Phase transitions in the antiferroelectric-ferroelectric mixed systems

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Phase diagram of solid solutions of antiferroelectric and ferroelectric materials like PbZr\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3} (PZT), Rb\textsubscript{x} (NH\textsubscript{4})\textsubscript{1-x}H\textsubscript{2}PO\textsubscript{4} (RADP) is calculated at the region \(0 < x < 1\). Antiferroelectric and ferroelectric order parameters (which correspond respectively to the difference and sum of two sublattices ions shifts) were introduced for antiferroelectric host lattice. Small admixture of ferroelectric component was considered as a random electric field source. The influence of this field on both aforementioned order parameters was calculated. Self consistent averaging with calculated random field distribution function made it possible to obtain the system of equations for order parameters of mixed system. The antiferroelectric \(T_a\) and ferroelectric \(T_c\) phase transition temperature concentrational dependence was expressed through the transition temperatures of the composition and members. The obtained \(T_a(x)\) dependence was shown to fit pretty good the observed values for PZT and RADP. The application of the proposed theoretical approach to other types of mixed systems is discussed.

I. INTRODUCTION

Mixed antiferroelectric-ferroelectric systems like PbZr\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3} (PZT), Rb\textsubscript{x} (NH\textsubscript{4})\textsubscript{1-x}H\textsubscript{2}PO\textsubscript{4} (RADP) (0 \(\leq\) \(x\) \(<\) 1) attract much attention of scientists because of their unusual properties and phase diagram peculiarities. These anomalies made PZT material useful for many technical application [1]. In particular compositions of PZT enriched by Zr \((x < 0,1)\) appeared to be useful for application in the novel branches of electronic technique (see e.g. [2], [3] and ref. therein). Theoretical description of the properties and phase diagram nearby antiferroelectric phase transition is hard problem because of complexity of description of antiferroelectric phase itself. The proximity of free energies of antiferroelectric and ferroelectric state is known to be the characteristic feature of antiferroelectrics [4]. This proximity lead to dielectric permittivity anomalies and to the possibility to induce ferroelectric order by application of small enough electric field. The latter can be the clue of the reasons of ferroelectric phase appearance even at small \(x\) values. Small content of ferroelectric material in the mixed system can be considered as the source of electric dipoles and induced by them random electric field. Calculation of this field magnitude allowing for dipole-dipole interaction via ferroelectric and nonferroelectric soft modes had shown that mean field is induced by the interaction via ferroelectric soft mode whereas other soft modes increase mean square field [5]. The supposition that nonzero internal mean field can destroy antiferroelectric order by the same way as external field made it possible to describe semiquantitatively the observed phase diagram [5].

In present work we performed detailed calculations of phase diagram of mixed antiferroelectric-ferroelectric system for the region of small concentration of ferroelectric material. The obtained data fitted pretty good measured phase diagram for PZT and RADP. The application of proposed method for calculation of phase diagrams in different mixed ferroelectrics is discussed.

II. GENERAL EQUATIONS

Let us begin with the description of antiferroelectric phase. In Ising model free energy \(F\) can be written as [4]:

\[
F = \frac{1}{2} J_S \sigma^2 + \frac{1}{2} J_A S^2 - p^* E \sigma - T \frac{1}{2} \ln \left[ 2 \cosh \left( 2 \beta \left( p^* E + J_S \sigma \right) + 2 \cosh \beta J_A S \right) \right]
\]

(1)

where \(\beta \equiv 1/(kT)\), effective dipole moment \(p^* = (\varepsilon_a - 1) \gamma_a b / 3\), \(\varepsilon_a\) and \(\gamma_a\) are antiferroelectric component susceptibility and Lorentz factor respectively, \(p = Zb\) (\(\pm b\) are the positions of two-well potential minima), \(E\) is electric field, \(\sigma\) and \(S\) are respectively ferroelectric and antiferroelectric transition order parameters (\(\sigma = \xi/\eta, S = \eta/b\), \(\eta\) being mean homogeneous and inhomogeneous displacements respectively): \(J_A = T_A\) and \(J_S = T_S\) are respectively antiferroelectric transition and...
Curie temperatures. Note, that in this model mean dipole moment of the unit cell has the form:

\[ d_r = Z(\bar{e} \pm \eta) \]  

(2)

Thus we consider the simplest two-sublattice model of antiferroelectric.

### A. Order parameters

Eq. (1) leads to the following expressions for the order parameters:

\[ \sigma = \frac{sh2\beta(p^*E + J_S\sigma)}{ch2\beta(p^*E + J_S\sigma) + ch(2\beta J_A S)} \]  

(3)

\[ S = \frac{sh2\beta E f + J_S\sigma + ch(2\beta J_A S)}{ch2\beta(p^*E + J_S\sigma) + ch(2\beta J_A S)} \]

Eqs. (3)-4 describe antiferroelectric component, i.e. mixed system at \( x = 0 \). Ferroelectric component corresponds to \( x = 1 \) and its order parameter \( L \) in Ising model has the form [4]

\[ L = \frac{th\beta(E_0 L + d^*E)}{E_0 L} \]  

(4)

where \( E_0 = T_{cmf} \) is mean field, that defined ferroelectric transition temperature, \( d^* \) is effective dipole moment of ferroelectric component ions.

Addition of small amount of ferroelectric component to antiferroelectric one leads to appearance of random electric field \( \varepsilon \), induced by electric dipoles of this component in the mixed system. Mean field in the mixed system has to include the contribution from ferroelectric component and from ferroelectric order parameter of antiferroelectric component namely

\[ \bar{e} = J_S(1-x)\sigma + xE_0 L \]  

(5)

This field as the most probable one has to define the position of maximum of random field distribution function \( f(\varepsilon, \sigma, L) \). It is equal to \( \delta(\varepsilon - J_S(1-x)\sigma - xE_0 L) \) in mean field approximation. Beyond of this approximation one has to take into account random field, i.e. to substitute \( E + \varepsilon \) (\( E \neq 0 \)) or \( \varepsilon \) (\( E = 0 \)) for \( E \) in Eqs. (3), (4) and to perform averaging with random field distribution function. This yields:

\[ \sigma = \int_{-\infty}^{\infty} \frac{sh2\beta p^*(\varepsilon + E) f(\varepsilon, \sigma, L)d\varepsilon}{ch2\beta p^*(\varepsilon + E) + ch(2\beta J_A(1-x) S)} \]

\[ S = \int_{-\infty}^{\infty} \frac{sh2\beta J_S(1-x)S f(\varepsilon, \sigma, L)d\varepsilon}{ch2\beta p^*(\varepsilon + E) + ch(2\beta J_A(1-x) S)} \]  

(6)

\[ L = \int_{-\infty}^{\infty} th(\beta d^* (\varepsilon + E)) f(\varepsilon, \sigma, L)d\varepsilon \]

One can see that in mean field approximation when \( f(\varepsilon, \sigma, L) \) has the form of \( \delta \)-function Eqs. (3) give Eqs. (3) at \( x = 0 \) and Eq. (3) at \( x = 1 \).

Eqs. (3) are general expressions for order parameters dependence on concentrations and characteristics of mixed system components. Note, that in the case \( S = 0 \) (both components of mixed system are ferroelectrics) the equations for \( \sigma \) and \( L \) have the same form as it has to be expected.

### B. Transition temperatures

Let us proceed now to calculations of the transition temperatures \( T_a \) (to antiferroelectric phase) and \( T_c \) (to ferroelectric phase) dependence on concentration. For the phase transitions of the second order these temperatures can be obtained from Eqs. (3) in the limit of \( \sigma \to 0, S \to 0, L \to 0 \). In such a limit one can simplify the integrands in Eqs. (3) substituting \( ch2\beta J_A S \approx 1, sh2\beta J_A S \approx 2\beta J_A S \) and representing the distribution function in the form:

\[ f(\varepsilon, \sigma, L) = f_0(\varepsilon) - \left( \frac{J_S x \sigma}{p^*} + E_0 x L \right) \left( \frac{df}{d\varepsilon} \right)_{\sigma=L=0} \]  

(7)

Here \( f_0(\varepsilon) \) is the distribution function in the case of mean field absence.

Keeping in mind that \( f_0(\varepsilon) \) is even parity function in aforementioned limit Eqs. (3) give:

\[ \sigma = \left[ (1-x)J_S \sigma + xE_0 L \frac{p^*}{d^*} \right] \beta I(x) \]

\[ S = (1-x)\beta J_A SI(x) \]

\[ L = \left[ (1-x)J_S \sigma \frac{d^*}{p^*} + E_0 x L \right] \beta I(x) \]

\[ I(x) = \int_{-\infty}^{\infty} f_0(y)dy \]  

(8)

Integral (8) has to depend on concentration because of dependence on \( x \) of the distribution function width.

The solution of the system of Eqs. (3) yields:

\[ T_a = (1-x)J_AI_a(x), T_c = [(1-x)J_S + xE_0] I_c(x) \]  

(10a)

or in dimensionless variables
\[ \tau_a = \frac{T_a}{T_A}, \tau_c = \frac{T_c}{T_S}; \lambda = \frac{T_{\text{emf}}}{T_S} \] (10b)

Eq. (10b) can be rewritten as

\[ \tau_a = (1 - x) I_a(x); \tau_c = [x \lambda + (1 - x)] I_c(x) \] (10c)

Here \( I_a(x) \) and \( I_c(x) \) are integrals at \( \beta = \beta_a \) and \( \beta = \beta_c \) respectively. One can see, that the transition temperatures are defined by the corresponding transition temperatures and concentrations of the components of mixed system and random field distribution function characteristics.

Equations (10) define concentrational dependence of transition temperature, i.e. phase diagram of mixed system for small concentration of ferroelectric component. One can see, that Eqs. (10) give the correct values in mean field approximation:

\[ T_a = T_A, T_c = T_S \text{ at } x = 0 \text{ and } T_a = 0, T_c = E_0 = T_{\text{emf}} \text{ at } x = 1. \]

C. Critical concentrations

Random field induced by electric dipoles of ferroelectric component of mixed system can destroy completely antiferroelectric phase at some concentration of the dipoles. This concentration \( x = x_{ca} \) is known to be critical concentration at which \( T_a = 0 \), so that antiferroelectric phase exists at \( x < x_{ca} \) only. On the other hand ferroelectric phase in the mixed system arises at \( x > x_{cc} \) where \( x_{cc} \) is critical concentration for ferroelectric phase transition. It has to be \( T_c \geq T_A \) at \( x \geq x_{cc} \). Therefore critical concentrations \( x_{ca} \) and \( x_{cc} \) in the region \( x \ll 1 \) can be obtained from the equations \( T_a = 0 \) (\( x_{ca} \)) and \( T_c = T_A \) (\( x = x_{cc} \)). Let us limit ourselves by the case \( \Delta = 0 \), which is of importance both for case of PZT and RADP on the "edges" of phase diagram. To perform the calculations on the base of Eqs. \( (10c) \) we have to know concentrational dependence of integrals \( I_{a,c}(x) \) defined by the distribution function \( f_0(y) \). For electric dipoles as random field sources it can be represented in Gaussian form (see [6] for details):

\[ f_0(y) = \frac{1}{2 \sqrt{\pi \sigma}} \exp \left( -\frac{y^2}{4 \sigma} \right) \] (11)

\[ c = \frac{16\pi}{15} d^2 r_c^{-3} \xi = c_0 x \] (12)

Here \( \varepsilon_0, a \) and \( r_c \) are respectively dielectric permittivity, lattice constant and correlation radius connected with soft ferroelectric mode of antiferroelectric component of mixed system. Parameter \( \xi \geq 1 \) takes into account dipole-dipole interaction via antiferroelectric and other nonferroelectric soft modes [5]. Performing changing of variables in integrals \( I_{a,c} (\beta_m E = u) \), we obtain that this reduces just to renormalization of parameter \( c_0 \) in \( (12) \), giving \( c_m = c_0 m^2, m = p^*, d^* \).

To map correctly the interval \( 0 < z < \infty \) into interval \( 0 < x < 1 \) we adopt following parametrization for \( z_{ca} \)

\[ z_{c,a} = \varphi_{c,a}(x) p^3; \rho = \frac{r_c}{a}, \varphi_c(x) = \frac{1 - x}{1 - (1 - x) \rho}, \varphi_a(x) = \frac{x}{1 - x \rho}, \mu \rightarrow \infty. \] (13)

Let us begin with critical concentration for antiferroelectric phase transition.

At \( \beta = \beta_a \) Eqs. (10a) with respect to Eqs. (11), (12) at \( \beta_a \rightarrow \infty \) yields

\[ I_a(x) = \frac{1}{\sqrt{x}} \frac{\tau_a}{\sqrt{\pi} q_a}; q_a = \frac{c p^*}{T_A} \] (14)

Substitution of Eq. (14) into the expression for \( \tau_a \) (see Eqs. (10c)) gives the following equation for critical concentration \( x_{ca} \):

\[ \frac{x_{ca}}{1 - x_{ca}} = \frac{1}{\pi q_a^2}. \] (15)

Eq. (15) has been solved numerically during the calculation of \( \tau_a \).

Critical concentration for ferroelectric phase transition can be obtained by the same way, but in the limit of \( T_c \rightarrow T_A \), i.e. \( \tau_c \rightarrow T_A/T_S \), this ratio being larger or close to unity. Since in such a limit integral \( I_c(x) \) can be calculated only numerically we shall obtain \( x_{cc} \) value in the next section devoted to numerical calculations with two fitting parameters \( \lambda = T_{\text{emf}}/T_S \) and \( q_c = c_d^*/T_S \).

III. PHASE DIAGRAM OF MIXED ANTIFERRO-FERROELECTRIC SYSTEM

Phase diagram, i.e. concentrational dependence of antiferroelectric and ferroelectric phase transition temperature was calculated with help of Eqs. (10). Integrals \( I_{a,c}(x) \) were calculated numerically. The obtained phase diagram is represented in Fig.1 in the region of small concentration of ferroelectric component for several values of dimensionless parameters \( q_a, q_c \) and \( \lambda \) (see Eq. (10b)). One can see from Fig.1 that antiferroelectric phase transition critical concentration \( x_{ca} \) increases with \( q_a \) decrease, its values being close to those calculated on the base of Eq. (15). The obtained critical concentration of ferroelectric phase transition several times smaller than that for antiferroelectric transition. This seems to be the result of proximity of free energies and may be of \( T_S \) and \( T_A \) which is characteristic feature of antiferroelectrics. The dimensionless transition temperature to antiferroelectric phase \( \tau_a \) decreases with concentration increase for all the considered parameters, whereas the behaviour of that to ferroelectric phase \( \tau_c \) depends on the choice of the parameters values. In particular \( \tau_c \) can increase or decrease with increase of electric dipoles concentration (see Fig.1).
Physically these types of behaviour depend on distribution function width and ratio ($\lambda$) of ferroelectric phase transition temperatures $T_{cmf}$ of ferroelectric component of mixed system to that of antiferroelectric component $T_S$: the smaller the distribution function width and the larger $\lambda$ value, the larger ferroelectric phase transition temperature in the mixed system.

**IV. DISCUSSION**

4.1. Let us begin with comparison of obtained data with experiment. The prominent example of mixed ferro-antiferro system is known to be $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ($0 \leq x \leq 1$), where $\text{PbZrO}_3$ is antiferroelectric with transition temperature from cubic paraelectric phase to rhombic antiferroelectric phase at $T_A = 500$ K and $\text{PbTiO}_3$ is ferroelectric with transition temperature from cubic paraelectric phase to tetragonal ferroelectric phase at $T_{cmf} = 763$ K. Phase diagram of mixed PZT system was investigated in many papers, but mainly at $T \geq T_{room}$ (see e.g. [6] and ref. therein). Therefore critical concentration $x_{ca}$ is known, and $T_a = 300$ K at $x = (5 - 6)\%$. One can see that the curve for $q_a = 1.7$ gives $T_a \simeq 300$ K at $x = 0.06$ and $x_{ca} \approx 0.11$. General form of calculated $\tau_a$ concentration dependence looks like experimental curve at $x < 0.1$ (Fig.1). There is a scattering of experimental data for ferroelectric phase transition temperature at small $\text{PbTiO}_3$ content ($x < 0.05$) because of influence of some uncontrolled defects and impurities on $T_c$ value. The most probable behaviour of $T_c$ is its slight increase (Fig.1) [6]. Such behaviour is similar to the calculated curve with $q_c = 1.7$ and $\lambda = 7$.

Another important example of mixed ferro-antiferro system is $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ ($0 \leq x \leq 1$) as a representative of hydrogen-bonded material. It was studied in many details (see e.g. [7]). $\text{RbH}_2\text{PO}_4$ (RDP) undergoes a ferroelectric phase transition at $T_{cmf} = 146$ K, $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) becomes antiferroelectric near $T_A = 148$ K. In mixed RADP system antiferroelectric transition temperature $T_a$ decreases with increase of RDP content and $T_a = 0$ K near $x = 0.2$ of RDP admixture, i.e. $x_{ca} \approx 0.2$ [8]. Substitution of this $x_{ca}$ value into Eq. (14) gives $q_a \approx 1$. One can see from Fig.2 that the curve, which corresponds to $q_a = 1.175$ fits the experimental points. Contrary to PZT there is no data about existence of ferroelectric phase transition at small ($< 10\%$) content of RDP. The reason for this difference can be the approximately equal values of $T_{cmf}$ and $T_A$ in RADP whereas they are different in PZT. Because of this theoretical parameter $\lambda \approx T_A/T_S \sim 1$ in RADP and at $\lambda = 1$ $\tau_c = T_c/T_S$ curve may be lower than $\tau_a$ curve and only antiferroelectric phase transition exists. One can see from Fig.2, that proposed theory explains the observed behaviour of ferroelectric phase transition decrease with increase of antiferroelectric component concentration and observed critical concentration $x_{cc}$ ($q_c = 1.424$, $\lambda = 1.1$).

Note that tuneling has to be taken into account for mixed systems of KDP family. Preliminary calculations have shown, that tuneling result into change of fitting parameters values.

Therefore the proposed theory describes pretty good phase diagrams of PZT and RADP for small $x$ values. Note, that only for small $x$ ($x < 0.2$) Ti and Rb ions can be considered as impurities randomly distributed in $\text{PbZrO}_3$ and $\text{NH}_4\text{H}_2\text{PO}_4$ matrices so that they can be the sources of random field.

4.2. The proposed theory can be applied for another types of mixed systems. For example, mixture of two ferroelectric systems $(F_1)_{1-x}(F_2)_x$ at $x < 0.1$ described with the help of Eqs. (6), (8) at zero antiferroelectric phase order parameter ($S = 0$). In this case the Equations for $\sigma$ and $L$ completely the same, i.e. $\sigma \equiv L$. In such situation mean field $E_0 = T_{cmf}$ is ferroelectric phase transition temperature of $F_1$ component whereas $F_2$ component defines the form and width of random field distribution function. Because the main physical idea of the proposed model is the inhibition and distortion of long range ferroelectric or antiferroelectric order by random electric field of different sources this model can be useful for description to relaxor ferroelectrics like $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN), $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ (PST), $\text{Pb}_1\text{La}_y\text{Zr}_{0.65}\text{Ti}_{0.35}\text{O}_3$ (PLZT, $y = 0.08; 0.09$). But the relaxors like PMN, PST are not solid solutions of two component, and in PLZT La ions are the impurities. Thus in all these materials there is only one ferroelectric component known as Burns reference phase (see [9] and ref. therein), which is $\text{PbZr}_{0.65}\text{Ti}_{0.35}\text{O}_3$ in the of PLZT. The transition temperature from para- to ferroelectric phase of the reference phase $T_{cmf} \equiv E_0$ defines the position of random field distribution maxima whereas the substitutional disorder, vacancies of lead and oxygen, impurities like La in PLZT define the distribution function width. Namely such a model has been proposed recently [10]. It permitted to describe the observed phase diagram of the relaxors, their dynamic and static properties peculiarities (see e.g. [11] and ref. therein).

Since the model is able to describe the distraction of long range order by any random field sources it can be useful also for description of solid solutions of ferroelectric and dielectric components, e.g. $\text{Ba(Ti}_{1-x}\text{Sn}_x\text{O}_3$ ($x < 0.1$). The observed in this material relaxor-like behaviour as well as change of phase transition order [12] can be the consequence of strong random field influence as it was shown recently [11,13]. Note that some residual ferroelectric domains were observed in another relaxor PLZT $(9/65/35)$ [14]. As the matter of fact, the dipole glass and mixed ferroglass phases (which appear in the relaxors with temperature lowering) can be considered as the reentrant phases with respect to this residual ferroelectric phase existing near the Burns temperature.

Therefore the generality of proposed model gives a possibility to apply it to various mixed systems which are solid solutions of ferro- and antiferroelectrics, two ferroelectrics, ferroelectric and dielectric etc. as well as to
ferroelectric relaxors.

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\( \tau_a : q_a = 1.5, x_a = 0.112 \)

\( \tau_c : q_c = 1.7, \lambda = 7 \)
Theory

Experiment (Fig.1 from Courtens, Ferroelectrics, 1987, v.72, p.234)

$q_a = 0.82$

$q_c = 1.8, \lambda = 3.4$

$\tau_a, \tau_c$