega_i$ and $\Omega'_m$ are the individual tunneling frequencies. $J_{ij}$ and $J'_{mj}$ are the host-host and host-dopant pseudospin interaction constants, respectively. $i$ and $j$ sum over all host pseudospins, and $m$ sums over dopant pseudospins. The thermal average of the $z$ component of a host pseudospin is[6]

$$\langle S_i^z\rangle = \frac{F_i^z}{2|\mathbf{F}_i|}\tanh\frac{|\mathbf{F}_i|}{2k_BT}, \tag{2}$$

where $\mathbf{F}_i$ is the effective field on the $i$th pseudospin, $\mathbf{F}_i = (-\Omega_i, 0, -\Sigma_j J_{ij}\langle S_j^z\rangle - \Sigma_m J'_{im}\langle\sigma_m^z\rangle)$, and $k_B$ is the Boltzmann constant. An analogous equation holds for the dopant pseudospin component $\langle\sigma_m^z\rangle$ except that the effective field becomes $\mathbf{F}_m = (-\Omega'_m, 0, -\Sigma_j J'_{mj}\langle S_j^z\rangle)$. Thus, Eq. (2) represents a system of coupled nonlinear equations involving pseudospin components $\langle S_i^z\rangle$ and $\langle\sigma_m^z\rangle$ with various individual interaction parameters $\Omega_i$, $\Omega'_m$ and $J_{ij}$, $J'_{im}$. The spontaneous polarization $P$ is proportional to the average $z$ component of the pseudospin. Despite the mean-field approximation, which makes the bilinear exchange interaction tractable, the solutions bear local characteristics in the same sense as experienced, e.g., in the treatment of surfaces.[7]

In order to simplify our calculations, the impurities are assumed to be distributed uniformly in the crystal. Only nearest-neighbor interactions are considered at this stage. The calculations are carried out with two procedures. In one calculation, $J_{ij}$ and $J'_{im}$ are assumed to be the same while $\Omega'_m$ is smaller than $\Omega_i$. In the other calculation, $J'_{im}$ is assumed to be larger than $J_{ij}$, and the tunneling frequencies are independent of the kinds of pseudospins. In both cases, $2\Omega_i$ is assumed to be larger than $\Sigma_j J_{ij}$, but $2\Omega'_m$ is smaller than $\Sigma_j J'_{mj}$. The two procedures give coherent results. The spontaneous polarization and Curie temperature of the system are obtained by calculating the value and stability limit of the pseudospins.

## III. RESULTS AND DISCUSSION

Figure 1 shows the polarization profile on the (001) plane of a KTL-like crystal at $T=0$. It is calculated for a dilution $x=0.016$, pseudospin vectors of length $|S|=1/2$, interaction constants $J_{ij}=1.0$ and $J'_{mj}=1.5$ for host-host and host-dopant pseudospin interactions, respectively, and a tunneling frequency $\Omega_i=\Omega'_m=3.05$. Similar results are found when

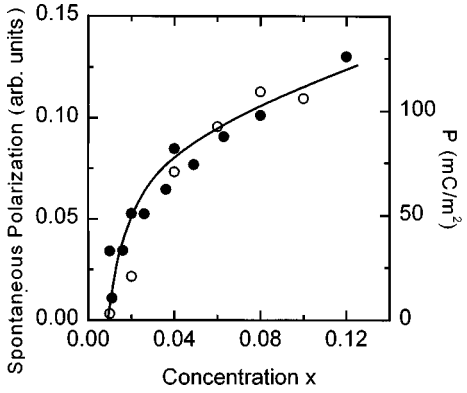


FIG. 2. Average polarization as a function of concentration as calculated with parameters as in Fig. 1 (solid line, left-hand scale) and as measured at $T\to 0$ on KTL (Refs. 11,12) and KTN (Ref. 13) (multiplied by 1.66) (solid and open circles, respectively; right-hand scale).

choosing $J_{ij}=J'_{mj}=1.0$ for all pseudospin pairs and $\Omega_i=3.05$ and $\Omega'_i=2.0$ for host and dopant pseudospins, respectively. The polarization at the pinning point (doped impurity) is much higher than that in the remaining area. The nearer the point to the doped ion, the larger the spontaneous polarization. That means that the ferroelectric distortion in the crystal is not uniform. The largest distortion is at the dopant sites similarly as has been found from lattice dynamical calculations.[10] This is easily understood from Eq. (2), e.g., in the case $J_{ij}=J'_{mj}$, where $\langle S_i^z\rangle/\langle\sigma_m^z\rangle = |\mathbf{F}_m|/|\mathbf{F}_i|$. Here, $\langle\sigma_m^z\rangle > \langle S_i^z\rangle$ follows immediately from $\Omega'_m < \Omega_i$. A similar argument holds for the case $J'_{mj} > J_{ij}$.

The average spontaneous polarization at $T=0$ as a function of concentration $x$ is shown in Fig. 2, for the same set of parameters used for Fig. 1. The polarization appears at a critical concentration $x_c=0.009$ and increases quickly when $x$ is small. The increase gets slower and slower with increasing $x$. The solid and open circles are the experimental data obtained at $T\to 0$ on KTL (Refs. 11,12) and KTN,[13] respectively. Obviously, the calculated concentration dependence agrees within errors with the experimental results.

The spontaneous polarization at the dopant sites is much higher than the average value. Figure 3 shows the ratio of the polarization at the dopant sites to the average value at different $x$. It is interesting to find that this ratio increases with

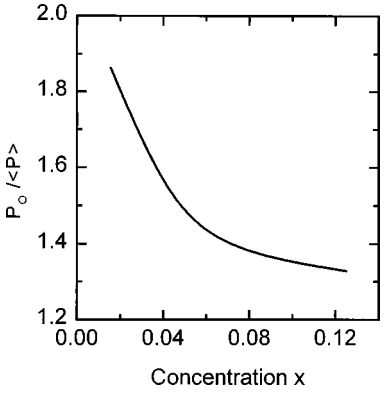


FIG. 3. The ratio of the polarization at dopant sites to the average value as a function of concentration at $T=0$.

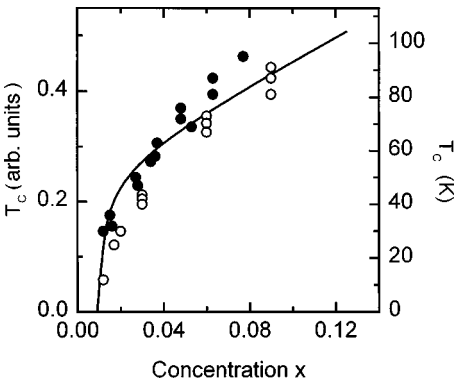


FIG. 4. Concentration dependence of the Curie temperature as calculated with parameters as in Fig. 1 (solid line, left-hand scale) and as measured on KTL (Ref. 12) and KTN (Ref. 5) (solid and open circles, respectively; right-hand scale).

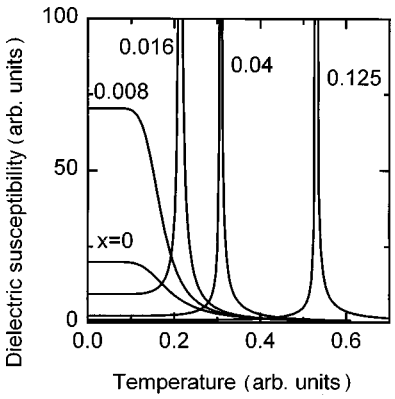


FIG. 5. The temperature dependences of the dielectric susceptibility of doped quantum paraelectrics for various impurity concentrations (labeled on the curves). Calculation parameters are the same as in Fig. 1.

decreasing $x$ or increasing temperature (not shown). At large $x$ or low temperature, the polarization profile is more uniform than that at small $x$ or high temperature. At small $x$ or high temperature the ferroelectric distortion is concentrated at the dopant sites while the distortion in the matrix is nearly zero. This result agrees well with the lattice dynamical calculation on KTL (Ref. 10) and the experimental observations in KTN (Ref. 14) and SCT.[15] In these materials, the dopant ions are considered to be the nuclei of polar clusters. They increase in size upon cooling and condensate at $T<T_c$ to form ferroelectric domains on a nanometric scale.

The Curie temperature as determined self-consistently from Eq. (2) also increases with increasing $x$ (see Fig. 4), quickly when $x$ is small and slowly at larger $x$. This is in accordance with the $x$ dependence of the spontaneous polarization. It can be seen that the theoretical prediction is compatible with experimental observations as shown by the common plot with data of KTL (Ref. 12) and KTN.[5] In the literature,[2] it has been pointed out that $T_c$ is proportional to $(x-x_c)^{1/2}$ when $x$ is small. This relation gives a reasonable fit to the experimental results at small $x$ but is not valid at large $x$. According to Fig. 4 both experimental and theoretical data vary linearly with concentration in the large $x$ limit.

The remaining differences between the observed and the calculated dependences of $T_c$ vs $x$ in Fig. 4 might partially be remedied by choosing more appropriate individual parameters entering Eq. (1). In addition, effects of randomness have finally to be taken into account. We do not expect large changes due to compositional fluctuations of the impurities. Preliminary calculations involving random distributions of the impurity pseudospins $\sigma_m$ seem to show that both $T_c(x)$ and $P_s(T\rightarrow 0)$ are quite stable against these microscopic fluctuations. More significant effects, however, are expected to arise from unavoidable intrinsic random fields.[5] They are known to smear the phase transitions of doped quantum paraelectrics and give rise to nanodomain structures below $T_c(x)$.[15,16] Because of their disordering nature they are expected to shift $T_c(x)$ to lower temperatures. Systematic studies of these effects are presently underway.

Irrespective of remaining deviations our model qualitatively reveals all basic features of doped quantum paraelectrics, e.g., as shown in Fig. 5, the calculated $x$ and $T$ dependences of the dielectric susceptibility $\chi=dP/dE$ come very close to the observed ones.[16] In particular, below the critical concentration $x_c$ the low-$T$ susceptibility becomes strongly enhanced when compared with the $x=0$ value, whereas critical divergences are observed at $T_c(x)$ when $x>x_c$. Details will be published elsewhere.

## IV. CONCLUSION

Our calculations have shown that many aspects of the phase transitions observed in doped quantum paraelectrics can be described by a transverse Ising model involving a regular distribution of impurities with appropriate exchange and tunneling parameters. Further studies have to take into account explicitly the effects of microscopic randomness, in particular in the vicinity of $x_c$, and of intrinsic random fields. In addition, the concentration, temperature, and electric field dependences[8] of the dielectric susceptibility will be of great importance for understanding the interesting properties of doped quantum paraelectrics.

## ACKNOWLEDGMENT

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