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Динамика решетки сегнетоэлектриков с примесями

Обсуждается динамика решетки сегнетоэлектриков с примесями на основе модели сегнетоэлектрика типа смещения. На основе метода самосогласованного фоионного поля совместно с приближением когерентного потенциала вычисляется фононный спектр неупорядоченной решетки и определяются зависимость постоянной Кюри-Вейсса $C(x)$ и температуры Кюри $T_0(x)$ от концентрации x для $0 \leq x \leq 1$. Получено качественное согласие с экспериментом для твердых сегнетоэлектрических растворов $Ba_{1-x}Sr_xTiO_3$ и $Pb_{1-x}Sr_xTiO_3$ и для $K(H_{1-x}D_x)_2PO_4$.

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Aksienov V.L., Braeter H., Plakida N.M. **E17 - 10782**

Lattice Dynamics of Ferroelectrics with Impurities

Lattice dynamics of displacive type ferroelectrics with impurities is considered. Using the self-consistent phonon theory and the coherent potential approximation the phonon spectrum of a disordered lattice is obtained and the dependence of Curie-Weiss constant and Curie temperature on the concentration x are calculated for $0 \leq x \leq 1$. Nonferroelectric impurities that can suppress the phase transition at some critical concentration, are also considered. Qualitative agreements with experiments for the solid solutions $(Ba-Sr)TiO_3$, $(Pb-Sr)TiO_3$ and $K(H-D)_2PO_4$ are obtained.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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Introduction

At the present time large experimental material is accumulated on the influence of defects on the properties of ferroelectrics (FE) (see, for example, refs. /1-3/). Under their influence the temperature of the phase transition (PT) changes essentially, and also the order of the PT. Defects, apparently, are the main reason for the appearance of the central peak /4/. For the understanding of the effects a detailed investigation of the dynamics of the disordered lattice of FE, having in accordance with the concept of Ginsburg-Anderson-Cochran unstable soft modes, is necessary. Although at present the lattice dynamics with defects is worked out well, there are only few works considering this problem for FE. In particular, in the work /5/ there was considered the influence of defects on the parameters of the vibronic model of FE, and in the work /6/ a Hamiltonian was proposed in the mean-field approximation for the description of the lattice dynamics of FE with defects. In these works it was shown, that in certain approximation the change of the temperature of the PT in ferroelectric solid solutions is connected with the change of the constant of anharmonic interaction and the limit frequency of the soft mode (see also the analysis of experimental data in ref. /7/). In this case for the description of displacive PT one can make use of a simple model of ferroelectrics /8/, generalized by us for the case of disordered lattice /9/.In this model only the dynamics of the sublattice of active atoms with harmonic coupling is considered, where each active atom is in an effective single-particle double minimum potential, caused by the other nonactive atoms. Assuming, that the random constants for the ferroelectric solid solution are the mass of the active atoms and the parameters of the single-particle potential, we use the coherent-potential approximation (CPA) together with the self-consistent phonon field approximation (SPFA), employed earlier by us for disordered FE /10/.The SPFA was used also in /11/ for the interpretation of the instability of the anharmonic lattice with vacancies.

In the next section the Hamiltonian of the model is considered, in Sec. 3 the phonon Green's functions of FE with defects are calculated. The determination of the Curie-temperature and the Curie-Weiss-constant is considered in Sec. 4, and in Sec. 5 the comparison of theoretical values with the experiments for the solid solutions $(Ba,Pb)_{1-x}Sr_xTiO_3$ /2/ and $K(H_{1-x}D_x)_2PO_4$ is made.

2. The Effective Model Hamiltonian

For the description of the PT in FE it is possible to pick out the group of atoms, which character of motion depends sufficiently on the temperature, so that they can

be considered as responsible for the PT in FE. The simplest model in this approximation is the dynamic model of harmonically coupled atoms, every of which is in a single-particle double minimum potential /8/. Assuming, that the active atoms can be of two sorts, $\alpha = 1,2$, we introduce the projection operators $t_{i\alpha}$, or

$$t_{i1} = t_i , \quad t_{i2} = 1 - t_i , \tag{1}$$

where $t_i = 1$ (or 0), if at the lattice site i is an atom of the sort 1 (or 2). We write the disordered model Hamiltonian of FE in the form:

$$H = \sum_{\alpha i} t_{i\alpha} \left(\frac{p_{i\alpha}^2}{2m_\alpha} - \frac{A_\alpha}{2} s_{i\alpha}^2 + \frac{B_\alpha}{4} s_{i\alpha}^4 \right) + \\ + \frac{1}{2} \sum_{\alpha\beta} \sum_{ij} t_{i\alpha} t_{j\beta} \phi_{ij} \frac{1}{2} (s_{i\alpha} - s_{j\alpha})^2 , \tag{2}$$

where the parameters A_α and B_α define, respectively, the height of the potential barrier, $u_{0\alpha} = A_\alpha^2 / 4B_\alpha$, and the distance between the two minima, $2s_{0\alpha} = 2\sqrt{A_\alpha / B_\alpha}$, in the potential, caused by the surrounding of the atom of the sort α. As usual, in the given model for simplicity only one mode is considered, which describes the displacement of the atoms $s_{i\alpha}$ along one of the crystal axes.

Defining the equilibrium atomic displacements below the phase transition point $b_\alpha = \langle s_{i\alpha} \rangle$ and the dynamic displacements $u_{i\alpha} = s_{i\alpha} - b_\alpha$, we introduce the effective harmonic Hamiltonian /10/

$$H_0=\sum_{i\alpha} t_{i\alpha}\{\frac{p_{i\alpha}^2}{2m_\alpha}+A_1\frac{\Delta_\alpha}{2}u_{i\alpha}^2\}+\frac{1}{4}\sum_{ij\alpha\beta}\sum t_{i\alpha}t_{j\beta}\phi_{ij}(s_{i\alpha}-s_{j\beta})^2. \quad (3)$$

In the SPFA/12/ the parameters of the Hamiltonian are defined from the variational principle by Bogolubov for the free energy

$$F_1=F_0+<H_0-H>_0, \quad \frac{\delta F_1}{\delta b_\alpha}=0, \quad \frac{\delta F_1}{\delta \Delta_\alpha}=0, \qquad (4)$$

where F_0 and $<\ldots>_0$ are the free energy and the statistical average for the system with the Hamiltonian (3). As a consequence we get the equations for the parameters Λ_α :

$$\Lambda_1=3(\eta_1^2+y_1)-1, \quad \Lambda_2=3\kappa(\eta_2^2+y_2)-\gamma \qquad (5)$$

and the equations for the parameters $\eta_\alpha = b_\alpha\sqrt{B_1/A_1}$; which are the equilibrium conditions for the atom of the sort α at the cell $i\,(t_{i\alpha}=1)$:

$$\eta_1^3-\eta_1(1-3y_1)+t_2f_0(\eta_1-\eta_2)=0,$$
$$\eta_2^3-\eta_2(\frac{\gamma}{\kappa}-3y_2)+t_1\frac{f_0}{\kappa}(\eta_2-\eta_1)=0, \qquad (6)$$

where $y_\alpha=<u_{i\alpha}^2>(B_1/A_1)$, $f_0=\sum_j\phi_{ij}/A_1$, $\gamma=A_2/A_1$ and $\kappa=B_2/B_1$. The average number of atoms of the sort α $t_\alpha=<t_{i\alpha}>_c$ is defined by the average $<\ldots>_c$ over all defect configurations. The system of equations (5), (6) describes the temperature-behaviour of the order-parameter η_α in the model in dependence on the values of the average quadratic displacements $<u_{i\alpha}^2>$, which are calculated self-consistently on the basis of the Green function (GF) method/13/.

3. The Phonon Spectrum of FE with Impurities

Let us consider the GF for displacement operators

$$D_{ij}(t-t')=<<u_i(t);u_j(t')>>=\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}e^{-i\omega(t-t')}D_{ij}(\omega), \qquad (7)$$

where the usual notations are used/12/. Taking into account (3) we get for the Fourier components of the GF (7) the equation:

$$[m_\alpha\omega^2-A_1\Lambda_\alpha]t_{i\alpha}D_{ij}(\omega)=\delta_{ij}+\sum_k\phi_{ik}D_{kj}(\omega). \qquad (8)$$

This equation is obtained for a given configuration of particles $\{t_{i\alpha}\}$ in (3), where it is taken into consideration that the random quantities are the potential Λ_α and the mass m_α only. In this case we can use for the calculation of the configuration averaged Green function the single site CPA, which describes quite well the main features of the vibrational spectrum of the disordered lattice.

Following the CPA/14/, we shall introduce a basic lattice of atoms of one sort (for definitness $\alpha=1$), every one of which is in a single-particle potential $\Delta_0(\omega)$, complex in general. Introducing the effective GF for the basic lattice in accordance with the equation:

$$[m_1\omega^2-A_1\Delta_0(\omega)]D_{ij}^{\circ}(\omega)=\delta_{ij}+\sum_k\phi_{ik}D_{kj}^{\circ}(\omega), \qquad (9)$$

we can write (8) in the form of the Dyson equation:

$$D_{ij}(\omega) = D^{\circ}_{ij}(\omega) + \sum_{k\alpha} D^{\circ}_{ik}(\omega) t_{k\alpha} V_{k(\alpha)} D_{kj}(\omega). \qquad (10)$$

The diagonal perturbation potential $V_{k(\alpha)}$ has the form:

$$\begin{aligned} V_{k(1)} &= A_1[\Delta_1 - \Delta_0(\omega)], \\ V_{k(2)} &= A_1[\Delta_2 - \Delta_0(\omega)] + (m_1 - m_2)\omega^2. \end{aligned} \qquad (11)$$

To obtain the coherent potential $\Delta_0(\omega)$ we shall employ the theory of multiple scattering. In accordance with this theory the equation (10) can be written, after the configuration averaging, in the form:

$$\begin{aligned} \bar{D}_{ij}(\omega) &= \langle D_{ij}(\omega) \rangle_c = D^{\circ}_{ij}(\omega) + \\ &+ \sum_{\ell k\alpha} D^{\circ}_{i\ell}(\omega) \langle T_{\ell(\alpha)k}(\omega) \rangle_c D^{\circ}_{kj}(\omega). \end{aligned} \qquad (12)$$

The scattering matrix $T_{\ell(\alpha)k}$ satisfies the equation:

$$T_{\ell(\alpha)k}(\omega) = V_{\ell(\alpha)}\delta_{\ell k} + \sum_{i\beta} V_{\ell(\alpha)} D^{\circ}_{\ell i}(\omega) T_{ik(\beta)}(\omega). \qquad (13)$$

Using now the single site approximation in the multiple scattering theory we get from the condition $\langle T_{\ell(\alpha)k}(\omega) \rangle_c = 0$ the equation for the coherent potential:

$$\sum_{\alpha} t_{\alpha} \frac{V_{k(\alpha)}}{1 - V_{k(\alpha)} D^{\circ}_{kk}(\omega)} = 0. \qquad (14)$$

Thus, the configuration averaged GF in (12) coincides with the effective one, which is translational invariant and can be written in the form:

$$\bar{D}_{ij}(\nu) = D^{\circ}_{ij}(\nu) = \frac{1}{A_1 N} \sum_{\vec{q}} \frac{e^{i\vec{q}(\vec{x}_i - \vec{x}_j)}}{\nu^2 - (\Delta_0(\nu) + f_0 - f_{\vec{q}})}, \qquad (15)$$

where the dimensionless quantities $\nu^2 = m_1\omega^2/A_1$ and $f_{\vec{q}} = (1/A_1)\sum_j \phi_{ij} \exp\{i\vec{q}(\vec{x}_i - \vec{x}_j)\}$ are introduced, $\vec{x}_i$ are the lattice sites of the three-dimensional lattice.

Besides configuration averaged GF (15) it is necessary to find the conditional averaged GF $\bar{D}_{i(\alpha)j}(\omega)$, which is determined by equation (8) under the condition, that there is an atom of sort α at the lattice site i and the average involve all possible configurations of the remaining (N-1) sites. In the same single site approximation of the CPA we obtain:

$$\bar{D}_{i(\alpha)j}(\omega) = \frac{D^{\circ}_{ij}(\omega)}{1 - V_{i(\alpha)} D^{\circ}_{ii}(\omega)}. \qquad (16)$$

This GF allowed to close the self-consistent system of equations (5), (6), so far as we have now the equation for the function $y_\alpha = \langle u^2_{i\alpha} \rangle B_1/A_1$:

$$\begin{aligned} y_\alpha &= \frac{\lambda}{2} \int_0^\infty \frac{d\nu^2}{\nu} \operatorname{cth}\frac{\lambda\nu}{2\theta} \left(-\frac{A_1}{\pi} \operatorname{Im} \bar{D}_{i(\alpha)i}(\nu + i\epsilon)\right) \approx \\ &\approx \theta \int_0^\infty \frac{d\nu^2}{\nu^2} \left[-\frac{A_1}{\pi} \operatorname{Im} \bar{D}_{i(\alpha)i}(\nu + i\epsilon)\right] = -\theta A_1 \operatorname{Re} D_{i(\alpha)i}(0), \end{aligned} \qquad (17)$$

where the approximate equality is written for classical case of high temperatures, $\theta \gg \lambda\nu_{max}$, and the dispersion relation for the retarded GF is used. Here the dimensionless temperature $\theta = kT/(A_1^2/B_1)$ and the quantum parameter $\lambda = (\hbar\sqrt{A_1/m_1})/(A_1^2/B_1)$ are also introduced. The phonon spectrum of the disordered lattice of FE is determined by the function $\rho(\nu^2) = -(A_1/\pi)\,\mathrm{Im}\bar{D}_{ii}(\nu + i\epsilon)$.

4. The Determination of the Curie-Temperature and Curie-Weiss-Constant

The Curie-temperature of FE with defects or FE solid solutions is determined usually from the maximum of the dielectric constant in the static $(\omega = 0)$, homogeneous $(\vec{q} \to 0)$ field. The general expression for the latter can be written in the presence of defects in the form:

$$\epsilon(\vec{q},\omega) = \epsilon_L - \frac{4\pi}{v_c}\frac{1}{N}\sum_{\substack{ij\\ \alpha\beta}}\langle t_{i\alpha}t_{j\beta}z_{i\alpha}z_{j\beta}D_{ij}(\omega)e^{-i\vec{q}(\vec{x}_i-\vec{x}_j)}\rangle_c, \tag{18}$$

where ϵ_L is the nonsingular at the PT part of dielectric constant of the lattice, $z_{i\alpha}$ is the effective charge of the ion of the sort α, $v_c = V/N$ is the volume of the unit cell. Assuming for simplicity, that $z_{i\alpha} \approx z$, we get for the static dielectric constant according to (15):

$$\epsilon(T) - \epsilon_L = \frac{\lambda}{\omega_0^2}\mathrm{Re}\frac{1}{\Delta_0(\nu = 0)} \approx \frac{C}{T - T_0}\Big|_{T \gtrsim T_0}, \tag{19}$$

where $\lambda = 4\pi z^2/v_c m_1$, $\omega_0^2 = A_1/m_1$. Therefore, the Curie-temperature is determined from the condition $\Delta_0(T_0) = 0$, which is equivalent to the vanishing of the gap in the phonon spectrum $\rho(\nu^2)$. For the Curie-Weiss-constant we get the equation:

$$C = \frac{\lambda}{\omega_0^2}\mathrm{Re}\left\{\frac{d\Delta_0(T)}{dT}\right\}^{-1}_{T \gtrsim T_0}. \tag{20}$$

To obtain the coherent potential from eqs. (14), (15) it is necessary to define the form of the function $f_{\vec{q}}$ or the model density of phonon states for the ideal lattice. It is convenient to choose the latter in the form:

$$\rho_0(\nu^2) = \frac{1}{N}\sum_{\vec{q}}\delta(f_0 - f_{\vec{q}} - \nu^2) = \frac{2}{\pi f_0^2}\sqrt{f_0^2 - (\nu^2 - f_0)^2}, \tag{21}$$

where $\nu^2 \leq 2f_0$. The integration over $\vec{q}$ with this spectrum in eq. (15) gives at $\Lambda_0(\nu = 0)$

$$\mathrm{Re}D^{\circ}_{ii}(\nu = 0) = -\frac{2}{f_0 A_1} \tag{22}$$

and the equation (14) for the determination of the Curie-temperature $\Delta_0(T_0)$ takes the form:

$$\frac{(1-x)\Delta_1}{1 + (2\Delta_1/f_0)} + \frac{x\Delta_2}{1 + (2\Delta_2/f_0)} = 0. \tag{23}$$

Substituting here $\Delta_\alpha(T)$ from (5) for $\eta_1 = \eta_2 = 0$ and using the expression for the correlation function (17) which, with eqs. (16), (22), has the form

$$y_a = \frac{2\theta}{f_0(1 + 2\Delta_a/f_0)} \qquad (24)$$

we find the dependence of the Curie-temperature on the concentration of defects $x = t_2$. For the calculation of the Curie-Weiss-constant $C(x)$ according to (19), it is necessary to investigate the solution of the system of equations (5), (14) - (17) for $T \gtrsim T_0$ and to determine $\Delta_0(\nu = 0, T)$. For the qualitative investigation we consider firstly the approximation $\Delta_a/f_0 \ll 1$ which is equivalent to the mean field approximation. In this case we can neglect the corrections in the denominator (23) and (24) and obtain for the coherent potential the expression:

$$\Delta_0(\nu = 0, T) = (1 - x)\Delta_1 + x\Delta_2 \qquad (25)$$

which is well-known in the literature as the virtual crystal approximation (VCA). For the Curie-temperature and the Curie-Weiss-constant we get the simple dependence

$$\frac{T_0(x)}{T_0(0)} = \frac{1 + (\gamma - 1)x}{1 + (\kappa - 1)x}, \quad \frac{C(x)}{C(0)} = \frac{1}{1 + (\kappa - 1)x}, \qquad (26)$$

where $T_0(0) = (\phi_0/6)(A_1/B_1)$, $C(0) = (4\pi z^2/v_c)(\phi_0/6B_1)$ are the parameters of the pure FE without defects.

Near the temperature $T_0(x)$ the single gaps in the spectrum

$$\Delta_1(T_0) = x\frac{\gamma - \kappa}{1 + (\kappa - 1)x}, \quad \Delta_2(T_0) = -(1 - x)\frac{\gamma - \kappa}{1 + (\kappa - 1)x} \qquad (27)$$

differ in sign which is determined by the relation of the width of the single particle potential in the defect site and in the matrix site: $\gamma - \kappa = (B_2/A_1)(s_{02}^2 - s_{01}^2)$. The increase (or decrease) of the Curie-temperature $T_0(x)$ in (26) is connected only with the increase, $s_{02} > s_{01}$, (or decrease, $s_{02} < s_{01}$) of the width of the single particle well, and the change of the Curie-Weiss-constant (and the deviation $T_0(x)/T_0(0)$ from the straight line) is determined by the change of the anharmonic constant $\kappa - 1 = (B_2/B_1) - 1$. If we take into consideration in the Hamiltonian (2) the dependence of the force constant ϕ_{ij} on the kind of atoms $\phi_{ij}^{\alpha\beta} = \{\phi_{ij}^{11}, \phi_{ij}^{12}, \phi_{ij}^{22}\}$ then in the mean field approximation the factor $s(x) = (1 - x)^2 + x^2(\phi_0^{22}/\phi_0^{11}) + 2x(1 - x)(\phi_0^{12}/\phi_0^{11})$ appears on the right-hand side (26), however, the relation

$$R(x) = \frac{T_0(x)}{C(x)} = \frac{T_0(0)}{C(0)}[1 + (\gamma - 1)x] \qquad (28)$$

keeps the same form. The comparison of (26), (28) with the experiment shows, that the mean field approximation, $\Delta_a/f_0 \ll 1$, does not work for the solid solutions of perovskites /2, 7/, - the function (28) is nonlinear, but describes sufficiently well FE of the KDP-type. The investigation of nonferroelectric-active defects, $A_2 < 0$, $\gamma = (A_2/A_1) < 0$ (see for example, Ca for $BaTiO_3$), represents some interest, too. In such systems a critical concentration x_c exists, when $T_0(x_c) = 0$. According to (26) we get $x_c = 1/(1 + |\gamma|)$.

5. The Comparison with Experiment

Besides qualitative estimations in the mean field approximation (26)-(28), we have also numerically solved the system of equations (5), (6) in the classical limit of high temperatures, taking into account (14)-(17) and (21). For the choice of the model parameters and the comparison with experiments the most investigated solid solutions of perovskites $(Ba,Pb)_{1-x}Sr_xTiO_3$ /2/ and $K(H_{1-x}D_x)_2PO_4$ /3/ were considered. In the first case we can assume, that the introduction of the defects Sr changes the effective single particle potential for the active complex TiO_3 , and in the second, according to the model /15/, the deuterization leads to the change of the parameters of the effective potential for the complexes K-PO_4, which undergo a transition of displacive type. The three parameters of the model, $\gamma = A_2/A_1$, $\kappa = B_2/B_1$ and $f_0 = \phi_0/A_1$, can be estimated through the characteristic energies:

$$\omega^2_{0a} = \frac{A_a}{m_a}, \quad \omega^2_D = \frac{\phi_0}{m_a}, \quad \tilde{B}_a = \frac{6B_a}{m^2_a}, \tag{29}$$

which can be determined by the low frequency phonon spectra of pure FE, (by the soft mode $\Omega^2_c(T) \approx \omega^2_0(T/T_0 - 1)$, by the average frequency of the spectrum ω_D) and by the thermodynamic data: $T_0 = \omega^2_0\omega^2_D/\tilde{B}$, $C = \lambda T_0/\omega^2_0$. In particular, making use of the data from /16/, for the system $Ba_{1-x}Sr_xTiO_3$ we obtain the estimations $\gamma \approx (T_{02}/T_{01})(C_1/C_2) \approx 0.2$; $\kappa \approx C_1/C_2 \approx 2$; $f_0 \approx 5$, , which correspond to $\omega_0 = 2.3 \cdot 10^{12}$ Hz and $\omega_D \approx 5 \cdot 10^{12}$Hz for the pure $BaTiO_3$.

The numerical solutions of the system of equations for $T < T_0(x)$ with these parameters are presented in Fig. 1 $(x = 0.1)$ and Fig. 2 $(x = 0.8)$. So far as in this case the coupling between the ions is sufficiently strong $(f_{01} = \phi_0/A_1 = 5,\ f_{02} = \phi_0/A_2 = 25)$, the equation (6) permits only solutions for the equilibrium positions η_1 and η_2 which differ slightly from each other. They vanish simultaneously with the coherent gap $\Delta_0(\nu = 0, T)$ for $T \to T_0(x)$. The single particle energies $\Delta_1(T)$ and $\Delta_2(T)$ differ according to the estimation (27) considerably from each other: for small concentration of defects their equilibrium positions are determined in the main by the ions of the matrix, that leads to an anomalous large gap, $\Delta_2 \gg \Delta_1$, in the case of smaller single particle well in the defect site $(x = 0.1)$ and to large negative values, $\Delta_1 < 0$, , for broader defect wells $(x = 0.8)$. Some difference in the behaviour of $\eta_1(T)$ and $\eta_2(T)$ for $T \to T_0(x)$ in the cases $x = 0.1$ and $x = 0.8$ is connected with the different values of the fluctuation effects in the calculation of the correlation function (17) within the SPFA. According to /17/ they appear in the temperature region $|T - T_0|/T_0 \sim 1/f_0$ and are large for $x = 0.1$, where the complexes with the weaker coupling constant, $f_{01} = 5$, take the leading part, and they are small for $x = 0.8$, where the complexes with the coupling constant $f_{02} = 25$ give the main contribution. The solution of the equations for $T \gtrsim T_0(x)$ allows one to determine $T_0(x)$ and $C(x)$. The numerical results and the comparison with the experimental data /2/ for the solid solution $Ba_{1-x}Sr_xTiO_3$ are shown in Fig. 3. Here the parameters γ and κ were taken from the condition, that the curves coincide with the experiment for the pure

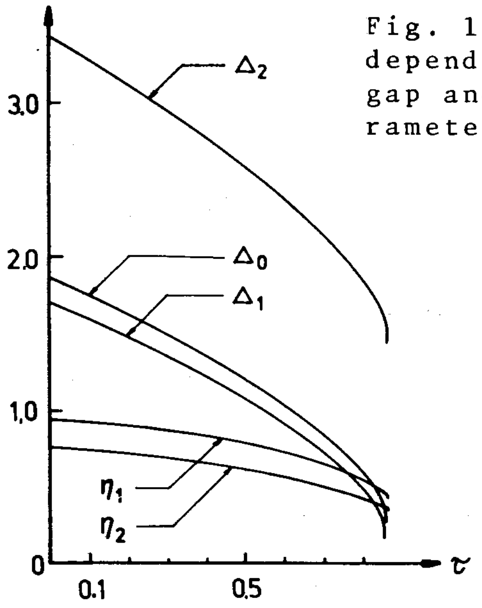

Fig. 1. The temperature dependence of the phonon gap and of the order parameter at x = 0.1.

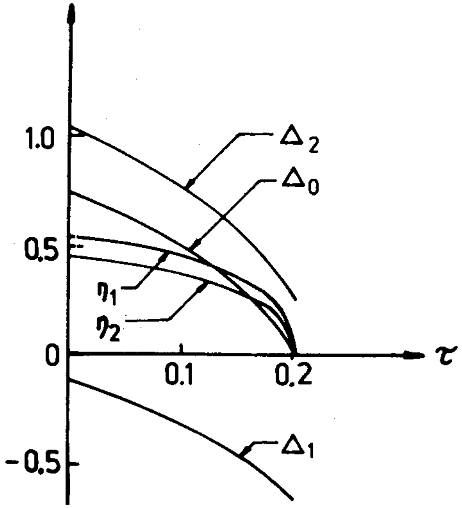

Fig.2. The temperature dependence of the phonon gap and of the order parameter at x = 0.8.

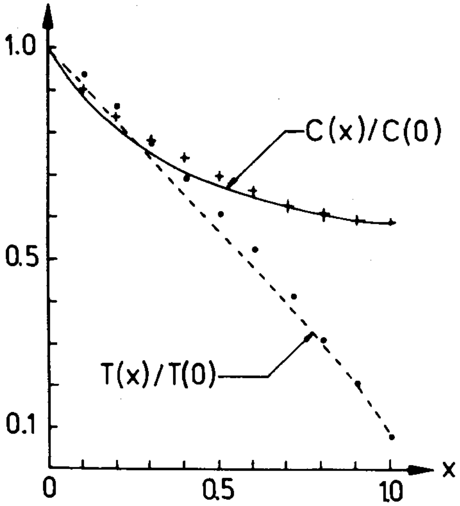

Fig.3. The concentration dependence of the Curie-Weiss-constant C and Curie temperature for Ba$_{1-x}$Sr$_x$TiO$_3$ (lines-theory, points and crosses experiment).

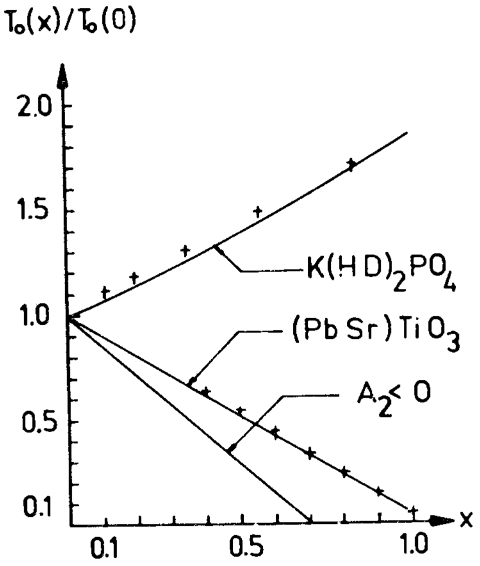

Fig.4. The concentration dependence of the Curie-temperature for Pb$_{1-x}$Sr$_x$TiO$_3$ /2/, K(H$_{1-x}$D$_x$)$_2$PO$_4$ /3/ and for the model with nonferroelectric defects ($A_2 < 0$) (lines-theory crosses-experiment).

FE (x = 0, x = 1), and the coupling constant was chosen from the condition, that the numerical results are close to the experimental data for the intermediate values of concentration. A reasonable agreement with the experiment was got for $f_0 = 2$, that corresponds to the relation $\omega_D/\omega_0 \approx 1.4$ for the pure BaTiO$_3$.

The numerical results and experimental data of $T_0(x)$ for (PbSr)TiO$_3$ ($\kappa = 2.3$; $\gamma = 0.087$; $f_0 = 2$) and K(HD)$_2$PO$_4$ ($\kappa = 0.71$; $\gamma = 1.31$; $f_0 = 10$) are presented in Fig.4. There is also shown the concentration dependence of $T_0(x)$ for the model with nonferroelectric defects ($\kappa = 1$; $\gamma = -1$; $f_0 = 5$). For K(HD)$_2$PO$_4$ the parameter f_0 was chosen from the estimations for the soft mode frequency which were obtained in /18/ : $f_0 = \omega_D^2/\omega_0^2$. So far as in this case $f_0 \gg 1$ the formulas (26) can be used which are obtained in the mean field approximation.

In (26) the parameter f_0 does not appear and therefore its value does not influence the results in numerical calculations too. In the case of perovskites the mean field approximation is rather bad, $\Delta_a/f_0 \sim 1$, , and it is necessary to employ more complicated methods as the CPA in the given work.

Rather a good agreement of the theoretical curves with the experimental results, where there are only three fitting parameters for the pure FE, shows that the proposed model describes the main features of ferroelectric solid solutions. We would note some uncertainty in our calculation of Curie-Weiss-constant the reason for which is as follows. The model (2) has the one soft mode only therefore the comparison of the calculated $C(x)$ with experimental one has sense in the vicinity of PT point, where the fluctuation effects becoming rather large (different in $BaTiO_3$ and $SrTiO_3$ /17/). We can get a further refinement of the model for the solid FE solutions considering the anisotropy of the phonon spectrum for soft mode and its coupling with the other low frequency phonon modes. In the case of KDP type FE it is necessary to consider in an explicit way the vibrational modes of the proton and their interaction with the active optical mode.

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