

# Some features of the cooperative behavior of paraelectric defects in strongly polarizable crystals

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(Submitted 14 February 1980)

Zh. Eksp. Teor. Fiz. 79, 947-952 (September 1980)

It is shown that ferroelectric ordering of paraelectric defects is possible in strongly polarizable crystals exhibiting soft phonon modes. A phase transition producing such ordering occurs if  $nr_c^3 \gg 1$  ( $n$  is the impurity concentration and  $r_c$  is the correlation radius) and it modifies the crystal lattice giving rise to a spontaneous polarization. The average field approximation is used to find the transition temperature and an expression for the permittivity of the lattice with impurities. At low concentrations ( $nr_c^3 \ll 1$ ), dipole impurities in strongly polarizable crystals form a "dipole glass," in the same way as in ordinary lattices.

PACS numbers: 77.80.Bh, 77.30. + d

1. Collective properties of electric dipole impurities in solids are being investigated intensively by theoretical and experimental methods. The greatest attention has been given to alkali halide crystals containing molecular ion impurities such as  $\text{OH}^-$  and  $\text{CN}^-$  and noncentral defects of the  $\text{Li}^+$  type in  $\text{KCl}$  (Ref. 1). For example, Fiory<sup>2</sup> observed permittivity anomalies due to the interaction of impurity dipoles. However, these anomalies are not accompanied by the appearance of a spontaneous polarization and are typical of "polar glass" systems<sup>3</sup> in which there is no ferroelectric order. A theoretical investigation of the physical properties of crystals with randomly distributed dipoles is usually made employing the Hamiltonian of the interaction of dipoles in a polarizable medium<sup>4</sup>

$$\mathcal{V}_{dd} = \sum_{i < j} \frac{1}{\epsilon_0} \left[ \frac{(\mathbf{d}_i \cdot \mathbf{d}_j)}{r_{ij}^3} - \frac{3(\mathbf{d}_i \cdot \mathbf{r}_{ij})(\mathbf{d}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right], \quad (1)$$

where  $\mathbf{d}_i^* = \mathbf{d}_i(\epsilon_0 + 2)/3$  is the effective dipole moment of an impurity including a correction for the local field in cubic crystals,  $\mathbf{d}_i$  is the permanent dipole moment of the impurity, and  $\epsilon_0$  is the permittivity of the pure crystal.

Fairly general assumptions which are not related to the mean field approximation are used in Ref. 5 to show that, in principle, ferroelectric ordering is impossible in a system of randomly distributed dipoles with the Hamiltonian (1), which is a consequence of the fact that the configurational average  $\overline{\mathcal{V}_{dd}} = 0$  vanishes.

Systems of paraelectric defects in strongly polarizable crystals characterized by low-frequency optical vibrations and a large polarization correlation radius  $r_c$ , which are of considerable current interest, represent a special case.<sup>6,7</sup> It is physically clear that when the correlation radius is sufficiently large, the random distribution of impurities should not have a significant effect on the observed properties of the system.

The cooperative behavior of paraelectric defects in lattices with large correlation radii is the subject of the present paper. We shall use the average field approximation to show that ferroelectric ordering of impurities is possible in such systems and that it is due

to a modification of the Hamiltonian of the dipole-dipole interaction. The Hamiltonian of this interaction in strongly polarizable crystals contains not only the usual anisotropic term of the type (1) but also an isotropic component whose magnitude depends strongly on  $r_c$ . Consequently, the average field acting on a dipole no longer vanishes and if  $nr_c^3 \gg 1$  ( $n$  is the impurity concentration), a ferroelectric phase transition can occur in the impurity system. At a temperature  $T_c$  of this transition we can expect the appearance of a spontaneous polarization of the lattice in view of the linear relationship between the average dipole moment of the impurities and the lattice polarization.

In the opposite limiting case of  $nr_c^3 \ll 1$ , the situation does not differ qualitatively from that encountered in alkali halide crystals.

2. The Hamiltonian of a system of  $N$  dipoles interacting with the lattice polarization can be written in the form

$$H = - \sum_i \mathbf{d}_i \mathbf{E}(\mathbf{r}_i) + \sum_{\mathbf{k}, j} \hbar \omega_{\mathbf{k}, j} a_{\mathbf{k}, j}^+ a_{\mathbf{k}, j}, \quad (2)$$

where  $a_{\mathbf{k}, j}^+$  and  $a_{\mathbf{k}, j}$  are the creation and annihilation operators of phonons of frequency  $\omega_{\mathbf{k}, j}$  ( $\mathbf{k}$  is the phonon wave vector and  $j$  is the polarization index);  $\mathbf{E}(\mathbf{r})$  is the electric field due to the polarization  $\mathbf{P}(\mathbf{r})$  associated with the lattice vibrations:

$$\mathbf{E}(\mathbf{r}) = \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \left[ \frac{4\pi}{3} \gamma \mathbf{P}_{\mathbf{k}} - 4\pi \frac{\mathbf{k}}{k^2} (\mathbf{k} \cdot \mathbf{P}_{\mathbf{k}}) (1 - \delta_{\mathbf{k}, 0}) \right], \quad (3)$$

where  $\mathbf{P}_{\mathbf{k}}$  are the Fourier components of the polarization. The first term in Eq. (3) corresponds to the local field taken in the Lorentzian form, which holds for wave vectors  $k \ll a^{-1}$  ( $a$  is the lattice constant),<sup>8</sup> and  $\gamma$  is the Lorentz factor. The second term in Eq. (3) corresponds to a macroscopic field and  $\delta_{\mathbf{k}, 0}$  is the Kronecker delta. Equation (3) allows for the fact that the crystal is under such conditions that a homogeneous polarization does not produce a macroscopic field. In the case of polyatomic lattices we shall sum with respect to  $j$  in Eq. (2) only for one group of triply degenerate, at  $k=0$ , soft optical branches responsible for the anomalous permittivity  $\epsilon_0$ . [If  $k \neq 0$ , this corresponds to allowance for two transverse ( $j_{\perp}$ ) and one lon-

gitudinal ( $j_{||}$ ) branches.]

Introducing, as usual, the normal coordinates  $Q_{kj}$ , we shall represent  $P_k$  in the form

$$P_k = \frac{Z^2}{(mN_0)^{1/2} v} \sum_j e_j^{-1} Q_{kj} \lambda(k, j), \quad (4)$$

where  $Z$  and  $m$  are the effective charge and mass of a vibration,  $N_0$  is the number of unit cells of volume  $v$ ,  $\lambda(k, j)$  is a unit polarization vector,  $\epsilon_{j||} = \epsilon_\infty$  is the high-frequency permittivity, and  $\epsilon_{j\perp} = 1$ .

We shall determine the local field  $\langle E(r) \rangle$  for a fixed impurity configuration (angular brackets denote quantum-statistical averaging) using the equation of motion for the normal coordinates and the equilibrium condition  $\langle \dot{Q}_{kj} \rangle = 0$ .

This gives

$$\langle E_\alpha(r_i) \rangle = \sum_{j\beta} (K_{\perp i\alpha}^{j\beta}(r_{i\alpha}) + K_{|| i\alpha}^{j\beta}(r_{i\alpha})) \langle d_{j\beta} \rangle, \quad (5)$$

$$K_{\perp}^{j\beta}(r) = -\frac{4\pi}{9V} \gamma^2 (\epsilon_0 - \epsilon_\infty) \sum_k \cos(kr) \frac{1}{1+r_{c\perp}^2 k^2} \left[ \delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2} (1 - \delta_{\alpha\beta}) \right], \quad (6)$$

$$K_{||}^{j\beta}(r) = -\frac{4\pi}{9V} \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0 \epsilon_\infty} (3 - \gamma)^2 \sum_{k \neq 0} \cos(kr) \frac{1}{1+r_{c||}^2 k^2} \frac{k_\alpha k_\beta}{k^2}, \quad (7)$$

where we have used the well-known relationship between the soft-mode frequency  $\omega_0$  and the permittivity of a crystal  $\epsilon_0 - \epsilon_\infty = 4\pi z^2 / mv \omega_0^2$  and we have assumed that the dispersion law of the vibrations is<sup>8</sup>

$$\omega_{k\perp}^2 = \omega_0^2 + s_\perp^2 k^2, \quad \omega_{k||}^2 = \omega_0^2 + s_{||}^2 k^2, \quad \omega_s^2 = \epsilon_0 \omega_0^2 / \epsilon_\infty; \\ r_{c\perp} = s_\perp / \omega_0, \quad r_{c||} = s_{||} / \omega_0,$$

$V = N_0 v$  is the volume of a crystal;  $\alpha$  and  $\beta$  are Cartesian coordinates.

Equation (6) is derived ignoring the lattice anharmonicity, which may generally be significant in the presence of a soft mode. The criterion of validity of the harmonic approximation deduced from estimates by the iteration method is

$$B \left( \frac{\epsilon_0}{4\pi r_c} \right)^2 \left( \frac{d\gamma}{3} \right)^2 \ln \left( \frac{r_c}{a} \right) \ll 1,$$

which imposes restrictions on the permissible dipole moment  $d$  of the impurities<sup>11</sup> ( $B$  is the anharmonicity constant).

In summing over  $l$  in Eq. (5) we have to separate the term with  $l=i$ . This is the average reactive field due to the dipole-induced polarization acting on a dipole. Such a reactive field may result in a local phase transition in a system of isolated dipoles in the lattice.<sup>9</sup> The other terms in the sum (5), which we shall then consider, represent a random molecular field associated with an indirect interaction of dipoles via a field of optical phonons (the randomness is due to the chaotic distribution of impurities). The Hamiltonian of this indirect interaction,

$$\mathcal{V} = \sum_{i,l,\alpha,\beta} K_{i\alpha}^{l\beta} d_{i\alpha} d_{l\beta}, \quad (8)$$

can be obtained also directly<sup>10</sup> ( $K = K_{\perp} + K_{||}$ ). Thus,  $K_{\perp}$  and  $K_{||}$  are the constants of the indirect dipole-dipole interaction via transverse and longitudinal optical pho-

nons, respectively.

It should be noted that whereas  $r_{c||} \sim a$ , the quantity  $r_{c\perp}$  depends significantly on the permittivity  $\epsilon_0$  and in the case of strongly polarizable crystals it may be considerably greater than  $a$ . However, in the case of crystals with the usual values of the permittivity, we find that  $r_{c\perp}$  is again of the order of  $a$ . For such crystals we can assume approximately that  $r_c \approx 0$  in Eqs. (6) and (7) and assume that the distances between the dipoles are  $r > a$ . Allowing not only for Eqs. (6) and (7), but also for the interaction of dipoles in a medium with the permittivity  $\epsilon_\infty$  (if  $\epsilon_\infty = 1$ , this corresponds to an allowance for the interaction of dipoles in vacuum), we obtain the Hamiltonian (1) in which we now have  $d^* = d[3 + \gamma(\epsilon_0 - 1)]/3$ . However, in the case of strongly polarizable crystals the dipole-dipole interaction does not reduce to the Hamiltonian (1). We shall now find the explicit form of this interaction.

It follows from Eqs. (6) and (7) that if  $\epsilon_0 \gg \epsilon_\infty$ , the interaction of dipoles via transverse phonons predominates and the contribution of longitudinal phonons can be ignored. Extending summation over the wave vectors in Eq. (6) to infinity, which is permissible if  $r > a$ , and going over to integration, we obtain

$$K^{\alpha\beta}(r) = -\frac{\gamma^2}{9} (\epsilon_0 - \epsilon_\infty) \left\{ \frac{2}{3} \delta_{\alpha\beta} \frac{1}{r r_c^2} e^{-r/r_c} + \frac{4\pi}{3V} \delta_{\alpha\beta} + (3n_\alpha n_\beta - \delta_{\alpha\beta}) \left[ \frac{1}{r^3} - e^{-r/r_c} \left( \frac{1}{r^3} + \frac{1}{r^2 r_c} + \frac{1}{3r r_c^2} \right) \right] \right\}, \quad (9)$$

where  $n = r/r_c$ ,  $r_c \equiv r_{c\perp}$ . The second term in Eq. (9) is approximate. It does not influence the nature of the interaction between dipoles which are a finite distance apart but it is important in order to obtain the correct value of the integral  $\int d^3 r K(r)$ .

Equations (8) and (9) give the interaction energy of dipoles in strongly polarizable crystals. In particular, the configurational average is  $\overline{\mathcal{V}} \neq 0$ , which is why ferroelectric ordering of paraelectric centers is possible.

3. In the molecular field approximation the statistical behavior of a system of dipoles is given by Eq. (5). The ordering temperature can be estimated in the usual way from the expression for the average dipole moment. Near the ordering temperature we have

$$\langle \overline{d_{i\alpha}} \rangle = -\frac{d^2}{3k_B T} \sum_{j\beta} K_{i\alpha}^{j\beta} \langle d_{j\beta} \rangle, \quad (10)$$

where  $d$  is the magnitude of a dipole. The random distribution of impurities gives rise to fluctuations of the local field and, therefore, the configurational average in Eq. (10) can be replaced by the product of the averages

$$\sum_{j\beta} K_{i\alpha}^{j\beta} \langle d_{j\beta} \rangle \rightarrow \sum_{j\beta} K_{i\alpha}^{j\beta} \langle \overline{d_{j\beta}} \rangle$$

only if we ignore fluctuations, which corresponds to introduction of an average field. This approximation is valid if

$$\left( \sum_j K_{ij} \right)^2 \gg \sum_j K_{ij}^2, \quad (11)$$

or, bearing in mind Eq. (9), if  $n r_c^2 \gg 1$ . Then, a ferro-

electric phase transition occurs in a system of dipoles at a temperature  $T_c$  given by

$$k_B T_c = \frac{4\pi}{27} d^2 \gamma^2 n [\epsilon_0(T_c) - \epsilon_\infty]. \quad (12)$$

Equation (12) allows for the usual (in the case of soft lattices) temperature dependence of  $\epsilon_0$ .

Below  $T_c$  we find that in addition to a ferroelectric ordering of impurities the lattice becomes spontaneously polarized because of the linear relationship between the average dipole moment of the impurities and the lattice polarization. In fact, by analogy with Eq. (5), we obtain

$$\langle \bar{P} \rangle = \frac{\gamma}{3V} (\epsilon_0 - \epsilon_\infty) \sum_i \langle \bar{d}_i \rangle. \quad (13)$$

If we consider the polarization of a crystal in an external field using Eqs. (10) and (13), we obtain the impurity-renormalized lattice permittivity  $\epsilon$  at temperatures  $T \geq T_c$ :

$$\epsilon(T) - \epsilon_\infty = \frac{C}{(T - T_c)(T + T_c - T_0)/T}, \quad (14)$$

where the permittivity  $\epsilon_0(T)$  is described by an approximation in the form of the Curie-Weiss law  $\epsilon_0(T) - \epsilon_\infty = C/(T - T_0)$ .

The average field approximation is equivalent to an inclusion in the sum (3) only of the terms with  $k=0$ , corresponding to the homogeneous polarization.<sup>11</sup> However, in the case of finite correlation radii it is important, as demonstrated above, to allow for the spatially inhomogeneous fluctuations of the polarization and if  $n r_c^3 \ll 1$ , such inhomogeneous fluctuations suppress a ferroelectric phase transition.

It is clear from Eq. (11) that if  $n r_c^3 \ll 1$ , the dispersion of a local field is considerably greater than the average value and, therefore, this situation does not differ qualitatively from that occurring in ordinary crystals with dipole impurities when  $\bar{\mathcal{V}} \neq 0$  and there is no ferroelectric order. If  $\bar{\mathcal{V}} \neq 0$ , the molecular field theory predicts the possibility of local ordering of dipoles. In the low-temperature phase (called the polar glass by analogy with the spin glass concept), it is found that  $\langle \bar{d}_i \rangle = 0$  but  $\langle \bar{d}_i \rangle^2 \neq 0$  at  $T < T_g$ .

We shall estimate the temperature  $T_g$  for the case of strongly polarizable crystals when  $n r_c^3 \ll 1$ . Following Ref. 12, we shall carry out configurational averaging in Eq. (10) after squaring the right- and left-hand parts on the assumption that  $\bar{K}_{ij} \approx 0$ . This gives

$$k_B T_g = \frac{1}{27} \gamma^2 d^2 \left( \frac{4\pi}{3} \frac{n}{r_c^3} \right)^{1/2} [\epsilon_0(T_g) - \epsilon_\infty]. \quad (15)$$

A polar glass in a strongly polarizable  $\text{KTaO}_3$  crystal with noncentral  $\text{Li}^+$  ions was recently discovered by Höchli *et al.*<sup>7</sup>

We shall conclude by noting that the self-consistent field approach adopted in the present paper reflects

only very approximately the main features of the cooperative behavior of impurity dipoles. However, there is little doubt about the possibility of ferroelectric ordering of polar impurities in materials with large correlation radii, which is based on the appearance of a new isotropic term in the Hamiltonian of the dipole-dipole interaction. Moreover, an estimate of the temperature of such phase transition should be qualitatively correct.<sup>2)</sup> As far as the transition to a polar glass phase is concerned, recent investigations<sup>14</sup> have shown that the molecular field theory describes only long-lived metastable states in real three-dimensional space. For example, in the case of paraelectric defects in alkali halide crystals the value of  $T_g$  calculated in Ref. 3 similarly to Eq. (15) is in qualitative agreement with the position of a maximum of the low-frequency permittivity<sup>2</sup> right up to frequencies  $\omega \sim 10^2$  Hz. Equation (15) can be used to study such quasistationary effects in strongly polarizable crystals.

The authors are grateful to M. A. Krivoglaz for his interest and discussion of the results.

<sup>1)</sup>For example, in the case of noncentral Li and Na impurities in  $\text{KTaO}_3$  ( $\gamma \sim 0.1$ ), detected in Refs. 6 and 7, the permissible value of the noncentral shift (equal to the length of the dipole) is  $x_0 < 0.5 \text{ \AA}$ .

<sup>2)</sup>A discussion of the validity of the average field approximation in dealing with the problem of the influence of impurities on the temperature of a second-order phase transition can be found, for example, in Ref. 13.

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Translated by A. Tybulewicz