5. The dependence \(i_0\) reproduces the experimental curve for additional optical absorption in \(\text{PbTe}\text{In}\) [5]. A verification of Eq. (5) is facilitated by a study of optical absorption in \(\text{PbSe}\text{In}\), where the resonance level is situated above the Fermi level [5]. Equations (7) and (8) may be verified in experiments on absorption of slow electromagnetic waves \(\omega < \nu_{\text{F}}\) in metalloids and degenerate semiconductors, where the wave number exceeds the diameter of the Fermi sphere. Verification of Eqs. (4) and (5) is possible in Al with alloys of transition electrons under conditions when the magnetic moments of the extrinsic atoms are absent [3].

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LITERATURE CITED


ELASTIC EFFECTS IN THERMODYNAMIC DESCRIPTION OF FLUCTUATING ELECTRON STATES IN FERROELECTRICS

V. Yu. Topolov and A. V. Turik

The effect of internal mechanical stresses of electrostriction nature on fluctuating electron states in ferroelectrics of \(\text{BaTiO}_3\) type during the para-ferroelectric phase transition has been considered for the first time within the framework of thermodynamic theory. A criterion has been obtained for the occurrence of a ferroelectric phason inside the crystalline matrix, and its main characteristics have been calculated.

Studies of fluctuating electron states [1-3] in ferroelectrics near critical points of first-order phase transitions were performed without taking into account internal mechanical stresses, which invariably occur when crystal lattice parameters undergo a sudden change due to the contact of the two coexisting phases [4, 5]. In this paper, simultaneous treatment of fluctuation and elastic effects (of the electron and mechanical subsystems) in ferroelectric crystals near the Curie point \(T_c\) has been performed for the first time, using the first-order phase transition between the cubic paraelectric and the tetragonal ferroelectric phases of \(\text{BaTiO}_3\) crystal as an example.

Similarly to [2], we shall consider the simplest case of a stabilized spherical fluctuation captured by an electron, which has the form of a seed of a new phase - the phason. Vectors of the homogeneous spontaneous phason polarization \(P\) and of the surrounding crystalline matrix \(P_0\) have parallel orientations along one of the pseudocubic crystal axes. Following [6] and based on the thermodynamic theory of small particles [7, 8], we shall write down the formula for the free energy of a ferroelectric phason, with the additive contribution of the elastic energy taken into account, in the following form:

\[
F(P, R) = R^3 [z^2 P^2 + (\delta + 3) P^4/2 + \tau^2 P^6/3] + R^2 z^2 P^2 - R^2 z^2 P^2 \tag{1}
\]
Here, \( R \) is the effective phason radius; \( \alpha_d = \alpha_d^V + \alpha_d^x \), \( \beta^V < 0 \) and \( \gamma^V > 0 \) are bulk coefficients of the thermodynamic potential \( \alpha_d^V = \alpha_d(T - T_0) \), \( T_0 \) is the Curie-Weiss temperature, \( \alpha_d = \alpha_d^V/2 = \alpha_d(T - T_0)/3 \) [9] is the coefficient describing the contribution to \( F(P, R) \) from the energy of the depolarizing field \( F_d = \alpha_d P^2 R^3 \); \( \delta \) is the electrostriction parameter [4, 5, 10], which describes the contribution to \( F \) from the elastic energy

\[
F_{\text{el}} = \delta P^4 R^3.
\]

(2)

In Eq. (1), only first terms in the expansion in \( P \) of the surface \( F_{\text{sur}} \) and of the fluctuation energy \( F_{\text{fl}} \) have been taken into account [2], i.e.,

\[
F_{\text{sur}} = x^P R^2,
\]

\[
F_{\text{fl}} = -x^P R^2 R^2
\]

(3)

(4)

where \( \alpha_s^P \) and \( \alpha_s^R \) are expansion coefficients.

The system of equations of state \( \partial F/\partial R = 0 \), \( \partial F/\partial P = 0 \)

\[
\alpha_s^P P^2 + (\beta + \delta) P^2 + \gamma P R^2 = 0;
\]

(5)

allows two solutions \( (P(T), R(T)) \), from which one should select a solution, which satisfies stability conditions at a fixed temperature in the temperature interval in which the solution for a ferroelectric phason exists:

\[
\frac{\partial^2 F}{\partial P^2} > 0, \quad \frac{\partial F}{\partial P} \frac{\partial^2 F}{\partial R^2} > 0.
\]

(6)

The expression for the optimal radius of a ferroelectric phason, found from Eq. (5) with elastic effects taken into account

\[
R = -x^P [2\alpha_s^P + (\beta + \delta) P^2]^2 - 1
\]

(7)

differs from that obtained in [2, 3, 9] by the parameter \( \delta \), which puts an additional significant restriction on the possibility of occurrence of a ferroelectric phason. Indeed, conditions (6) and \( R > 0 \) (as the physical meaning of radius) lead to the following inequality:

\[
\beta + \delta < 0
\]

(8)

for \( P^2 > 4\alpha_d^P/(\beta + \delta) \) (because \( \alpha_s^P > 0 \) [2, 3, 9] and \( \alpha_d^P > 0 \) for any \( T > T_0 \)). Criterion (8) was satisfied earlier [2, 9] automatically because it was explicitly assumed that \( \delta = 0 \). We note that Eq. (7) may be obtained from Eqs. (1) and (5) independently of the contribution of \( F_{\text{fl}} \) to Eq. (1), including the case of \( F_{\text{fl}} = 0 \).

When elastic effects are taken into account [4, 5], the temperature of the phase transition into the ferroelectric phase \( T_{\text{FE}} \) and into the paraelectric phase \( T_{\text{PE}} > T_{\text{FE}} \) are different. At these temperatures, equality of free energies of ferroelectric and paraelectric phases are achieved, i.e., \( F = 0 \). Analysis of solutions (5) in the point \( T = T_{\text{PE}} \) shows that one of the solutions satisfies Eq. (6) and allows one to obtain the critical radius of the ferroelectric phason \( R_0 \), which is approximately equal to \( 0.5\alpha_s^P/\alpha_s^R \) [2, 3]. The other solution gives \( P = \sqrt{-3(\beta + \delta)/(4\gamma^V)} \) and \( R \to \infty \) (more precisely, \( R \gg R_0 \)), which one should consider as the appearance of spontaneous polarization over the total volume of the crystal. In the latter case, supercritical seeds are formed, which are described within the framework of the theory of Frenkel heterophase fluctuations [1]. As \( R \to \infty \), it is meaningful to perform a transformation from Eq. (1) to the free energy density \( f(P) = \lim_{R \to \infty} F/R^3 \). Analysis of \( f(P) \) shows that for \( T = T_{\text{PE}} \), \( f(P) = 0 \), \( df/dP = 0 \), and \( d^2f/dP^2 > 0 \), which makes the phase transition into the ferroelectric phase possible. The limit \( R \to \infty \) for \( T = T_{\text{PE}} \) allows one to obtain from Eq. (5) known relations [10] of the thermodynamic of supercritical seeds (with depolarization energy taken into account). For \( T \leq T_{\text{PE}} \) (supercooling) it is necessary that criteria of the seed formation [4, 5, 10], which are related to the elastic compression of seeds of the new phase appearing in the crystalline matrix, be satisfied. The first solution (5) \( (R(T_{\text{PE}}) = R_0) \) maintains thermodynamic stability for finite \( R \) up to a certain temperature \( T_0 < T' < T_{\text{FE}} \), however, for \( T < T_{\text{FE}} \) it is energetically less favorable, compared with the solution for a supercritical seed, which gives \( R \to \infty \), \( f(P) < 0 \), and \( d^2f/dP^2 > 0 \) over the whole interval \( T_0 < T < T_{\text{FE}} \). The temperature interval in which the ferroelectric phason exists is restricted from above by the temperature of the phason decay \( T_{\text{FE}} \) [3], which corresponds to the reduction of the effective phason radius down to the size of the cloud of a localized electron.