Pis'ma v ZhETF, vol.65, iss.5, pp.425 - 429 © 1997 March 10

SELF-LOCALIZED CARRIER STATES IN DISORDERED FERROELECTRICS

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Submitted 15 Junuary 1997

A theory of self-localized states of free carriers near polarization fluctuations (fluctuons) in disordered ferroelectrics is developed. Calculations are carried out for the model disordered ferroelectric $K_{1-x}Li_xTaO_3$ ($x << 0.05$). The basic characteristics of the fluctuon – the energy and radius of the fluctuon state — are calculated as functions of the impurity dipole concentration and temperature. The theory predicts the appearence of stable fluctuon states in both the mixed ferroelectric–dipole-glass phase (a dipole glass is the electric analog of a spin glass) and the dipole-glass state of disordered ferroelectrics. The possible role of fluctuons in kinetic phenomena such as conductivity in these substances is discussed.

PACS: 71.38.+i, 77.80.-e

Self-localized states of the charge carrier (electon, hole, or sometimes exciton), namely polarons [1] and fluctuons [2], play an important role in the physics of insulators and semiconductors. While a great deal of scientific work has been devoted to investigations of polaron states (see, e.g., [1, 4]), the available information about fluctuon states is very limited. Since a fluctuon is known to be a carrier trapped near a polarization fluctuation [2, 3], the carrier can interact with fluctuations induced by both longitudinal and transverse phonons. The latter are especially important in ferroelectrics for which the spontaneous polarization is due to transverse phonons. A theory of fluctuon states in ordinary ferroelectrics was developed in [5], where the domain walls were considered as the main source of polarization fluctuations in the ferroelectric phase. However, the presence of short-range polar order in the dipole-glass state or a mixture of short- and long-range polar order in the mixed ferroglass phase is peculiar to disordered ferroelectrics (see, e.g., [6] and the references cited therein). In such a system polarization fluctuations are a basic characteristic of those phases. In view of the existence of a fundamental electric current in many disordered ferroelectrics [7–9], the appearence of fluctuon states in these systems seems to be very probable. In the present work we propose a theory of self-localized (fluctuon) states of the charge carrier in disordered ferroelectrics with random electric dipoles which induce concentrational phase transitions of the dipole-glass–mixed-phase–ferroelectric type. The calculations are carried out for the model disordered ferroelectric $K_{1-x}Li_xTaO_3$ (KLT) ($x << 0.05$), the impurity Li^+ ions being electric dipoles with random site and orientation.

The disordered ferroelectric KLT is known to have an ordinary ferroelectric phase transition for $x > 0.05$ and dipole-glass–mixed-ferroglass phase transitions for $x \leq 0.05$ at low temperatures ($T << 50$ K) [10]. The latter two phases correspond to $nr_c^3 \leq 1$ ($n = x/a^3$, and x, r_c, and a are the dipole concentration and the host lattice correlation radius and lattice constant, respectively). It is known [10] that in this concentration interval the effects of disorder are quite strong (at large Li

concentrations we simply have the case of the ordered ferroelectric $LiTaO_3$), so that spatial nonuniformity of the polarization should be taken into account.

The fluctuon energy functional, allowing for the interaction of the charge carrier with the polarization P in the effective mass approximation for strong coupling of thee carrier to the polarization, can be written as in [1]:

$$W = \frac{\hbar^2}{2m^*} \int \left| (\nabla \Psi)^2 \right| d^3r - \int \mathbf{P} \cdot \mathbf{D} d^3r + \int f d^3r \tag{1}$$

where f is the free-energy density of the disordered ferroelectric, m^* and $\Psi(r)$ and D are the effective mass and wave function of the carrier and the electric displacement produced by the carrier, respectively. The last is given by

$$\mathbf{D}(\mathbf{r}) = -e \int |\Psi(\mathbf{r}_1)|^2 \frac{(\mathbf{r} - \mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|^3} d^3\mathbf{r}_1 \tag{2}$$

The free energy f was calculated recently [11] for the case of 8-orientation dipoles and can be written in the form

$$f = -\frac{4\pi}{c} \left[\frac{1}{2} P^2 + \frac{d^{*2}}{V_0^2 \beta} \int_0^\infty \frac{(1 - \cos(\rho P_1 E_0(\rho))) \exp(F_1(\rho)) d\rho}{\rho E_0(\rho) \sinh(\frac{\pi\rho}{2\beta})} \right], \tag{3}$$

$$c = \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}$$

where $d^* = \gamma d \varepsilon_0 / 3$ is the effective dipole moment of the impurity, γ is the Lorentz factor, ε_0 and ε_∞ are the low- and high-frequency dielectric permittivities of the host lattice, $E_0(\rho)$ is the average electric field induced by the dipoles, $F_1(\rho)$ is the width of the distribution function of the random fields, calculated in [11], V_0 is the unit cell volume, and $\beta \equiv 1/kT$. Note that the factor c appears in (3) because only the inertial part of the polarization contributes to the energy of the self-localized carrier state.

Equation (1) in reference to (2) and (3) determines the properties of the fluctuon. Independent variation of (1) with respect to Ψ and P gives the following equations for the fluctuon structure:

$$-D[\Psi] + \frac{4\pi}{c} \left[P - \frac{d^*}{V_0 \beta} \int_0^\infty \frac{\sin(\rho P_1 E_0(\rho)) \exp(F_1(\rho)) d\rho}{\sinh(\frac{\pi\rho}{2\beta})} \right] = 0, \tag{4a}$$

$$-\frac{\hbar^2}{2m^*} \Delta \Psi - eP(\Psi) \int \Psi(\mathbf{r}_1) \frac{(z - z_1)}{|\mathbf{r} - \vec{r}_1|^3} d^3\mathbf{r}_1 = 0 \tag{4b}$$

$$P_1 \equiv \frac{PV_0}{d^*}$$

System (4a), (4b) should be solved under the normalization condition

$$\int |\Psi|^2 d^3r = 1 \tag{4c}$$

Equation (4a) gives the relation between D and P. It therefore determines the dependence of the electric field of the carriers on the concentration of impurity

dipoles, the characteristics of the host lattice, and the parameters of the distribution function of the random fields of the impurity dipoles (the latter were used in the calculation of the free energy 3; see [11]). We must emphasize that in the case of a ferroelectric phase induced by electric dipoles ($nr_c^3 \gg 1$) the integral in Eq. (4a) can be calculated in the mean field approximation, which is valid at large impurity concentrations (see [10,11]), and turns out to equal βP_1. It is easy to see that the expression in the brackets in Eq. (4a) equals zero, so that $D = 0$ and the fluctuon does not exist. This is because we did not take into account the domain walls, which have been shown [5] to be the main source of polarization fluctuations in ordinary ferroelectrics. Note that the system (4a), (4b) can also be applied to investigation of the influence of charge carriers on the polarization of disordered ferroelectrics. This influence has been shown to be important in many disordered ferroelectrics [7-9]. Since the system (4a), (4b) is rather complicated, we were not able to find its analytical solution. We shall therefore study the fluctuon properties by a direct variational method. To do this, we must substitute (4a) into (1) in reference to (2) and minimize the resulting expression subject to condition (4c) with some trial function Ψ.

To obtain the energy of fluctuon ground state we shall choose the one-parameter trial function which gives the lowest energy as compared to any other one-parameter trial function, in a form similar to [1]:

$$\Psi = \frac{1}{\sqrt{7\pi} r_0^{3/2}} \left(1 + \frac{r}{r_0}\right) \exp\left(-\frac{r}{r_0}\right) \tag{5}$$

where r_0 is a variational parameter. Minimization of functional (1) in reference to relations (4a) and (2) and with the parameters values for KLT leads to the following form for the fluctuon energy:

$$W_\Psi = \frac{3\hbar^2}{14 m^* r_0} - \frac{0.428332 e^2 c}{6\Phi(\nu,\tau) r_0}, \tag{6}$$

$$\Phi(\nu,\tau) = \left(\frac{dP_1}{dD}\right)_{P_1 = P_0} \tag{7}$$

where P_0 is the equilibrium homogeneous polarization ($D(P_0) = 0$), $\nu \equiv nr_c^3$, and $\tau = T/T_{cmf}$ (T_{cmf} is the ferroelectric phase transition temperature calculated in the mean field approximation).

A calculation of $\Phi(\nu,\tau)$ in reference to relation (4a) shows that the dependence of P_1 on D has a hysteretic character: on the $P_1(D)$ curve there are parts with $dP_1/dD << 0$ and parts with $dP_1/dD > 0$. It follows from Eqs.(6) and (7) that the parts where $dP_1/dD << 0$ and the parts where $dP_1/dD > 0$ can lead to the maximum and minimum fluctuon energy, respectively. In the latter case the fluctuon is stable, and its energy and radius of localization are as follows:

$$r_{\min} = \frac{6\hbar^2 \Phi(\nu,\tau)}{m^* e^2 c},$$

$$W_{\min} = -0.0054946 \frac{m^* e^4 c^2}{\hbar^2 \Phi^2(\nu,\tau)} \tag{8}$$

These parameters are depicted in Fig.1 along with the general form of the dependence of the fluctuon energy on r_0 as calculated on the basis of Eqs.(6) and

(7) in reference to relation (4a). It is seen from relation (4a) that the dependence of the dimensionless radius of the fluctuon state on the dipole concentration and temperature is determined by $\Phi(\nu,\tau)$. The temperature dependence of $\Phi(\nu,\tau)$ is shown in Fig.2 for parameters which correspond to the dipole glass ($\nu << \nu_{cr}$) and to the mixed phase ($1 \geq \nu > \nu_{cr}$) with coexistence of short- and long-range polar order, i.e., with the onset of spontaneous polarization. It is seen from Fig.2 that in the latter case the localization radius has a temperature dependence similar to that of the spontaneous polarization. This is truly a manifestation of the fluctuon nature of the carrier localization in disordered ferroelectrics. Indeed, the increase of the spontaneous polarization with decreasing temperature means that its fluctuations are inhibited, which in turn decreases the fluctuon nucleation probability. This behavior also follows from Eq.(8) and Fig.2, because $|W_{\min}| \sim 1/r_{\min}^2$, i.e., the localization radius growth decreases the depth of the fluctuon energy minimum. Points at which $\Phi(\nu,\tau) = 0$ correspond to the onset of spontaneous polarization, i.e., to the phase transition temperature [11].

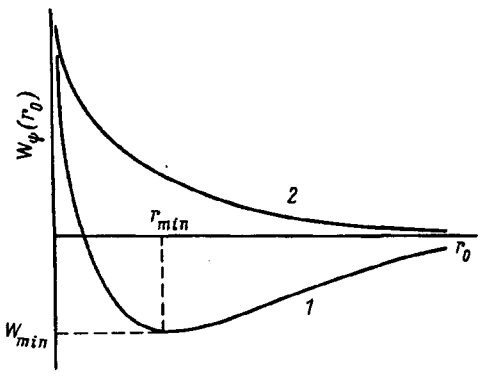

Fig.1.Energy of fluctuon ground state as a function of the variational parameter r_0 for stable (1) and unstable (2) states of the fluctuon

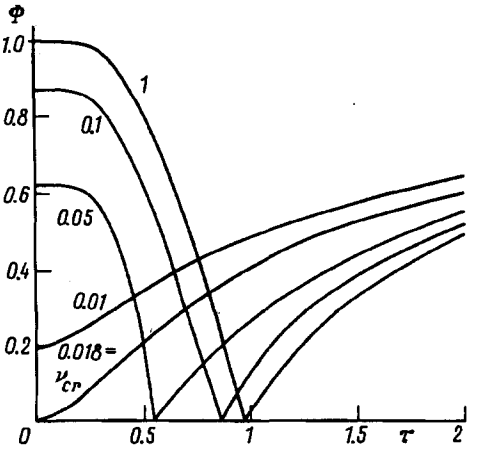

Fig.2. Dimensionless localization radius $\Phi(\nu,\tau)$ versus the dimensionless temperature $\tau = T/T_{cmf}$. The curves are labeled with the values of $\nu = nr_c^3$

At these points $r_{\min} \to 0$ while $W_{\min} \to -\infty$. This means that the fluctuon collapses at phase transition points. At $T > T_c$ (paraelectric phase) $r_{\min} \neq 0$ and the localization radius is finite on account of polarization fluctuations induced by the random electric fields of the impurity dipoles. Fluctuons can also be stable in the dipole-glass state, where polar clusters of short-range order can induce strong polarization fluctuations (see Fig.2).

The calculations have shown that disordered ferroelectrics are suitable media for revealing and investigating self-localized fluctuon states of carriers. It can be supposed that the fluctuon contribution to the electric current (and photocurrent, which was observed recently in KLT [9]) might be substantial. This contribution depends on the position of the fluctuon local level in the ferroelectric band gap. To shed light on this question, let us make some numerical estimates of $r_{\min}$

and $W_{\min}$. We have from Eq. (8)

$$r_{\min} = 3.18\frac{\Phi}{\alpha c}(\text{Å}),$$

$$W_{\min} = -0.16\frac{\alpha c^2}{\Phi^2}\ (\text{eV}), \tag{9}$$

where $\alpha = m^*/m_0$, m_0 is free electron mass. For validity of the effective mass approximation we must have $r_{\min} \geq (3\text{–}4)a$ (for $KTaO_3$ $a \simeq 4$ Å). Putting $r_{\min} = 3a$ in (9), we have $\Phi/\alpha c \simeq 3.8$, which gives

$$W_{\min} \simeq -\frac{0.01}{\alpha}\ (\text{eV}) \tag{10}$$

Therefore $|W_{\min}| \leq 0.01$ eV, i.e., fluctuons produce very shallow local levels in the lattice band gap near the valence band bottom for electrons. Note that the observed temperature anomalies of the photocurrent in KLT have been explained on the assumption that a very shallow local level exists near the valence band ceiling [9]. This level could be of a fluctuon nature. More-precise estimates of the fluctuon characteristics in disordered ferroelectrics and of their contribution to the conductivity and other kinetic phenomena require additional experimental and theoretical investigations.

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Edited by Steve Torstveit