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A deviation from the Coulomb law for interacting microscopic impurities in a perovskite-like lattice

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Abstract. Formulae for calculating the electric field produced by microscopic impurities in perovskite-type oxides have been derived. By way of illustration, dipole and monopole impurities in KTaO_3 , $\text{YBa}_2\text{Cu}_3\text{O}_6$ and La_2CuO_4 were considered. It was found that the lattice polarization leads to a gigantic enhancement of the interaction between dipole impurities that can explain many phenomena in polar lattices.

1. Introduction

Strongly polarizable lattices often show intriguing features. So, perovskite-type oxides have revealed high-temperature superconductivity in parallel with the long-explored ferroelectric property. The same phenomenon was then also discovered in the polar lattice of fullerites.

When studying polar lattices, it was detected that even a very small concentration of off-centre impurities in them can lead to phase transition phenomena [1, 2] and to a drastic change in the critical temperature of superconductivity. The interaction between microscopic impurities is seemingly weakened just due to the high lattice polarizability. However, in fact, the reverse is sometimes true. It was rigorously proved in [3–5] that, in the simple-cubic lattice, the interaction between the two widely separated microscopic dipoles is, in reality, $[(\epsilon + 2)/3]^2$ times stronger than is given by the Coulomb law written for continuous media with the dielectric constant ϵ . Thus, one can expect that, at large ϵ , the interaction between the dipoles will be sufficiently enhanced.

The aim of the present paper is to generalize the result obtained earlier for the simple-cubic lattice to more complex lattices of perovskite-type oxides. The results, which we shall give in sections 2 and 3 are of common character irrespective of the nature of the microscopic dipoles. They can provide the basis for the explanation of dissimilar phenomena which will be briefly discussed in section 4.

2. Theory

Let us consider a polar crystal consisting of microscopic impurities. The coordinates of the impurities can be arbitrary. In particular, they can occupy lattice sites substituting for ions in the host lattice. They can be atomic vacancies or complexes of microscopic defects.

We shall consider the polar crystal to consist of polarizable sites. For simplicity, as a first step, we shall study polarization in this lattice with the use of the point-polarizable-ion model. Our choice of the model stems from the possibility of achieving analytical results

within this approach. Moreover, this model can be readily generalized to the case when partial covalent bonding as well as atomic size are taken into account.

The site's polarizability may include both the electronic and the ionic contributions. The latter can describe slight ion shifts from the atomic sites. If the ion displacements are large, we shall treat them in another way. This is expected in the nearest vicinity of the microscopic impurities. The real change in the ion positions will be taken into account in this case.

As a first stage, let us consider the case when the ion displacements are small. In this case, the electric fields produced by the displacements are the same as the electric field of point dipoles located at the ion sites. Thus, the local electric field at the i th site of the n th cell can be written as the sum of the unscreened field e_{ni}^0 produced by the microscopic impurities and a field produced by polarization [6]:

$$e_{ni}(\mathbf{r}) = e_{ni}^0(\mathbf{r}) - \mathcal{V} \sum_{mj} \Phi_{ni,mj}(\mathbf{r}) \cdot \mathbf{P}_{mj} \quad (1)$$

where \mathcal{V} is the volume of the unit cell, \mathbf{P}_{mj} is the vector of the polarization on the j th site in the m th cell and $\Phi_{ni,mj}$ is the tensor of the dipole-dipole interaction

$$\Phi_{ni,mj} = (\mathbf{I} - 3\hat{\mathbf{R}}_{ni,mj}\hat{\mathbf{R}}_{ni,mj})/R_{ni,mj}^3. \quad (2)$$

Here \mathbf{I} is the identity matrix and $\mathbf{R}_{ni,mj}(\mathbf{r}) = \mathbf{r}_{ni} - \mathbf{r}_{mj} + \mathbf{r}$, \mathbf{r}_{ni} is the radius vector of the i th site in the n th cell given by $\mathbf{r}_{ni} = \mathbf{r}_{0i} + \mathbf{R}_n$, \mathbf{R}_n is the radius vector of the n th cell and $\hat{\mathbf{R}} = \mathbf{R}/R$ is the unit vector directed along the vector \mathbf{R} .

Within the linear approximation, we have

$$\mathbf{P}_{mj} = \frac{1}{\mathcal{V}} \Lambda_j^0 \cdot e_{mj}(0) \quad (3)$$

where Λ_j^0 is the tensor of the atomic polarizabilities.

If the unscreened field e_{ni}^0 is determined by the point dipole \mathbf{d}_{0j} located at the point $\mathbf{r}_{0j} + \mathbf{r}'$, then

$$e_{ni}^0(\mathbf{r}) = -\Phi_{ni,0j}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{d}_{0j}. \quad (4)$$

In the case when the unscreened field is produced by the point charge q_{0j} ,

$$e_{ni}^0(\mathbf{r}) = \mathbf{W}_{ni,0j}(\mathbf{r} - \mathbf{r}') q_{0j} \quad (5)$$

where

$$\mathbf{W}_{ni,0j}(\mathbf{r}) = \frac{\mathbf{r} + \mathbf{r}_{ni} - \mathbf{r}_{0j}}{|\mathbf{r} + \mathbf{r}_{ni} - \mathbf{r}_{0j}|^3}. \quad (6)$$

Equations (1)–(4) allow one to find the electrostatic field produced by the microscopic impurities.

To solve these equations, let us introduce the following quantities [7]:

$$\begin{aligned} e_i(\mathbf{k}, \mathbf{r}) &= \sum_n \exp[i\mathbf{k} \cdot (\mathbf{r}_{ni} + \mathbf{r})] e_{ni}(\mathbf{r}) \\ e_i^0(\mathbf{k}, \mathbf{r}) &= \sum_n \exp[i\mathbf{k} \cdot (\mathbf{r}_{ni} + \mathbf{r})] e_{ni}^0(\mathbf{r}) \\ \Phi_{ij}(\mathbf{k}, \mathbf{r}) &= \sum_n \exp[i\mathbf{k} \cdot (\mathbf{r}_{ni} + \mathbf{r} - \mathbf{r}_{0j})] \Phi_{ni,0j}(\mathbf{r}) \\ \mathbf{W}_{ij}(\mathbf{k}, \mathbf{r}) &= \sum_n \exp[i\mathbf{k} \cdot (\mathbf{r}_{ni} + \mathbf{r} - \mathbf{r}_{0j})] \mathbf{W}_{ni,0j}(\mathbf{r}). \end{aligned} \quad (7)$$

After making use of the Fourier transformation, equations (1) take the form

$$e_i(\mathbf{k}, \mathbf{r}) = e_i^0(\mathbf{k}, \mathbf{r}) - \sum_j \Phi_{ij}(\mathbf{k}, \mathbf{r}) \cdot \Lambda_j^0 \cdot e_j(\mathbf{k}, \mathbf{0}). \quad (8)$$

The solution of these equations can be readily obtained by proceeding as follows. First, substituting $\mathbf{r} = \mathbf{0}$, we obtain homogeneous equations. Then, substituting the solution of these equations into equation (8), we have

$$e_i(\mathbf{k}, \mathbf{r}) = e_i^0(\mathbf{k}, \mathbf{k}) - \sum_n \Phi_{ij}(\mathbf{k}, \mathbf{r}) \cdot \chi_{jn}(\mathbf{k}) e_n^0(\mathbf{k}, \mathbf{0}) \quad (9)$$

where χ_{ij} is the matrix of susceptibilities defined as follows:

$$\sum_j (\Lambda_j^{-1} \delta_{ij} + \Phi_{ij}(\mathbf{k}, \mathbf{0})) \chi_{jm}(\mathbf{k}) = \delta_{im} \mathbf{1}. \quad (10)$$

Reverse motion to the ordinary space is given by the Fourier integral

$$e_{ni}(\mathbf{r}, \mathbf{r}') = \frac{1}{\Omega} \int \exp[-i\mathbf{k} \cdot (\mathbf{r}_{ni} + \mathbf{r})] e_i(\mathbf{k}, \mathbf{r}) d^3k \quad (11)$$

where Ω is the volume of the Brillouin zone.

Thus, the microscopic electric field in the vicinity of the microscopic impurities can be found by integration of the Fourier transform over the Brillouin zone. The Fourier transforms can be readily calculated by, for example, Ewald's method. For example, the transform of the tensor of the dipole-dipole interaction is

$$\begin{aligned} \Phi_{ij}(\mathbf{k}, \mathbf{r}) = & \frac{4\pi}{\mathcal{V}} \hat{\mathbf{k}} \hat{\mathbf{k}} - \frac{4\pi}{\mathcal{V}} \sum_{g \neq 0} \exp(-i\mathbf{g} \cdot \mathbf{r}) \hat{\mathbf{G}} \hat{\mathbf{G}} \exp\left(-\frac{g^2}{4\lambda^2}\right) \\ & - \exp[-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_{0j})] \frac{\partial^2}{\partial \mathbf{r} \partial \mathbf{r}} \sum_n' \frac{\operatorname{erfc}(\lambda|\mathbf{r} + \mathbf{r}_{ni} - \mathbf{r}_{0j}|)}{|\mathbf{r} + \mathbf{r}_{ni} - \mathbf{r}_{0j}|} \exp(i\mathbf{k} \cdot \mathbf{r}_{ni}) \end{aligned} \quad (12)$$

where $\mathbf{G} = \mathbf{k} + \mathbf{g}$, in the second sum $(ni) \neq (0j)$, and the parameter λ has an arbitrary value which may be chosen on the basis of rapidly converging sums in both the ordinary and the reciprocal spaces. Note that this parameter is well defined if one wants to take into account the size of the ions in the lattice. In this case, the second sum in the ordinary space vanishes.

Now, it is not difficult to calculate the energy of the lattice polarization:

$$E_{pol} = \frac{1}{2} \sum_{ni\alpha} \Lambda_{i\alpha}^0 e_{ni\alpha}^2. \quad (13)$$

Indeed, substituting solution (11) into equation (13), one can see that the summation over the number n of the cells can be performed analytically. The final result is

$$E_{pol} = \frac{1}{2\Omega} \sum_{j\alpha} \Lambda_{j\alpha}^0 \int |e_{j\alpha}(\mathbf{k}, \mathbf{0})|^2 d^3k. \quad (14)$$

Thus, to calculate the energy of polarization, one should perform the integration of the squared transform of the microscopic electric field over the Brillouin zone. In the case when the lattice is polar, this approach seems to be much easier than the ordinary cluster method because, in the cluster approach, one should use a huge cluster to be sure it is adequate for the polar crystal lattice and, moreover, one should carry out the calculation of the electric field at each site and then perform summation (13) over the sites.

Let us now briefly discuss the case when the ion displacements near the microscopic impurities are large. Let it hold for the set of the sites $L = \{ni\}$. To take into account the real displacements, we redefine the unscreened electric field

$$\bar{e}_{ni}^0(\mathbf{r}) = e_{ni}^0(\mathbf{r}) + \sum_L [\Phi_{ni,L}(\mathbf{r}) \cdot \Lambda_L^0 \cdot e_L(\mathbf{0}) - \Phi_{ni,L}(\mathbf{r} - \Delta\mathbf{r}_L) \cdot \Lambda_L \cdot e_L(\Delta\mathbf{r}_L)] \quad (15)$$

where $\Delta\mathbf{r}_L$ is the ion displacement, e_{ni}^0 is the unscreened electric field produced by the microscopic impurities and, by the shifted ions, the tensor Λ_j^0 is constructed from the polarizabilities which do not depend on the number n of unit cells, but the tensor Λ_{nj} can have arbitrary values. Thus, we take into account the ion displacements as well as the change in the polarizabilities of the ions. In particular, one can consider the case when an ion is not shifted but has changed polarizability. Note that the atomic displacements should satisfy the ordinary equilibrium conditions.

Substituting definition (15) into equation (11), one can obtain a set of equations of the following general form:

$$e_{ni}(\mathbf{r}) = A_{ni}(\mathbf{r}) + \sum_L B_{ni,L}(\mathbf{r})e_L(\mathbf{0}) + \sum_L C_{ni,L}(\mathbf{r})e_L(\Delta\mathbf{r}_L) \quad (16)$$

where A_{ni} , $B_{ni,L}$ and $C_{ni,L}$ can be readily defined on the basis of equations (9), (11) and (16). To solve these equations, one should substitute $\mathbf{r} = \mathbf{0}$ and $\mathbf{r} = \Delta\mathbf{r}_L$, which results in a set of homogeneous equations. Having found the solution of these equations, one can then calculate the local electric field at any one of the points of the lattice by means of equation (16).

Thus, the approach in use allows one to compute the microscopic electric field, produced by the microscopic impurities, without resorting to the cluster approach. In this method, the polarization of the whole crystal as well as the interdependence of the polarization of all the lattice sites are taken into account without making use of both the Mott–Littleton approach and the continuous-media approximation. This is very important because, as will be shown later, the asymptotic behaviour of the electric field in the crystal lattice differs from that in the Mott–Littleton and continuous-media approximations.

Let us now return to the case when the displacements are small but let us turn to the asymptotic behaviour of the electric field. At a considerable distance from the dipole, only small values of \mathbf{k} in the integral (11) are important. The Fourier transforms of the tensor of the dipole–dipole interaction have a particularly simple form near the point $\mathbf{k} = \mathbf{0}$. Only the first contribution in equation (12) can be taken into account in this case.

Noting that function (11) is determined by only the direction of the vector \mathbf{k} but not by its modulus, the integral over the modulus of \mathbf{k} in (11) can be performed analytically by making use of the following formula:

$$\int_{-1}^1 \int_0^\infty \exp(-ikt) k^2 f(t) dt dk = -\frac{\pi}{l^3} f''(0) \quad (17)$$

where $t = \cos\theta$. Note that the infinite upper limit of the integration over k is justified by the fact that only small k contribute to the integral at high l .

To find the derivative in equation (17), we employ equation (12) together with the definition of susceptibility (10). The latter gives

$$\begin{aligned} \chi'_t &= -\chi \Phi'_t(\mathbf{k}, \mathbf{0}) \chi \\ \chi''_{tt} &= -\chi \Phi''_{tt}(\mathbf{k}, \mathbf{0}) \chi - \chi'_t \Phi'_t(\mathbf{k}, \mathbf{0}) \chi - \chi \Phi'_t(\mathbf{k}, \mathbf{0}) \chi'_t. \end{aligned} \quad (18)$$

It is very important that the derivatives Φ'_t and Φ''_{tt} for small values of \mathbf{k} do not prove to depend on the atomic site

$$\begin{aligned} \frac{\mathcal{V}}{4\pi} \Phi'_t &= \left. \frac{\partial}{\partial(\cos\theta)} \hat{\mathbf{k}} \hat{\mathbf{k}} \right|_{\cos\theta=0} \\ \frac{\mathcal{V}}{4\pi} \Phi''_{tt} &= \left. \frac{\partial^2}{\partial(\cos\theta^2)} \hat{\mathbf{k}} \hat{\mathbf{k}} \right|_{\cos\theta=0}. \end{aligned} \quad (19)$$

The final result is

$$\mathbf{e}_{ni}(\mathbf{r}) = \frac{1}{2\pi} \int_0^{2\pi} \mu_i^+(\varphi, \mathbf{r}) \mathbf{G}(\varphi) \mu_j(\varphi, \mathbf{r}') \mathbf{d}_{0j} d\varphi \quad (20)$$

where

$$\mu_i^+(\varphi, \mathbf{r}) = \left. \sum_m \left(\delta_{im} \mathbf{I} - \sum_j \Phi_{ij}(\varphi, \mathbf{r}) \chi_{jm}(\varphi) \right) \right|_{\cos\theta=0} \quad (21)$$

$$\mu_i(\varphi, \mathbf{r}) = \left. \sum_j \left(\delta_{ij} \mathbf{I} - \sum_m \chi_{jm}(\varphi) \Phi_{mi}(\varphi, -\mathbf{r}) \right) \right|_{\cos\theta=0}$$

$$\mathbf{G}(\varphi) = \left. \frac{2\pi^2}{\Omega l^3} \left(\Phi''_{tt} - 2 \sum_{ij} \Phi'_t \chi_{ij} \cdot \Phi'_t \right) \right|_{\cos\theta=0}. \quad (22)$$

Thus, one can consider the energy E_{12} of the interaction between two dipoles in the lattice as the average (over the directions of the unit vector $\hat{\mathbf{k}}$ in the x - y plane) of the matrix product of the tensors of the effective dipole moments $\mu_1 \mathbf{d}_1$ and $\mu_2 \mathbf{d}_2$ and of the effective (screened) interaction tensor \mathbf{G} .

Let us consider the case when the dipoles are located at a crystallographic axis and are directed along this axis. In this case, μ_i does not prove to depend on φ . As a result, equation (20) takes the form

$$\mathbf{e}_z \mathbf{e}_{ni}(\mathbf{r}, \mathbf{r}_{0j} + \mathbf{r}') = \mathbf{e}_z \mu_i^+(\mathbf{r}) \frac{2\langle \epsilon_{\perp}^{-1} \rangle}{l^3} \cdot \mu_j(\mathbf{r}') \mathbf{d}_{0j} \quad (23)$$

where \mathbf{e}_z is the unit vector directed along the z axis and

$$\langle \epsilon_{\perp}^{-1} \rangle = 1 - \frac{2}{\mathcal{V}} \int_0^{2\pi} \hat{\mathbf{k}} \cdot \sum_{ij} \chi_{ij} \hat{\mathbf{k}} \Big|_{\cos\theta=0} d\varphi. \quad (24)$$

The dielectric constant (24) describes the screening of the interaction between the two point charges in the lattice. In cubic crystals, it also coincides with the macroscopic dielectric constant. The coefficient μ_i has in this case the following sense. Let a uniform external electric field be applied to the crystal. Then, μ_i is the ratio of the local field on the i th site to the average field. In the simple-cubic lattice, this ratio is $\mu = (\epsilon + 2)/3$. This result is in accordance with the values obtained in earlier work [3–5].

In the case considered, the following sum rule holds:

$$\frac{4\pi}{\mathcal{V}} \sum_i \alpha_i \mu_i(0) = \epsilon - 1. \quad (25)$$

Furthermore, there is the following condition of normalization:

$$\frac{1}{\mathcal{V}} \int_{unit\ cell} \mu_i(\mathbf{r}) d^3r = 1 \quad (26)$$

where the integration is performed over the unit cell.

Thus, the effective dipole moment can be much greater than the real dipole moment. However, this holds only if the dipoles are directed along the z axis. In the case when the dipoles are directed perpendicular to this axis, in the simple-cubic lattice, $\mu = (\epsilon + 2)/3\epsilon$ while $G = \epsilon$, i.e., the effective dipole moment has a comparatively low value while the effective interaction between the dipoles is enhanced.

Along similar lines, we have derived an expression for calculating the electric field produced by the point charge q_{0j} located at the j th site of the zeroth cell. The dissimilarity from the previous case is only that the unscreened field must be rewritten in the form

$$e_i^0(\mathbf{k}, \mathbf{r}) = \mathbf{W}_{ij}(\mathbf{k}, \mathbf{r})q_{0j}. \quad (27)$$

At small \mathbf{k} , the vector \mathbf{W}_{ij} has a particularly simple form

$$\mathbf{W}_{ij}(\mathbf{k}, \mathbf{r}) = \frac{4\pi i}{\mathcal{V}} \frac{\mathbf{k}}{k^2}. \quad (28)$$

To perform the integration in (11), one can use the following formula:

$$\int_{-1}^1 \int_0^\infty \exp(-ikt) k f(t) dt dk = -i \frac{\pi}{l^2} f'(0). \quad (29)$$

The derivative in equation (29) can again be determined analytically by using equations (18) and (19). The final result is

$$e_i(\mathbf{r}, \mathbf{r}_{0j} + \mathbf{r}') = \frac{1}{2\pi} \int_0^{2\pi} \mu_i^+(\varphi, \mathbf{r}) \mathbf{F}(\varphi) \Big|_{\cos\theta=0} q_{0j} d\varphi \quad (30)$$

where

$$\mathbf{F}(\varphi) = \frac{1}{l^2} \left(\hat{\mathbf{k}}'_i - \sum_{ij} \varphi'_i \chi_{ij} \hat{\mathbf{k}} \right). \quad (31)$$

It is seen that, in this case, the electric field does not depend on the atomic site at which the point charge is located.

It is evident that, if the vector e_i is directed perpendicular to the z axis, the electric field (30) vanishes. In the case, when this vector is directed along the z axis, we have

$$e_z e_i(\mathbf{r}, \mathbf{r}_{0j} + \mathbf{r}') = e_z \mu_i^+(\mathbf{r}) \frac{(\epsilon_\perp)^{-1}}{l^2} q_{0j}. \quad (32)$$

Thus, the formulae obtained in this section allow one to calculate the electrostatic field produced by the point dipole as well as by the point charge in a complex crystal with the orthorhombic unit cell or in orthorhombic positions. This provides the basis for calculating the electrostatic field produced by impurities in perovskite-like crystals.

3. Results of the calculation

As a first example, we have chosen potassium tantalate in which phase transition phenomena at a low concentration of Li ions were observed [1]. Potassium tantalate has a cubic structure for low temperatures, but it is usually related to the incipient ferroelectrics [8, 9]. The Curie temperature, obtained in a nominally pure potassium tantalate by extrapolating experimental data, lies just below 0 K.

The computation was carried out using different values of the dielectric constant that corresponded to different temperatures and frequencies. We considered three cases. In the first (I) and second (II) cases, the lattice parameter was taken to be equal to 3.9884 Å [8], which was related to room temperature. The atomic polarizabilities of the potassium ion,

$\alpha_K = 1.14 \text{ \AA}^3$, and of the oxygen atom, $\alpha_{O\parallel} = 2.44 \text{ \AA}^3$ and $\alpha_{O\perp} = 0.93 \text{ \AA}^3$, were taken from [8]. The polarizability of the Ta atom was chosen so that the calculated dielectric constant is equal to the experimental value: $\epsilon_\infty = 5.15$ in the first case and $\epsilon_0 = 204$ in the second case [8]. The third (III) case describes the lowest temperatures for which the values $a = 3.9842 \text{ \AA}$ and $\epsilon_0 = 3840$ were employed [9].

The energy of two interacting dipoles is expressed as follows:

$$E_{12} = d_1 \gamma_1 \frac{\epsilon + 2}{3} \Phi_{12} \langle \epsilon_\perp^{-1} \rangle \frac{\epsilon + 2}{3} \gamma_2 d_2. \quad (33)$$

In the simple-cubic lattice, $\gamma_1 = \gamma_2 = 1$. In perovskite-type oxides, these quantities were determined by interpolation of the results of calculating the energies of pair interactions.

Table 1. The values of the parameter γ obtained for KTaO_3 .

Case	γ_K	γ_{Ta}	γ_{Oz}	γ_{Oxy}	ϵ
I	0.44	2.93	1.97	0.79	5.15
II	-0.21	5.20	3.72	0.24	204
III	-0.23	5.28	3.78	0.22	3840

From the data obtained (table 1) we note that the interactions between the dipoles located on the Ta and O_z sites are the greatest. The enhancement of the interaction between dipoles in these positions is of the order of the static dielectric constant ϵ_0 . Thus, the effective dipole moment in these sites appears to be approximately ϵ_0 times larger than the real dipole moment.

Table 2. The values of the parameter γ obtained for La_2CuO_4 : O(1) is the apical oxygen atom while O(2) and O(3) are the oxygen atoms lying in the a - b plane.

Case	Dipole		γ_{La}	γ_{Cu}	$\gamma_{O(1)}$	$\gamma_{O(2)}$	$\gamma_{O(3)}$	$\langle \epsilon_\perp^{-1} \rangle^{-1}$	ϵ
	direction	l direction							
I	c	c	0.37	1.17	1.11	0.86	0.86	4.49	4.45
I	a	c	1.70	0.87	0.85	1.24	1.26		
I	c	a	0.38	1.18	1.11	0.89	0.89	4.52	4.49
I	a	a	1.70	0.87	0.85	1.24	1.27		
II	c	c	0.12	1.28	1.15	0.82	0.82	45.1	23
II	a	c	4.73	0.84	0.62	2.74	2.72		
II	c	a	0.09	0.97	0.87	0.63	0.63	32.23	45.1
II	a	a	3.8	0.653	0.48	0.69	0.68		

Table 2 lists the calculated values of the parameter γ for the atomic sites of La_2CuO_4 . Two cases were considered. The first case employed the atomic polarizabilities $\alpha_{La} = 1.04 \text{ \AA}^3$, $\alpha_{Cu} = 0.001 \text{ \AA}^3$ and $\alpha_O = 2.46 \text{ \AA}^3$. These values are consistent with the high-frequency dielectric constant $\epsilon_\infty = 4.5$. The second case corresponded to the static dielectric constants $\epsilon_c = 23$ and $\epsilon_{a,b} = 45$ [10]. In the latter case, the oxygen polarizability was chosen so that the calculated static dielectric constants were equal to the experimental values. The oxygen polarizabilities proved to equal 4.369 \AA^3 along the c axis and 3.996 \AA^3 in the a - b plane.

Table 3 shows the results obtained for $\text{YBa}_2\text{Cu}_3\text{O}_6$. Again, two cases were considered. The first case corresponded to high frequencies while the second case was related to low

Table 3. The values of the parameter γ obtained for $\text{YBa}_2\text{Cu}_3\text{O}_6$: the same notation as in table 2 is used; the Cu(1) atom belongs to the Cu–O chain while the Cu(2) atom is related to the CuO_2 layer.

Case	Dipole		γ_Y	γ_{Ba}	$\gamma_{Cu(1)}$	$\gamma_{Cu(2)}$	$\gamma_{O(1)}$	$\gamma_{O(2)}$	$\gamma_{O(3)}$	$(\epsilon_{\perp}^{-1})^{-1}$	ϵ
	direction	l direction									
I	c	c	1.49	0.65	2.48	0.61	0.92	0.75	0.75	3.8	2.21
I	a	c	0.72	1.39	0.07	1.30	1.14	1.49	1.19		
I	c	a	1.38	0.63	2.23	0.58	0.84	0.71	0.71		
I	a	a	0.67	1.31	0.06	1.21	1.07	1.40	1.11		
II	c	c	1.58	0.32	3.65	0.45	0.95	0.59	0.59	90.2	3.73
II	a	c	1.33	4.37	-2.09	6.96	2.58	6.10	5.49		
II	c	a	0.51	0.09	1.21	0.14	0.30	0.18	0.18		
II	a	a	0.45	1.48	-0.71	2.35	0.87	2.06	1.85		

frequencies. The electronic polarizabilities were equal to 0.001 \AA^3 , 1.94 \AA^3 and 0.001 \AA^3 for the Y, Ba and Cu ions, respectively.

The oxygen polarizabilities were chosen in the following manner. First, we approximated the results of the shell-model calculations carried out for $\text{YBa}_2\text{Cu}_3\text{O}_7$ in [11] by the point-polarizable-ion model. We found the oxygen polarizabilities $\alpha_{Oa} = 2.22 \text{ \AA}^3$, $\alpha_{Ob} = 2.0465 \text{ \AA}^3$ and $\alpha_{Oc} = 2.0095 \text{ \AA}^3$ to be suitable for this purpose. Therefore, $\epsilon_{\infty a} = 3.66$, $\epsilon_{\infty b} = 3.58$ and $\epsilon_{\infty c} = 3.18$. Then, the average polarizability $\alpha_{Oab} = 2.12 \text{ \AA}^3$ in the a - b plane and $\alpha_{Oc} = 2.00 \text{ \AA}^3$ were employed for calculating the local fields in $\text{YBa}_2\text{Cu}_3\text{O}_6$. The oxygen polarizabilities in the second case were chosen along similar lines. It was found for $\text{YBa}_2\text{Cu}_3\text{O}_7$ that $\alpha_{Oa} = 4.0427 \text{ \AA}^3$, $\alpha_{Ob} = 3.912 \text{ \AA}^3$ and $\alpha_{Oc} = 4.198 \text{ \AA}^3$ and $\epsilon_{0a} = 15.497$, $\epsilon_{0b} = 13.68$ and $\epsilon_{0c} = 16.77$ respectively, which was in accordance with the values obtained in [11]. For $\text{YBa}_2\text{Cu}_3\text{O}_6$ we took $\alpha_{Oab} = 4.0 \text{ \AA}^3$ and $\alpha_{Oc} = 4.2 \text{ \AA}^3$. This led to the following results: $\epsilon_{ab} = 18.757$ and $\epsilon_c = 90.206$. The large values of the static dielectric constants are in agreement with numerous experiments showing ferroelectric-like properties in layered perovskite oxides. Furthermore, the coefficients γ_i were found to be not very sensitive to the value of the dielectric constant ϵ_0 at large ϵ_0 .

4. Discussion

The gigantic enhancement of the interaction between microscopic dipoles in the polar lattices of cubic and layered perovskite-type oxides can evidently lead to the formation of polarized regions. Indeed, they were observed in many research studies. An explanation of this phenomenon has been given in a few investigations (see the reviews in [1, 2]) where it was supposed that the indirect interaction between dipoles was a result of their interaction with a soft ferroelectric (optical) mode. This interaction lowers the frequency of the soft mode and, as a consequence, can lower the crystal symmetry. The evaluation of the coefficient of the enhancement of the interaction between microscopic dipoles in KTaO_3 was carried out in [1] in the following way. First, using Slater's [6] formulae, the local electric field produced by the ferroelectric polarization was calculated at an atomic site. Then, the ratio γ of this field to $4\pi P/3$ was found. Thereafter, the formulae obtained in [3] for calculating the electric field between microscopic dipoles in the simple-cubic lattice were multiplied by γ .

Our computations were carried out in a different manner. However, the values of $|\gamma|$

proved to be close to the values obtained in [1]. We found for the K site that $\gamma = -0.21$ and for the Ta site $\gamma = 5.25$. These values are in qualitative accordance with those obtained in [1, 12]: $\gamma = -0.1$ for the K site and $\gamma = 5$ for the Ta site [13].

Experiments on ESCR showed for the solution $\text{KTaO}_3\text{:Li}$ that the value of γ for the Li position was about 0.1 [1]. This result is somehow lower than the value which we obtained in our computations but there are good reasons for this. Indeed, the electric field which we have calculated (and also the field calculated in [1, 12]) is produced by the point dipole but, according to experimental data, the Li ion off-centre displacement is about 1.35 Å [8]. Our preliminary results and the condition of normalization (26) show that the Li ion displacement is accompanied by a change in the interaction. We believe that this would lower γ . Similarly, a study of the ESCR spectrum of the $\text{Fe}^{3+}\text{-V}_0$ complex yielded $\gamma = 0.05$ [13, 14] whereas this value is two orders lower than the value $\gamma = 5$ obtained for the Ta site. In fact, the computation was carried out for an ideal (no vacancies) lattice structure. The absence of the oxygen ion near the substitution could cause the decrease in γ . Rigorous consideration of such cases will be dealt with separately.

The huge values of the effective dipole moments for microscopic impurities in ferroelectrics can lead to many other interesting phenomena. One of them is the even field current. This phenomenon is as follows. If one applies to a ferroelectric monodomain crystal (or polarized ceramic) a voltage perpendicular to a ferroelectric axis, then current arises not only in the direction of the electric field but also along the polar axis, i.e. perpendicular to the direction of the voltage. This phenomenon was explained on the basis of the anisotropic scattering of hot electrons by dipole impurities [15]. However, as the hot electrons in dielectrics have very small wavevectors, their scattering by microscopic dipoles cannot explain the appearance of a current of the order of a few per cent. In connection with this, it was suggested in [16, 17] that a non-linear dependence of the field on polarization be taken into account. In fact, as is seen from the data obtained, anisotropic scattering of hot electrons can arise from the gigantic enhancement of the electric field of a microscopic dipole.

We wish to call attention to the following. The enhancement of the electrostatic field of microscopic impurities takes place only at definite positions in crystal. Averaging the field over the unit cell reduces the expression for calculating the field to the ordinary Coulomb law written for continuous media.

In connection with the discovery of the high-temperature superconductivity in perovskite-like oxides, many models have appeared in which attempts were made to study the consequences of the high polarizability of the lattice. In particular, in [18, 19], it was suggested that the localization of a hole on the oxygen ion could lead to an increase in the radius of the ion and, as a consequence, to its displacement from the usual position. Attraction between microscopic dipoles, sufficiently enhanced by the lattice polarization, can lead, in the authors' opinion, to the formation of local pairs. The results of our computations support the idea of gigantic enhancement of the interaction between the microscopic dipoles located on the oxygen sites.

Similar to the model described, it was shown in [20] that the two oxygen ions O^- near an acceptor substitution in KTaO_3 are shifted from the centrosymmetric positions so as to form a bipolaron. In our opinion, the main causes of this are the decrease in the atomic radius and the large enhancement of the dipole–dipole interaction.

In recent years, paired holes arising by means of dipole excitations (dipolarons) have been extensively studied [21]. The results of our computations support the idea of enhancement of the monopole–dipole interaction in perovskite-like lattices. However, according to our analysis, the charge–charge interaction, as in the simple-cubic lattice [3],

at a widely separated distance is described by the ordinary Coulomb law, i.e. the unscreened field must be divided by ϵ_0 . Apparently, enhancement of the field could arise at shorter distances.

It was shown in [22] that the oxygen vacancy in perovskite-type oxides can, under certain conditions, be a dipole centre. The experimental evidence that, in KTaO_3 , there are dipole centres the concentration of which is correlated with the degree of oxidation (reduction) of the sample is provided in [23]. From the data obtained, we note that the appearance of an ordered state of the oxygen vacancies in perovskites can be expected. In support of this conjecture, the phase transitions from the cubic phase to the tetragonal phase were experimentally observed for $\text{LaCuO}_{3-\delta}$ and $\text{BaPb}_{1/4}\text{Bi}_{1/4}\text{O}_{3-\delta}$ [24, 25] for an increased number of oxygen vacancies. However, there are other possible explanations of these facts. The oxygen vacancies are known to increase the volume of crystal which can trigger instability of the lattice [26].

Finally, let us pay attention to the fact that not only can the displacement of ions give rise to the appearance of the dipole moments in lattice but also dipoles may arise as a result of the dipole excitations of electrons on the same atom or between two atoms [21]. So, the charge-transfer excitation between the oxygen atom and the metal atom results in the formation of a dipole located anywhere between these two ions. The interaction between such electronic excitations in the polar lattice is sufficiently enhanced. As a result, under certain conditions, local pairs could arise. In similar way, the dipole arising from the charge-transfer excitation could attract a point charge, e.g. a hole.

The necessary condition for these phenomena is that the dipole excitation is localized in ordinary space. The electron (hole) localization can be a consequence of the electron correlation or of the strong electron-phonon interaction. It was shown numerically that the cluster approach is capable of describing the electron localization due to its interaction with the lattice polarization in alkali halides [27–30], binary oxides [31] and SiO_2 [32, 33]. However, we expect that, when applying the cluster approach to much more polar ionic systems such as the perovskite-type crystals, difficulties from the limited cluster size would arise. In this connection, the method proposed in the present paper could be very useful for calculating the energy of polarization near a microscopic impurity. An alternative approach, based on the Green-function method, was proposed in [34, 35]. In this method the shell model was used instead of the point-polarizable method. It should be remembered that our approach was capable of giving analytical results.

5. Conclusions

In the present paper, we have formulated a method for calculating the local electric fields produced by microscopic impurities in polar complex ionic lattices. This method allows one to calculate the electric fields and the energy of the lattice polarization without resorting to the cluster approach. Rather, integration over the Brillouin zone is to be performed for these purposes.

At a considerable distance, the energy of the interaction between microscopic defects was shown to be represented as the matrix product of the tensors of the effective dipole moments and of the tensor of the effective interaction. The latter is defined by the macroscopic dielectric constant while the former proves to be markedly enhanced. This is a consequence of the sum rule obtained in the present work. In the particular case of the simple-cubic lattice, the results obtained coincide with those published earlier [3–5]; the enhancement of the real dipole moment is $(\epsilon + 2)/3$.

Thus, the asymptotic behaviour of the electric field produced by the microscopic

impurities strongly differs from the field in the Mott–Littleton model as well as in the continuous-media approximation. We call attention to the fact that the method proposed does not use these models.

The calculations performed have shown that the effective dipole moment is markedly enhanced both in cubic KTaO_3 and in layered La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_6$. Moreover, we have found that the changes in the atomic polarizabilities, leaving the dielectric constant unchanged, does not lead to a change in this result. Thus, the enhancement of the dipole–dipole and monopole–dipole interactions is not a consequence of the appropriate choice of parameters. This is a general result which is based on the sum rule.

Where it was possible, we have carried out a comparison of our quantitative results with those obtained with the soft-mode model and by experiment. We have found that our results, obtained for KTaO_3 , agree with the experiment and calculation by Vugmeister and Glinchuk [1] very well. However, it should be emphasized that Vugmeister and Glinchuk calculated the interaction of a dipole with a soft ferroelectric mode while we made use of the other approach. The reason for the qualitative coincidence of our results is, in our opinion, as follows. We showed that the enhancement coefficient μ_i of the dipole moment acts in a sense as the ratio of the local field on the i th site, produced by the uniform external electric field, to the average field. Thus, at a considerable distance from the microscopic dipole, the polarization of the lattice looks like the ferroelectric distortion of the crystal. This is why the results obtained with the soft-mode model coincide with our straightforward calculations.

We have predicted a large enhancement of the effective dipole moment of microscopic impurities in layered copper oxides that can be checked by the ESCR method. We showed that the even field currents in ferroelectrics could be the result of the dipole moment enhancement. Our data supports the idea of a strong interaction between two holes localized on two oxygen ions in perovskite-type lattices.

It can be inferred from the sum rule and the norming condition that, in the unit cell, there are special points at which the electric fields are mostly enhanced. Thus, it is more probable that the greatest enhancement is achieved in complex lattices because, in this case, the unit cell comprises many atoms occupying different points in the cell. In this respect, the oxides of the perovskite family are peculiar. Their unit cells are very complex and, furthermore, the polarizabilities of the atomic sites are very large. As a consequence, the enhancement coefficient, for example, for the Ta site in KTaO_3 , is gigantic and equals $5.25(\epsilon + 2)/3$.

We also call attention to the possibility of checking cluster calculations by means of the comparison of their results with the analytical expressions obtained in the present paper.

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References

- [1] Vugmeister B E and Glinchuk M D 1990 *Rev. Mod. Phys.* **62** 993
- [2] Glinchuk M D and Bykov I P 1992 *Phase Trans.* **40** 1
- [3] Mahan G D 1967 *Phys. Rev.* **153** 983
- [4] Smith E R 1980 *J. Phys. A: Math. Gen.* **13** L107
- [5] Wielopolski P 1981 *J. Phys. A: Math. Gen.* **14** L263

- [6] Slater J C 1950 *Phys. Rev.* **78** 748
- [7] Born M and Huang K 1954 *Dynamical Theory of Crystal Lattices* (Oxford: Oxford University Press)
- [8] Van der Klink J J and Khanna S N 1984 *Phys. Rev. B* **29** 2415
- [9] Samara G A and Morosin B 1973 *Phys. Rev. B* **8** 1256
- [10] Reagor D, Ahrens E, Cheong S-W, Migliori A and Fisk Z 1989 *Phys. Rev. Lett.* **62** 2048
- [11] Baetzold R C 1990 *Phys. Rev. B* **42** 56
- [12] Vikhnin V S 1984 *Solid State Physics* vol 26 (New York: Academic) p 906
- [13] Vugmeister B E and Antimirova T V 1990 *Phys. Status Solidi b* **157** 183
- [14] Vugmeister B E 1993 *Ferroelectrics* **150** 77
- [15] Sturman B I and Fridkin V M 1992 *Photogalvanic Effect* (Moscow: Nauka)
- [16] Furman A C 1990 *Sov. Phys.-JETP* **97** 1626
- [17] Prosdandeyev S A, Chervonobrodov S P and Tennenboun I M 1994 *Ferroelectrics* **153** 279
- [18] Vugmeister B E and Glinchuk M D 1989 *Phys. Lett.* **139A** 471
- [19] Kristoffel N and Rubin P 1990 *Phys. Status Solidi b* **157** K93
- [20] Donnerberg H and Birkholz A 1995 *J. Phys.: Condens. Matter* **7** 327
- [21] Sharma R R 1994 *Physica C* **224** 368
- [22] Prosdandeyev S A, Teslenko N M and Fisenko A V 1993 *J. Phys.: Condens. Matter* **5** 9327
- [23] Fisher C, Auf der Horst C, Voigt P, Kapphan S and Zhao J 1994 *Proc. 7th Europhys. Conf. on Defects in Insulating Materials (Lyon, 1994)* p 36
- [24] Darracq S, Matar S and Demazeau G 1993 *Solid State Commun.* **85** 961
- [25] Hashimoto T and Kawazoe H 1993 *Solid State Commun.* **87** 251
- [26] Prosdandeyev S A and Tennenboun I M 1994 *J. Phys.: Condens. Matter* **6** 7013
- [27] Shluger A L, Kantorovich L N, Heifets E N, Shidlovskaya E K and Grimes R W 1992 *J. Phys.: Condens. Matter* **4** 7417
- [28] Heifets E N and Shluger A L 1992 *J. Phys.: Condens. Matter* **4** 8311
- [29] Kantorovich L N, Heifets E N, Lifshicz A, Kuklja M and Zapol P 1993 *Phys. Rev. B* **47** 14 875
- [30] Shluger A L, Itoh N, Puchin V E and Heifets E N 1991 *Phys. Rev. B* **44** 1499
- [31] Shluger A L, Heifets E N, Gale J D and Catlow C R A 1992 *J. Phys.: Condens. Matter* **4** 5711
- [32] Zhang X, Ong C K and Stoneham A M 1994 *J. Phys.: Condens. Matter* **6** 5647
- [33] Zhang X and Ong C K 1995 *J. Phys.: Condens. Matter* **7** 1603
- [34] Stachiotti M G and Migoni R L 1990 *J. Phys.: Condens. Matter* **2** 4341
- [35] Stachiotti M G, Migoni R L and Hochli U T 1991 *J. Phys.: Condens. Matter* **3** 3689