Stabilization of the dipole state of a polaron near an oxygen vacancy in oxides of the perovskite family

S. A. Prosandeev

Rostov State University, 344090 Rostov-on-Don, Russia

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This paper shows that in oxides of the perovskite family the symmetry of the one-electron wave function of a bound state of an oxygen vacancy can be lowered due to the interaction of the electron with the lattice polarization. The phenomenon explains the existence in nominally pure $KtAO_3$ of the dipole centers recently discovered by the second-harmonic generation method. The problem is analyzed theoretically both in the continuum approximation and by allowing for the real structure of the crystal. The lattice polarization energy is determined by numerically solving the problem for a cluster with roughly 160 atoms in the first region (closest to the defect) and about 2000 atoms in the second regions (at a distance from the defect). The asymptotic value of the electric fields obtained analytically is used in the second region. The covalent component of the energy is found from analytical calculations of lattice sums by the method of Green's functions. The electron Green's functions are determined by the alternate structure theory with a realistic description of electron dispersion in bands of allowed states, which are found by approximating the results of band calculations done by other researchers. © *1996 American Institute of Physics.* [S1063-7761(96)01510-7]

1. INTRODUCTION

As is known, the interaction between charge carriers and lattice polarization can lead to spatial localization of the carriers. The common approach is to consider bound states that are symmetric with respect to a certain lattice site, states that do not violate the point symmetry of the lattice. Only the spatial symmetry of the one-electron wave function is broken. However, lately it has been discovered that sometimes the state of the so-called molecular polaron proves to be energetically more advantageous.[1] In this state the polaron has equal weights on the two nearest anions of the lattice. Such states are stabilized by the decrease in the radii of the anions, the approach of the anions toward one another, and the resulting strengthening of the covalent component of the chemical bond.

This paper examines an entirely different possibility: that the wave function of a polaron coupled with a point defect acquires different weights on sites that are equivalent from the standpoint of the point symmetry of the defect. Such a nonequilibrium state can have a large lifetime, and in time it may transform into a similar state, but with a rotated polarization vector.

Actually such a state, we believe, was observed by Fisher *et al.*[2] in experimental studies of reduced $KTaO_3$. They applied the method of second harmonic generation at low temperatures and discovered in reduced $KTaO_3$ 10^{18} cm^{-3} dipole centers whose concentration increases under reduction and decreases under oxidation of the sample.

Earlier in studies of the electric conduction and optical spectra of oxides of the perovskite family we found that the theoretically calculated temperature dependence of the electrical conductivity is in good agreement with the experiment data if one assumes that the crystal contains 10^{18} cm^{-3} singly ionized oxygen vacancies V_O^+ (see Refs. 3 and 4). These defects are the basic ones in oxides of the perovskite family. If their concentration is in the vicinity of the above value, it can easily be controlled by heating in the respective (oxidizing or reducing) atmosphere.

It can be assumed that the experimentally discovered dipole centers are related in some way to $V_O{}^+$. We will see that under certain conditions V_O^+ has a dipole moment slowly fluctuating in time. For this to happen the ground state of V_O^+ must be formed differently from that in F-centers.

Usually an F-center is interpreted as an electron bound to an anion vacancy. It is assumed that the wave function of this electron is primarily located in the cavity formed in the crystal at the anion site. The reasons for such localization are well-studied. They are the strong reflection of the electron wave from the cations closest to the vacancy and to the decrease in the potential at the vacancy center because of the Madelung field.[5,6] However, the strong reflection of the electron wave occurs only if the first free eigenstates of the cations are highly excited. If cations have fairly low-lying states, as is the case in ion–covalent crystals, an entirely new possibility emerges. The wave function of an electron at V_O^+ in this case can be localized at the cations closest to V_O^+ This ground state was obtained in Refs. 7 and 8 and was found in accordance with the existing optical and electrical characteristics of oxides of the perovskite family.

The ions closest to the oxygen site in $KTaO_3$ are the two equivalent Ta ions. The electron wave function can have weights on these ions that are equal in absolute value, so that the corresponding defect state can be denoted by $Ta^{4.5}V_OTa^{4.5}$, where the number in the superscript indicates the formal valence of the ion. For the case of preferential localization of the electron at one of the Ta ions two other symmetrically reflected structures emerge: $Ta^{4+}V_OTa^{5+}$ and $Ta^{5+}V_OTa^{4+}$. These have dipole moments (with respect to the defect center) pointing in opposite directions.

In this paper we will show that the interaction of the electron at V_O^+ with the lattice polarization stabilizes the asymmetric states of a polaron of the $Ta^{4+}V_OTa^{5+}$ or $Ta^{5+}V_OTa^{4+}$ type. Section 2 is devoted to the general statement of the problem. For illustration we analyze the problem using two models: the continuum model (Sec. 3) and the model of exactly polarizable ions (Sec. 5). Here it must be immediately noted that the first model is too crude for obtaining quantitative results and is given here only because it possesses all the necessary features of a more complicated model but, in contrast to the latter, is exactly solvable. At the same time we found that to describe the phenomenon quantitatively one must allow the local field to differ from the mean field and include the interaction of the polarizations of lattice sites located in a broad region near a defect, which meant using the following approach. The entire region of the crystal surrounding a defect was divided into two parts. The first contained about 160 atoms for which the polarization of each site was determined self-consistently, i.e., the dipole moment of each site was determined by the field at the lattice site generated by all the other polarized sites. In the second region, which included about 2000 atoms, we employed the asymptotic behavior of the local fields. This behavior is studied in Sec. 4 by the inverse Fourier transformation method. Here it must be immediately noted that this behavior in polar crystals was found to differ considerably from the behavior in the often used Mott–Littleton model. The model assumes that the electric field generated by a point charge in a polar lattice far from the charge can be described by the Coulomb formula in the continuum approximation. Actually, however, this formula is true only in the mean field, i.e., if one calculates the mean field over a unit cell. The local (microscopic) field in polar crystals can differ considerably from the mean field. In particular, earlier in Refs. 9–11 it was found that the local field at the sites of a simple cubic lattice differs by a factor of $(\varepsilon+2)/3$ from the macroscopic field. Section 4 generalizes this result to the case of more complex lattices, in particular, to the case of the lattice of the perovskite family.

The chemical bond in oxides of the perovskite family is of an intermediate ion–covalent nature.[12] This means that in solving the problem one must accurately take into account the covalent effects. We show that these effects stabilize the symmetric state of the bound defect state. Estimates of the covalent contribution to the binding energy are made in Secs. 6 and 7 by a combination of the method of Green's functions and a realistic model for the electronic structure of a perfect crystal, the model being based on numerous band calculations by the density functional method. Analytical results for the lattice sums that emerge in calculating the covalent contribution to the energy were obtained. The method does not use perturbation theory techniques. In Sec. 8 we discuss the results and arrive at several conclusions.

2. GENERAL STATEMENT OF THE PROBLEM

When an atomic vacancy is created in a crystal, the potential V in the space surrounding the vacancy changes. Here and in what follows V is interpreted as the matrix element of the perturbation of the electron Hamiltonian in the atomic basis. The modified potential may cause a local level to appear in the forbidden band. This happens if

$$\det\|1-g(\varepsilon)V\|=0, \tag{1}$$

where $g(\varepsilon)=(\varepsilon-H)^{-1}$ is the resolvent of the Hamiltonian operator, or the Green's function of a perfect crystal. Here we consider a situation in which a local state exists and is occupied by a single electron.

An oxygen site in the $KTaO_3$ lattice is surrounded by two Ta ions positioned symmetrically with respect to the site. In this connection one would think that the wave function of the electron bound with the vacancy has equal weights on these ions. Below however, we will see that the interaction of the electron with the polarization of the surrounding medium makes the localization of the electron on one of the two Ta ions advantageous. In this case the one-electron wave function will have a symmetry that is lower than the point symmetry of the oxygen site. It is this solution of the problem that we are discussing in the present paper. Within the solution the electron polarizes the surrounding crystal, with the result that it is shifted, so to say, away from the center to one of the Ta ions closest to the vacancy. Obviously, this is possible only if the Ta^{4+} ion has a low-lying state (in comparison, say, to the position of the cation levels in alkali halide crystals). At the same time, in covalent semiconductors with low-lying levels this effect may not manifest itself because, first, as shown in Sec. 6, the covalent bond stabilizes the symmetric state of the defect and, second, as shown in Sec. 3, the effect is possible only if the local field differs considerably from the mean field.

We take the charges on the Ta atoms closest to V_O as the parameters of the problem:

$$q_1=-\frac{1}{\pi}\,\mathrm{Im}\int_0^{\varepsilon_F}G_1(\varepsilon)d\varepsilon,\quad q_2=-\frac{1}{\pi}\,\mathrm{Im}\int_0^{\varepsilon_F}G_2(\varepsilon)d\varepsilon. \tag{2}$$

Here G_1 and G_2 are the diagonal elements of the Green's function of the crystals with defects, and ε_F is the Fermi energy. Since the wave function of the electron on V_O^+ is symmetric with respect to the two Ta atoms, we have $q_1=q_2=q^0$. But is such a symmetric state stable?

We write the energy of the system as the sum of two contributions,

$$E=E_{\mathrm{pol}}+E_{\mathrm{cov}}, \tag{3}$$

where E_{cov} is the covalent component of the energy (see definition below) and E_{pol} is the polarization energy of the medium:

$$E_{\mathrm{pol}}=-\frac{1}{2}\sum_{ni\alpha}\Lambda_{i\alpha}e_{ni\alpha}^2. \tag{4}$$

Here the sum is only over occupied sites, $\Lambda_{i\alpha}$ is the polarizability of the ith site in the αth direction, e_i is the local field at the ith site (determined by the field e_i^0 of the charge source and the polarization field P_{mj}):

$$\mathbf{e}_{ni}(\mathbf{r})=\mathbf{e}^{0}_{ni}(\mathbf{r})-\mathscr{V}\sum_{mj}\Phi_{ni,mj}(\mathbf{r})\mathbf{P}_{mj}, \tag{5}$$

where $\mathscr{V}$ is the cell volume, and $\Phi_{ni,mj}$ is the dipole–dipole interaction tensor,

$$\Phi_{ni,mj}=\frac{\hat{I}-3\hat{R}_{ni,mj}\hat{R}_{ni,mj}}{R^{3}_{ni,mj}}. \tag{6}$$

Here $\hat{I}$ is the identity matrix and we have written $\mathbf{R}_{ni,mj}=\mathbf{r}_{ni}-\mathbf{r}_{mj}+\mathbf{r}$, where $\mathbf{r}_{ni}$ is the radius vector of the ith site of the nth cell ($\mathbf{r}_{ni}=\mathbf{r}_{0i}+\mathbf{R}_{n}$, with $\mathbf{R}_{n}$ the radius vector of the nth cell), and $\hat{\mathbf{R}}=\mathbf{R}/R$ is the unit vector directed along $\mathbf{R}$. We use the linear approximation, according to which

$$\mathbf{P}_{mj}=\frac{1}{\mathscr{V}}\Lambda_{j}\mathbf{e}_{mj}(0). \tag{7}$$

Note that the displacements of the atoms away from the lattice sites are assumed small, and because of this they can be taken into account by adding an ion component to the electron polarizability. We also note that numerical calculations show (more about this later in the paper) that the atomic displacements near a defect prove to be on the order of the ferroelectric displacements of ions in the polar phase (0.06 Å), which supports the use of the linear approximation.

The covalent energy E_{cov} can be found from the variations in the density of electron states:

$$E_{\mathrm{cov}}=\int_{0}^{\varepsilon_{F}}\varepsilon\Delta N(\varepsilon)d\varepsilon, \tag{8}$$

where

$$\Delta N(\varepsilon)=-\frac{1}{\pi}\,\mathrm{Im}\left[\frac{\partial}{\partial\varepsilon}\ln(\det\|1-g(\varepsilon)V\|)\right]. \tag{9}$$

We assume that when the deviations $\Delta q=q_{1}-q^{0}$ are small, the energy (8) can be written in the same way as in the two-level model (proof of this is given in Sec. 6):

$$E_{\mathrm{cov}}=2tf_{1}f_{2}+E^{0}_{\mathrm{cov}}, \tag{10}$$

where E^{0}_{cov} is the contribution of valence electrons to the energy (8), $t<0$ is the effective hopping integral between the first and second Ta ions, and f_{1} and f_{2} are the weights of the wave functions on these ions. To estimate the behavior of f_{1} and f_{2} as functions of the parameters of the problem we employ the following approximations:

$$f_{1}=\sqrt{q_{1}},\quad f_{2}=\sqrt{q_{2}},\quad q_{1}+q_{2}=2q^{0}, \tag{11}$$

which are a natural consequence of the two-level model. The validity of these assumptions has been verified numerically by the method of Green's functions.

Note that (3) incorporates only the one-particle part of the energy. The reason for this is the following. The possible effect of the electrostatic electron–electron interaction on the stability of the symmetric solution of the problem was analyzed in Refs. 13 and 14. There it was found that the Hubbard electron–electron interaction in transition elements can disrupt the symmetry of the defect. The present paper studies a different and, we believe, a much more important result of symmetry violation—the interaction of an electron with the polarization of the medium caused by the electron. For this reason we focus mainly on the one-particle part of the energy.

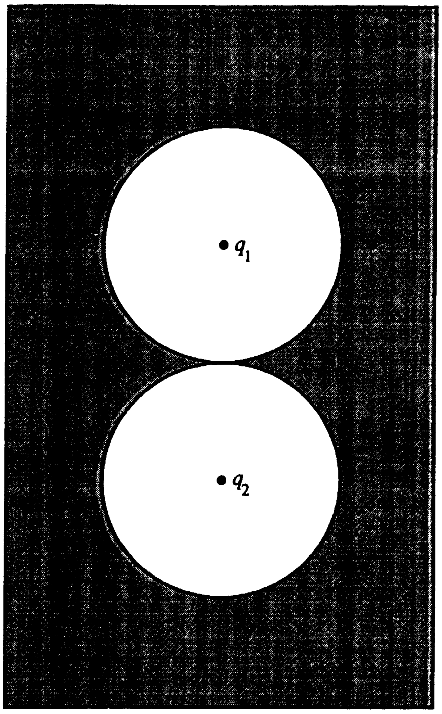

FIG. 1. Schematic of the continuum model used in the present work.

We expand the energy (3) in a power series in Δq at the point $q_{1}=q_{2}=q^{0}$ and restrict our discussion to second-order terms in Δq:

$$E=E^{0}+\beta(\Delta q)^{2}-\frac{t}{q^{0}}(\Delta q)^{2}, \tag{12}$$

where

$$\beta=\frac{1}{2}\frac{\partial^{2}E_{\mathrm{pol}}}{\partial q_{1}^{2}}\Big|_{q_{1}=q^{0}}. \tag{13}$$

This implies that the symmetric state of a defect proves unstable if

$$\beta q^{0}-t<0. \tag{14}$$

At the same time this condition describes the region of a stable dipole state. Clearly, since we have $t<0$, for (13) to be true β must be negative and must exceed $|t|/q^{0}$ in absolute value. This is possible in highly polar crystals but not in semiconductors. Below we will see that for (14) to hold the local field must differ from the mean field, but this difference is practically nil in semiconductors.

3. THE CONTINUUM APPROXIMATION

Let us take the following model (Fig. 1). Suppose that a uniform polarizable medium with a dielectric constant ε contains two point charges, q_{1} and q_{2} at points z_{0} and $-z_{0}$ and a charge q_{0} at the origin of the coordinate system. This third charge models an anion vacancy, while the first two model the two Ta ions closest to the vacancy. For simplicity we assume $q_0=\frac{1}{2}$, i.e., $q_1+q_2=1$.

We surround each of the first two charges by spheres of radius $\frac{1}{2}z_0$ and assume that inside the spheres the medium is unpolarizable. This ensures that the energy is not divergent and allows for the finite distance from the field sources to the ions closest to them.

Under these assumptions,

$$E=-A[q_1^2+(1-q_1)^2]-2Bq_1(1-q_1)+2t\sqrt{q_1(1-q_1)}, \tag{15}$$

where

$$A=\frac{\varepsilon-1}{z_0\varepsilon^2}\left(\frac{4}{5}+\frac{1}{16}\ln 15\right), \quad B=\frac{\varepsilon-1}{4z_0\varepsilon^2}. \tag{16}$$

The energy (15) for $B<A-t$ is minimal at the points

$$q_1=\frac{1}{2}\pm\sqrt{\frac{1}{4}-\frac{t^2}{4(A-B)^2}}, \tag{17}$$

which correspond to the two possible dipole states of the defect. The condition for the stability of the dipole state can be written as

$$|t|<0.72\frac{\varepsilon-1}{z_0\varepsilon^2}. \tag{18}$$

At $z_0=2$ Å we find $|t|<5(\varepsilon-1)/\varepsilon^2$eV, which holds for $|t|=0.1$ eV if $1.02<\varepsilon<49$. Thus, for $\varepsilon>49$ the dipole state proves unstable in the given model. The reason is that at high values of ε the electric field at distances $|r|>\frac{1}{2}z_0$ is extremely weak and hence the polarization energy can not counterbalance the covalent energy. In Sec. 4 we will see that the true asymptotic behavior of the electric field at the lattice sites of an ionic crystal for large values of ε is independent of ε, with the result that the condition (18) assumes the form

$$|t|<0.72\gamma^2\left(\frac{\varepsilon+2}{3}\right)^2\frac{4\pi\alpha}{\mathcal{V}z_0\varepsilon^2}, \tag{19}$$

where α is the atomic polarizability, and $\gamma\sim 1$. We see that for large values of ε the right-hand side of the inequality (19) is proportional to α. In the continuum approximation we have $a\sim\varepsilon-1$, but if we allow for the atomic structure of the crystal, according the Lorenz-Lorentz formula,

$$\frac{4\pi\alpha}{\mathcal{V}}=3\frac{\varepsilon-1}{\varepsilon+2}. \tag{20}$$

This implies that for large ε the value of α is independent of ε. Thus, for large ε the right-hand side of the inequality (19) has a maximum. The situation resembles the one in polaron theory,[15] which uses the quantity $\varepsilon^{-1}=\varepsilon_0^{-1}+\varepsilon_\infty^{-1}$, where ε_0 and ε_∞ are the low- and high-frequency dielectric constants, respectively. When ε_0 is large, we can ignore ε_0^{-1}, and $\varepsilon^{-1}=\varepsilon_\infty^{-1}$. This means that the depth of the polaron well for large ε_0 has a limit determined by the high-frequency dielectric constant ε_∞. Similarly, in our case we found that for large ε (here $\varepsilon\equiv\varepsilon_0$) the drop in the polarization energy when the symmetry of the defect is broken has a limit determined by the atomic polarizability.

For small values of ε ($\varepsilon\sim 1$) the right-hand side of the inequality (19) is proportional to $\varepsilon-1$, i.e., the larger the value of ε the stronger the effect.

Note that the polarizable medium is assumed to be in the paraelectric state, when the impurity electric field does not force the medium out of equilibrium. Because of this we also ignore the fluctuations of the medium polarization and the nonlinearity of the P vs E relationship. Actually, at temperatures close to the Curie point the impurities may transform the crystal into a ferroelectric state.[16] Near T_C, the polarization may fluctuate spatially even in the paraelectric phase, i.e., small polarized regions can exist. In such cases, obviously, the dipole state of a defect may become stable much more easily. Our analysis shows, however, that even in the paraelectric phase far from the Curie point stabilization of a state of V_O^+ with broken symmetry is possible. Below we examine this problem with allowance for the real geometry of the crystal lattice.

4. THE ASYMPTOTIC BEHAVIOR OF THE ELECTRIC FIELD OF A POINT CHARGE IN A LATTICE OF POLARIZABLE IONS

In this section we establish the asymptotic behavior of the electric field of a point charge in a polar crystal. We take a lattice consisting of polarizable sites and assume that the polarization of each site is determined by the total local field generated by the field source and all the other polarized sites. Solving this problem in general form requires taking account of an infinite number of linear equations (5) and (6). But if we are interested only in the asymptotic value of the field, there is a way of considerably simplifying the solution of the problem and even obtaining a solution in analytic form. Mahan[9] was the first to do this for a simple cubic lattice. The value of the energy of interaction between a point charge and a distant point dipole in a simple cubic lattice was found to be $(\varepsilon+2)/3$ times higher than that provided by the continuum approximation. This result was verified by Smith[10] and Wielopolski,[11] who found that the asymptotic value of the electric field of a point charge in a simple cubic lattice is $(\varepsilon+2)/3$ times larger than the one used in the Mott–Littleton model. These results were used by Vugmeister and Glinchuk[16] to explain the ferroelectric phenomena in a $KTaO_3$:Li solution. They calculated the interaction energy of Li impurities in the soft-mode approximation. Here we generalize the results obtained in Refs. 9–11 to the case of more complex lattices. In particular, we allow for the fact that the oxygen site in the perovskite lattice is axisymmetric. In this connection we are forced to discard the method of deriving finite expressions suggested in Ref. 9, since it is valid only for the atomic positions in cubic lattices that also possess cubic point symmetry.

We perform the inverse Fourier transformation of Eqs. (5) and (6). To this end we examine the following quantities:

$$\mathbf{e}_i(\mathbf{k},\mathbf{r})=\sum_n \exp[i\mathbf{k}(\mathbf{r}_{ni}+\mathbf{r})]\mathbf{e}_{ni}(\mathbf{r}),$$

$$\mathbf{e}_i^0(\mathbf{k},\mathbf{r})=\sum_n \exp[i\mathbf{k}(\mathbf{r}_{ni}+\mathbf{r})]\mathbf{e}_{ni}^0(\mathbf{r}),$$

$$\Phi_{ij}(\mathbf{k},\mathbf{r})=\sum_n \exp[i\mathbf{k}(\mathbf{r}_{ni}+\mathbf{r}-\mathbf{r}_{0j})]\Phi_{ni,0j}(\mathbf{r}),$$

$$\mathbf{W}_{ij}(\mathbf{k},\mathbf{r})=\sum_n \exp[i\mathbf{k}(\mathbf{r}_{ni}+\mathbf{r}-\mathbf{r}_{0j})]\mathbf{W}_{ni,0j}(\mathbf{r}), \tag{21}$$

where

$$\mathbf{W}_{ni,0j}(\mathbf{r})=\frac{\mathbf{r}+\mathbf{r}_{ni}-\mathbf{r}_{0j}}{|\mathbf{r}+\mathbf{r}_{ni}-\mathbf{r}_{0j}|^3} \tag{22}$$

is the electric field generated by a unit point charge. As a result we get

$$\mathbf{e}_i(\mathbf{k},\mathbf{r})=\mathbf{e}_i^0(\mathbf{k},\mathbf{r})-\sum_j \Phi_{ij}(\mathbf{k},\mathbf{r})\Lambda_j\mathbf{e}_j(\mathbf{k},0). \tag{23}$$

The general solution of this system is

$$\mathbf{e}_i(\mathbf{k},\mathbf{r})=\mathbf{e}_i^0(\mathbf{k},\mathbf{r})-\sum_n \Phi_{ij}(\mathbf{k},\mathbf{r})\chi_{jn}(\mathbf{k})\mathbf{e}_n^0(\mathbf{k},0), \tag{24}$$

where χ is the susceptibility tensor specified by the equations

$$\sum_j (\Lambda_j^{-1}\delta_{ij}+\Phi_{ij}(\mathbf{k},0))\chi_{jm}(\mathbf{k})=\delta_{im}I. \tag{25}$$

The inverse Fourier transform is

$$\mathbf{e}_{ni}(\mathbf{r})=\frac{1}{\Omega}\int \exp[-i\mathbf{k}(\mathbf{r}_{ni}+\mathbf{r})]\mathbf{e}_i(\mathbf{k},\mathbf{r})d^3k. \tag{26}$$

Let us examine the behavior of (26) for large n (far from the source). Only small k contribute to (26), i.e., values for which we can use the following approximations:

$$\Phi_{ij}(\mathbf{k},\mathbf{r})=\frac{4\pi}{\mathscr{V}}\hat{\mathbf{k}}\hat{\mathbf{k}}+\Phi_{ij}(\mathbf{r}),\quad \mathbf{W}_{ij}(\mathbf{k},\mathbf{r})=\frac{4\pi i}{\mathscr{V}}\frac{\mathbf{k}}{k^2}, \tag{27}$$

where $\hat{\mathbf{k}}=\mathbf{k}/k$, and $\Phi_{ij}(\mathbf{r})$ is the $\mathbf{k}$-independent part of the tensor.

In calculating the integral (26) we use the following formula:

$$\int_{-1}^{1}\int_0^\infty e^{-iklt}kf(t)dt\,dk=-i\frac{\pi}{l^2}f'(0), \tag{28}$$

where $t=\cos\theta$. Then the integral (26) assumes the form

$$\mathbf{e}_i(\mathbf{r})=\frac{1}{2\pi}\int_0^{2\pi}\mu_i^+(\varphi,\mathbf{r})F(\varphi)|_{\cos\theta=0}q_{0j}d\varphi, \tag{29}$$

where

$$F(\varphi)=\frac{1}{l^2}\left(\hat{\mathbf{k}}_t'-\sum_{ij}\Phi_t'\chi_{ij}\hat{\mathbf{k}}\right), \tag{30}$$

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

Here

$$\frac{\mathscr{V}}{4\pi}\Phi_t'=\frac{\partial}{\partial\cos\theta}\hat{\mathbf{k}}\hat{\mathbf{k}}\Bigg|_{\cos\theta=0}. \tag{31}$$

In the particular case where the field is directed along the z axis, which coincides with the crystallographic axis, we have

$$\mathbf{e}_z\mathbf{e}_i(\mathbf{r},\mathbf{r}_{0j}+\mathbf{r}')=\mathbf{e}_z\mu_i^+(\mathbf{r})\frac{\langle\varepsilon_\perp^{-1}\rangle}{l^2}q_{0j}, \tag{32}$$

where

$$\langle\varepsilon_\perp^{-1}\rangle=1-\frac{2}{\mathscr{V}}\int_0^{2\pi}\hat{\mathbf{k}}\sum_{ij}\chi_{ij}\hat{\mathbf{k}}|_{\cos\theta=0}d\varphi \tag{33}$$

is the average value of the reciprocal dielectric constant. The quantity $\mu(\mathbf{r})$, which represents the enhancement of the dipole moment, satisfies the following conditions:

$$\frac{4\pi}{\mathscr{V}}\sum_i\Lambda_i\mu_i(0)=\varepsilon-1, \tag{34}$$

$$\frac{1}{\mathscr{V}}\int_{\text{u.c.}}\mu_i(\mathbf{r})d^3r=1. \tag{35}$$

The first relates μ_i to the macroscopic dielectric constant ε, while the second shows that the mean (macroscopic) field coincides with the Coulomb field in a continuous medium. At the same time, the local (microscopic) field may be arbitrary. The coefficient μ is equal to $(\varepsilon+2)/3$ for a simple cubic lattice, which coincides with the result of Refs. 9–11; for complex lattices $\mu_i=\gamma_i(\varepsilon+2)/3$, and here the calculation[17] for $KTaO_3$ have yielded $\gamma=5.20$, -0.21, 3.72, and 0.24 for the Ta, K, O_z, and O_{xy} positions, respectively. The data are close to those of Vugmeister and Glinchuk[16] in the soft-mode model for the Ta and K positions. We see that at large distances the electric field in a polar lattice is greatly enhanced in comparison to the value provided by the continuum approximation.

5. DIRECT CALCULATIONS OF THE LATTICE POLARIZATION ENERGY

As noted earlier, the crystal was divided into two parts. The first had a diameter of about 16 Å. Inside it the system of equations (5) and (6) was solved numerically. The initial field e^0 was generated by the charge $1.2e$ of the vacancy cavity, the charges on two Ta ions, the charges on the ten oxygen ions nearest to the Ta ions, and by the dipole moments at the sites of the second region. We allowed for the covalence of the Ta–O chemical bond and the breaking of chemical bonds in the formation of an atomic vacancy. The degree of covalence s of the chemical bond is assumed equal to 0.5, which agrees with band calculations.[12] In view of this the real charge of the Ta^{5+} ion in the perfect lattice is $q_{Ta}=5se=2.5e$. This means that due to the covalence of the chemical bond $(2.5/3)e=0.8e$ of the charge is drawn away from each O^{2-} ion to the Ta^{5+} ions. Thus, the real charge of an oxygen ion is $q_O=-2e+0.8e=-1.2e$.

As a result of the breaking of two chemical bonds in the formation of an oxygen vacancy, the Ta ions closest to the vacancy acquire an additional charge equal to $2.5e/6=0.4e$.

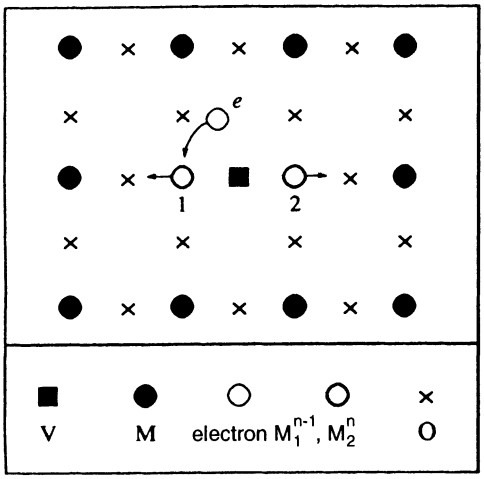

FIG. 2. The geometry of the nearest neighbors of an oxygen vacancy in oxides of the perovskite type AMO_3; n is the valence of the transition element.

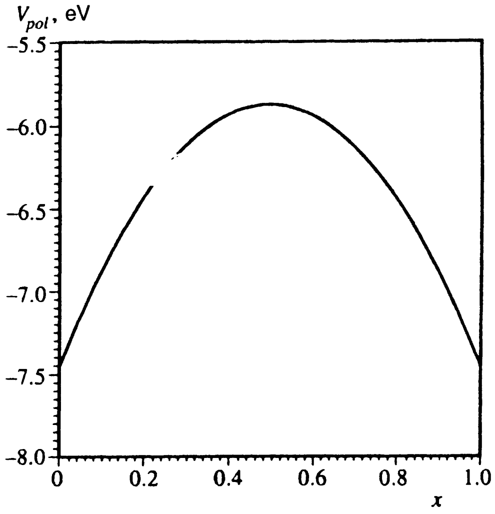

FIG. 3. The polarization energy as a function of the degree x of symmetry violation.

We distributed the additional charge created by the electron bound to the vacancy between the two TaO_5 fragments in the symmetric state in equal portions (Fig. 2), while for the asymmetric state the portions had corresponding weights. Inside each TaO_5 fragment the charge distribution was fixed in such a way that half was on the Ta ion and half was distributed uniformly between five oxygen ions. Such a distribution corresponds to the partial covalence of the chemical bond with $s=0.5$. As a result in the symmetric state the additional charge on each Ta ion was $1.5e$, and the additional charge on each of the oxygen ions was $-0.05e$. When the symmetry was violated, the charges were specified as follows:

$$q_1=(0.4-xs)e, \quad q_2=[0.4-(1-x)s]e,$$
$$q_{01}=-\frac{xs}{5}e, \quad q_{02}=-\frac{(1-x)s}{5}e, \tag{36}$$

with $0<x<1$, where $q_{01}(q_{02})$ is the charge on each of the oxygen ions closest to the first (second) Ta ion. The charge of the vacancy was not changed in the process of symmetry breaking.

The second region was roughly 64 Å in diameter. In this region the local field at a lattice site was determined by Eq. (32). The polarization energy was calculated by direct summation in (4). The ion polarizabilities ($\alpha_{Ta}=1.1$ Å^3, $\alpha_{O\parallel}=2.44$ Å^3, and $\alpha_{O\perp}=0.93$ Å^3) and lattice constant $a=3.9884$ Å were taken from Ref. 18. The degree of violation of the symmetry of the defect was taken into account in all calculations.

As a result of the calculations (Fig. 3) we found that E_{pol} has a maximum at $q_1=q_2=q^0$ equal to -5.87 eV and a minimum equal to -7.44 eV, provided that the electrons on one of the Ta ions and on the five oxygen ions closest to that Ta ion are totally localized. The lowering of energy proved to be greater than its increase caused by the change in the energy of the covalent bond (see Sec. 6).

The calculations imply that the defect state with broken symmetry has a lower energy than the symmetric state. However, the lattice constant and the atomic polarizabilities that we used correspond to room temperature. To study the dependence of the result on the model parameters we repeated the calculations for the lowest possible temperatures, at which $a=3.9842$ Å and $\varepsilon_0=3840$ hold (see Ref. 19); at room temperature we have $\varepsilon_0=204$ (see Ref. 18). We fixed the polarizabilities of all the atoms except Ta, and the polarizability of the Ta was selected in such a way that the calculated value of ε_0 coincided with the experimental value. The result was $a_{Ta}=1.08$ Å^3. Here the polarization energy remained practically unchanged. These data agree with the data obtained in the continuum approximation in Sec. 4.

We also did the following numerical experiment: α_{Ta} was increased from 1.08 Å^3 to 1.3 Å^3. Near the value $\alpha_{Ta}=1.3$ Å^3 we observed a sharp increase in polarization energy (by several orders of magnitude) and a significant rise in the energy difference between the symmetric and asymmetric states of the defect. We believe that the reason for this is the appearance at these values of α_{Ta} of a cluster that is unstable in the transition to the ferroelectric state (initiated by the dipole defect). In our opinion the fact that this was observed at values of α_{Ta} somewhat higher than in a bulk crystal is related to the finiteness of the cluster.

We also decreased α_{Ta} from 1.08 Å^3 to 0.1 Å^3. Here both the polarization energy and the energy difference between the symmetric and asymmetric states of the defect lowered. The energy difference at $\alpha_{Ta}=0.1$ Å^3 proved to be equal to 0.6 eV. Obviously, when the polarizability of all the other ions decreases, this value must vanish.

What is interesting is that the Ta ions closest to V_O^+ are shifted away from the vacancy by 0.06 Å. This implies that $KTaO_3$ must expand in reduction, which agrees with the experimental data. In some cases this expansion may lead to interesting physical phenomena.[20] Curiously, in the state with broken symmetry the shifts of the two Ta ions closest to V_O^+ are different: 0.0.067 and 0.0555 Å, respectively. But on the average the ions are shifted by 0.06 Å away from the vacancy. Note that in the ferroelectric state, at $\alpha_{Ta}=1.3$

Å^3, the Ta ions are shifted in the same direction by 0.025 and 0.184 Å, respectively.

Our estimates of the energy of the one-electron state of V_O^+ (see Ref. 8) using Green's functions show that the energy is about 0.3 eV. This means that at room temperature and at higher temperatures V_O^+ is partially ionized (here we take into account the relatively low concentration of V_O). Hence reliable observations of the effect are possible only at low temperatures.

We explain the observation of dipole centers in nominally pure $KTaO_3$ (Ref. 2) by means of second harmonic generation by the presence of defects of the form $Ta^{4+}V_OTa^{5+}$. Each such dipole defect creates a polarized region surrounding it. The size of the region can be estimated as follows. We expand the electric field of a point charge and a point dipole in a power series in $1/q$. Using the method developed bu Mahan and Mazo,[21] we find

$$E_z=\frac{\varepsilon+2}{3\varepsilon r^2}\left[1+\frac{2.110}{\varepsilon}(\varepsilon-1)\left(\varepsilon-\frac{3}{5}\right)\frac{a^2}{r^2}+\cdots\right], \tag{37}$$

$$C_{zz}=2\frac{(\varepsilon+2)^2}{9\varepsilon r^3}\left[1+\frac{5.908}{\varepsilon}(\varepsilon-1)\left(\varepsilon-\frac{3}{7}\right)\frac{a^2}{r^2}+\cdots\right]. \tag{38}$$

The expansions are valid if

$$r\gg a\sqrt{\frac{2.110}{\varepsilon}(\varepsilon-1)\left(\varepsilon-\frac{3}{5}\right)}, \tag{39}$$

$$r\gg a\sqrt{\frac{5.908}{\varepsilon}(\varepsilon-1)\left(\varepsilon-\frac{3}{7}\right)}, \tag{40}$$

respectively. On the other hand, these conditions make it possible to estimate the characteristic size of the polarized region. For instance, for large ε we have

$$R\sim a\sqrt{2.110\varepsilon}, \tag{41}$$

$$R\sim a\sqrt{5.908\varepsilon}, \tag{42}$$

respectively. We see that for large ε the asymptotic behavior of the electric field of the point charge is independent of ε, and the size of the polarized region increases with ε like $\sqrt{\varepsilon}$. This suggests that even when the defect concentration is fairly low but ε is large, the defects may form polarized regions on the nanometer scale. Note that in our case this result follows from the fact that the local field differs from the mean field.

6. CALCULATION OF THE COVALENT COMPONENT OF THE INTERACTION ENERGY OF IMPURITIES IN AN ION–COVALENT CRYSTAL

Earlier we noted that breaking of the symmetry of the one-electron wave function on a two-impurity center increases the covalent component of the energy. This increase is described by the simple formulas of the two-level model, provided that we know the value of the parameter t of the effective interaction between the impurities. Determining this value is a complicated problem, however. Indeed, since the vacancy site contains no oxygen ion, there can be no interaction between the two Ta ions closest to the vacancy, indirectly via the oxygen ion, just as there can be no such interaction in a perfect crystal. Such an interaction can be transmitted along long atomic chains connecting the Ta ions and bending around the vacancy (Fig. 2). The shortest chain consists of four Ta ions and three oxygen ions. Two of these Ta ions are far from the defect ($\simeq 4$ Å), with the result that they play little part in the transmission of the interaction, since the wave function of a local state decays exponentially with distance from the defect. In other words, even if in some way we do find the value of the effective interaction of the Ta ions in the Ta–O–Ta chain, this is generally insufficient for finding the effective interaction in the Ta–O–Ta–O–Ta–O–Ta chain. We must have additional data on the wave function of the local defect state. It would be a mistake to think that the interaction in a short chain is the same in order of magnitude as that in a long chain, since the effective interaction must rapidly decrease with the distance between the impurities.

We also note that the interaction is transmitted not by a single chain but by an infinite number of such chains. Even if we do establish what interaction is transmitted along one of the chains, we will still need to sum these interactions over the entire lattice of an unbounded crystal. Restricting the sum to the nearest chains is possible only if we have a clear idea about the rate at which the interaction weakens when the length of the chain increases and about the interaction between the chains. All this constitutes a separate complicated problem.

Another problem is that the chemical bond in $KTaO_3$ is of an intermediate ion–covalent nature. This means that the dispersion in the bands of allowed states is primarily determined by the nearest-neighbor interaction and is of the same order as the band gap. Strictly speaking, in these conditions we cannot employ perturbation theory techniques and write the energy of the interaction between the nearest Ta ions as $t_{pd\pi}^2/(\varepsilon_d-\varepsilon_p)$ (here we have used the $pd\pi$-interaction integral, since the ground state of V_O^+ is built from π orbitals[7,8]). Note that Harrisson's parametrization gives[12] $V_{pd\pi}=1.44$ eV, while the denominator $\varepsilon_d-\varepsilon_p$ is of order 3.5–5.5 eV (depending on whether energy is measured to the bottom of the conduction π-band or to the middle of the band). On the basis of these data it can easily be concluded that the effective interaction between the Ta ions in the Ta–O–Ta chain is a quantity on the order of several tenths of an electron-volt. However, this estimate, as noted earlier, is not rigorous and does not permit an estimate of the interaction of the two Ta ions nearest to V_O.

Below we suggest a rigorous solution of this problem based on a realistic description of the electron band structure in a perfect perovskite lattice and on the full knowledge of the local state of the defect. The method does not use perturbation theory techniques. To this end we employed the method of Green's functions, which makes it possible to analytically sum the interactions over the entire lattice surrounding the defect. The results of this section are very general in nature, are not linked to a specific representative of the huge collection of oxides belonging to the perovskite family, and are valid even for the broader class of ion–covalent crystals.

Thus, if the lattice of an ion–covalent crystal contains a point defect with which a local one-electron state is associated, the contribution of this state to the covalent component of the energy can be calculated by the formula

$$E_{\mathrm{cov}}=\frac{1}{2}\sum_{ni}\sum_{mj} f_{ni}t_{ni,mj}f_{mj}, \tag{43}$$

where f_{ni} are the amplitudes of the one-electron wave functions of the local state at the ith atom of the nth cell, and $t_{ni,mj}$ is the hopping integral. The amplitudes f_{ni} satisfy the following equation:

$$f_{ni}=\sum_{mj} g_{ni,mj}(\varepsilon)V_{mj}f_{ni}, \tag{44}$$

where V_{mj} and $g_{ni,mj}$ are the matrices of the perturbation potential and the Green's function of a perfect crystal (which were defined earlier), and ε is the energy of the local level specified by Eq. (1).

Plugging (44) into (43) yields

$$E_{\mathrm{cov}}=\frac{1}{2}\sum_{ni}\sum_{mj} E_{\mathrm{cov}}^{ni,mj}, \tag{45}$$

where

$$E_{\mathrm{cov}}^{ni,mj}=f_{ni}V_{ni}\sum_{ps}\sum_{uw} g_{ni,ps}(\varepsilon)t_{ps,uw}g_{uw,mj}(\varepsilon)V_{mj}f_{mj}. \tag{46}$$

The diagonal elements $E_{\mathrm{cov}}^{ni,ni}$ can be interpreted as the self-energy of the impurity at the nth site (here we are dealing with the covalent contribution to the energy caused by the electron bounded to the vacancy), while the off-diagonal can be interpreted as the impurity interaction energy.

To find the lattice sums in (46) we do the following. We write the equations determining the Green's functions of a perfect crystal:

$$(\varepsilon\hat{I}-\hat{H}_0-t)\hat{g}=\hat{1}, \tag{47}$$

where $\hat{I}$ is the identity matrix, $\hat{H}_0=\varepsilon_d\hat{I}$ at Ta ions, and $\hat{H}_0=\varepsilon_p\hat{I}$ at oxygen ions. We solve (47) for $\hat{t}\hat{g}$ and multiply the result by $\hat{g}$ from the left. The result is

$$\hat{g}\hat{t}\hat{g}=\hat{g}(\varepsilon\hat{I}-\hat{H}_0)\hat{g}-\hat{g}. \tag{48}$$

Below we use the special properties of the Green's functions in crystals with a chemical bond of an intermediate nature and show that when two Ta ions interact,

$$\hat{g}(\varepsilon\hat{I}-\hat{H}_0)\hat{g}=-\frac{(\varepsilon-\varepsilon_d)(\varepsilon-\varepsilon_p)}{\varepsilon-\varepsilon_0}\frac{d}{d\varepsilon}\hat{g}. \tag{49}$$

We plug (49) into (48) and the result into (46). After summation over the entire crystal lattice we get

$$E_{\mathrm{cov}}^{ni,mj}=-f_{ni}V_{ni}\times\left[\frac{(\varepsilon-\varepsilon_d)(\varepsilon-\varepsilon_p)}{\varepsilon-\varepsilon_0}\frac{d}{d\varepsilon}g_{ni,mj}(\varepsilon)+g_{ni,mj}\right]f_{mj}V_{mj}. \tag{50}$$

This formula is true for the interaction of two Ta ions and for the Ta–O interaction. The amplitude f_{ni} can be found by solving the system of equations

$$(\hat{I}-\hat{g}\hat{V})\hat{f}=0 \tag{51}$$

together with the normalization condition

$$\sum_{ni}|f_{ni}|^2=1. \tag{52}$$

The latter, after we have used Eq. (51) and the formula for summing Green's functions

$$\hat{g}\hat{g}=-\frac{d}{d\varepsilon}\hat{g}(\varepsilon), \tag{53}$$

can be written as

$$\mathbf{f}^*\hat{V}\left(-\frac{d}{d\varepsilon}\hat{g}\right)\hat{V}\mathbf{f}=1. \tag{54}$$

This notation is more convenient since it includes only the amplitudes f_{ni} of the sites that are closest to the defect at which the perturbation potential is finite.

Note that Eq. (53) can easily be obtained if we write the Green's function in the form

$$\hat{g}(\varepsilon)=\sum_{\tau\mathbf{k}}\frac{|\tau\mathbf{k}\rangle\langle\tau\mathbf{k}|}{\varepsilon-\varepsilon_\tau(\mathbf{k})}, \tag{55}$$

where τ is the number of the band, and $\mathbf{k}$ is the wave vector. Then

$$\begin{aligned}\hat{g}\hat{g}&=\sum_{\tau\mathbf{k}}\sum_{\kappa\mathbf{q}}\frac{|\tau\mathbf{k}\rangle\langle\tau\mathbf{k}||\kappa\mathbf{q}\rangle\langle\kappa\mathbf{q}|}{[\varepsilon-\varepsilon_\tau(\mathbf{k})][\varepsilon-\varepsilon_\kappa(\mathbf{q})]}\\&=\sum_{\tau\mathbf{k}}\frac{|\tau\mathbf{k}\rangle\langle\tau\mathbf{k}|}{[\varepsilon-\varepsilon_\tau(\mathbf{k})]^2}=-\frac{d}{d\varepsilon}\hat{g}.\end{aligned} \tag{56}$$

As Eq. (50) shows, we were able to express the impurity interaction energy caused by the covalent component of the bond in terms of the corresponding off-diagonal matrix element of the Green's function and its derivative. In this formula we did not employ the cluster approximation, i.e., the entire crystal is taken into account. The formula has been derived with full allowance for the electron band structure both in a perfect crystal and in a crystal with defects. It allows for the decay of the wave function of the defect as the distance to the defect increases and does not use any perturbation-theory techniques to calculate the covalent component of the energy, unlike the case of crystals with a weak covalent bond. Calculations of the case we are interested in are done in Sec. 7.

7. THE GREEN'S FUNCTION OF A PERFECT LATTICE OF OXIDES OF THE PEROVSKITE FAMILY

Calculating the desired quantity requires knowing the electron Green's functions. To this end we use the theory of alternant structures, which originated in the work of Coulson and Longuet-Higgins[22] devoted to alternant hydrocarbons. Later the theory was reformulated by Rebane for disordered crystals of the A_nB_m type.[23] For oxides of the perovskite family the theory was developed in the works of the present author (see the review in Ref. 24) and later was used for calculating the optical, electric, and magnetic properties of perfect crystals and for calculating the electronic structure of point and extended defects.[25–28] In the present paper we apply the theory to calculate the covalent component of the impurity interaction energy.

Equation (55) indicates that to calculate the electron Green's functions we must know the electron dispersion laws, $\varepsilon_\tau(\mathbf{k})$, and the state vectors $|\tau\mathbf{k}ni\rangle$. The electronic structure of oxides of the perovskite family has been thoroughly studied by different variants of the density functional method (see a review in Ref. 12). The results of these studies show that the dispersion in the bands is caused primarily by the nearest-neighbors interaction in the lattice (below for the sake of definiteness we speak of Ta and O), and in this approximation the Hamiltonian matrix can be factorized into submatrices of the π- and σ-type. Accordingly, the matrix of the Green's functions is also factorizable. The band pattern here is as follows. The lower conduction band is built from orbitals of the π-type, and its bottom is 3.5 eV above the valence band. The bottom of the conduction σ-band is 3.5 eV higher. When an oxygen vacancy is formed, the local level splits from the bottom of the conduction π-band. This state is built from π-type states.[7,8]

In Ref. 29 it was found that the dispersion laws and the densities of the electron states in the π-band are perfectly approximated in the Koster–Slater model (the tight-binding approximation) if the basis consists of only the $d\pi$-orbitals of Ta and the $p\pi$-orbitals of the oxygen ion. With allowance for the nearest-neighbors interaction we have

$$\begin{aligned} &-(\varepsilon-\varepsilon_d)C_{di}+\sum_j T_{ij}C_{pj}=0, \\ &-(\varepsilon-\varepsilon_p)C_{pi}+\sum_j T_{ij}^{*}C_{dj}=0, \end{aligned} \tag{57}$$

where the T_{ij} are the off-diagonal matrix elements of the secular equation of the tight-binding approximation. Since one $d\pi$-orbital can interact with two $p\pi$-orbitals of the cell, one of the solutions of the system (57), corresponding to the energy $\varepsilon=\varepsilon_p$, describes a bonding $p\pi$-state. The other two states can easily be obtained after eliminating the vector C_{pi} from (57):

$$C_{pi}=\frac{1}{\varepsilon-\varepsilon_p}\sum_j T_{ij}^{*}C_{dj}, \tag{58}$$

$$[-(\varepsilon-\varepsilon_d)(\varepsilon-\varepsilon_p)\hat{I}+\hat{T}\hat{T}^{*}]\mathbf{C}_d=0. \tag{59}$$

Let us denote the λth eigenvalue of the matrix TT^* by $v_\lambda=v_\lambda(\mathbf{k})$. Then the system of equations (59) has a solution if

$$(\varepsilon-\varepsilon_d)(\varepsilon-\varepsilon_p)=v_\lambda(\mathbf{k}). \tag{60}$$

This means that

$$\varepsilon_{\lambda\nu}(\mathbf{k})=\varepsilon_0+\sqrt{\Delta^2+v_\lambda(\mathbf{k})}, \tag{61}$$

where $\nu=\pm1$, and η_0 and Δ are, respectively, the half-sum and half-difference of the energies ε_d and ε_p. In Ref. 29 it was demonstrated that the function (61) accurately approximates the dispersion curves obtained by the density functional method. A parametrization based on this fact is given in Ref. 12.

Using the above tight-binding approximation, we can obtain the electron Green's functions. Before we do this, however, we note that the conditions for the normalization of the state vectors and Eq. (58) imply that for the bands (61) the following relationship is valid:

$$\begin{aligned} &\sum_i C_{di}^{\kappa*}C_{di}^{\tau}+\sum_i C_{pi}^{\kappa*}C_{pi}^{\tau} \\ &\quad=\sum_i C_{di}^{\kappa*}C_{di}^{\tau}\left[1+\frac{v_\lambda(\mathbf{k})}{(\varepsilon-\varepsilon_p)^2}\right]=\delta_{\kappa\tau}. \end{aligned} \tag{62}$$

Combining this with (61) yields

$$\sum_i C_{pi}^{\kappa*}C_{pi}^{\tau}=\frac{\varepsilon-\varepsilon_d}{2(\varepsilon-\varepsilon_0)}\delta_{\kappa\tau},\quad \sum_i C_{di}^{\kappa*}C_{di}^{\tau}=\frac{\varepsilon-\varepsilon_p}{2(\varepsilon-\varepsilon_0)}\delta_{\kappa\tau}. \tag{63}$$

Now we can easily see that after the state vectors and the dispersion laws (61) and (63) are plugged into the expression (55) for the Green's function and summation over τ is completed, we have

$$g_d(\varepsilon)=\frac{\varepsilon-\varepsilon_p}{2(\varepsilon-\varepsilon_0)}g(\varepsilon), \tag{64}$$

$$g_p(\varepsilon)=\frac{\varepsilon-\varepsilon_p}{4(\varepsilon-\varepsilon_0)}g(\varepsilon)+\frac{1}{2(\varepsilon-\varepsilon_0)}, \tag{65}$$

where g_d and g_p are the diagonal elements of the Green's function. The additional term in Eq. (65) is due to the contribution of the nonbonding states:

$$g(\varepsilon)=\sum_{\lambda\nu}\sum_{\mathbf{k}}\frac{1}{\varepsilon-\varepsilon_{\lambda\nu}(\mathbf{k})}. \tag{66}$$

This function can be expressed in terms of a universal function that allows reducing the multiband problem to the single-band problem:

$$g(\varepsilon)=\frac{2(\varepsilon-\varepsilon_0)}{4V_{pd\pi}^2}f(e), \tag{67}$$

where

$$e=\frac{(\varepsilon-\varepsilon_0)^2-\Delta^2}{4V_{pd\pi}^2}, \tag{68}$$

$$f(e)=\sum_\lambda\sum_{\mathbf{k}}\frac{1}{e-w_\lambda(\mathbf{k})+i\ \mathrm{sgn}(\varepsilon-\varepsilon_0)0}. \tag{69}$$

Here $w_\lambda(\mathbf{k})=v_\lambda(\mathbf{k})/4V_{pd\pi}^2$.

Up to this point the results were of a general nature and remain valid for all alternant lattices in which the electron states are described by Eqs. (57). To calculate the universal function $f(e)$ in $\mathrm{KTaO_3}$ we specify the form of $v(\mathbf{k})$ for π-bands:[24]

$$v_{\alpha\beta}(\mathbf{k})=2V_{pd\pi}^2[2-\cos(k_\alpha a)-\cos(k_\beta a)], \tag{70}$$

where a is the lattice constant, and $\alpha\beta=xy,xz,yz$. In (69) we transform the sum over k into an integral over a Brillouin zone. The integral with respect k_α can easily be evaluated by the theory of residues, and the integral with respect to k_β can be reduced to an elliptic integral. The final result is

$$g_d(\varepsilon)=-\frac{\varepsilon-\varepsilon_p}{2\pi x V_{pd\pi}^2}K\left(\frac{1}{x}\right), \tag{71}$$

$$g_p(\varepsilon)=-\frac{\varepsilon-\varepsilon_p}{2\pi x V_{pd\pi}^2}K\left(\frac{1}{x}\right)+\frac{1}{2(\varepsilon-\varepsilon_p)}, \tag{72}$$

where $x=1-e$, and

$$K(\xi)=\int_0^1\frac{dt}{\sqrt{(1-t^2)(1-\xi t^2)}} \tag{73}$$

is the complete elliptic integral of the first kind.

Earlier we obtained expressions for calculating the diagonal elements of the Green's function. The off-diagonal element can be found in similar way, but in cases Eq. (47) can be used to reduce them to diagonal elements. Indeed, among other things, Eq. (47) implies that

$$(\varepsilon-\varepsilon_d)g_d=1+4t_{10}g_{01}, \tag{74}$$

$$(\varepsilon-\varepsilon_d)g_{01}=t_{01}g_d+t_{02}g_{21}, \tag{75}$$

where the numbers 1 and 2 stand for the Ta ions that are closest to each other, and 0 stands for the oxygen site positions between these ions. The above formulas can easily be used to find the off-diagonal matrix elements of the Green's function that relate the closest Ta and O ions and the closest Ta ions:

$$g_{01}=\frac{\varepsilon-\varepsilon_d}{4V_{pd\pi}}g_d-\frac{1}{4V_{pd\pi}}, \tag{76}$$

$$\begin{aligned} g_{12}&=-\frac{\varepsilon-\varepsilon_p}{V_{pd\pi}}g_{01}+g_d\\ &=\left[1-\frac{(\varepsilon-\varepsilon_p)(\varepsilon-\varepsilon_d)}{4V_{pd\pi}^2}\right]g_d+\frac{\varepsilon-\varepsilon_p}{4V_{pd\pi}^2}. \end{aligned} \tag{77}$$

We see that the Green's functions of the electrons in the perfect perovskite lattice can be obtained if only two parameters of the theory are known, Δ and $V_{pd\pi}$. Twice the value of the first parameter gives the forbidden gap and hence can be found from experiments. The value of the second parameter fixes the dispersion in the π-bands of allowed states and can be deduced by approximating the results of band calculations done by the density functional method.[12]

Within this scheme we estimated the effective interaction of two Ta ions near an oxygen vacancy in KTaO$_3$. With 0.35 eV for the characteristic energy of the local level[8] we found that

$$\begin{aligned} &g_d=-0.70\ \text{eV}^{-1}, \quad g_d'=-1.03\ \text{eV}^{-2},\\ &g_{12}=-0.23\ \text{eV}^{-1}, \quad g_{12}'=-0.60\ \text{eV}^{-2}. \end{aligned} \tag{78}$$

The resulting value of the energy E_{cov}^{12} of the effective interaction was found to be -0.09 eV. Clearly, the increase in the covalent energy caused by lowering the defect symmetry cannot balance the relatively larger decrease in the polarization energy. Thus, the results of the calculations suggest that our model is valid.

In conclusion we prove the validity of Eq. (49) used in our calculations. We plug formula (55), which determines the one-particle Green's function, into the initial expression:

$$\begin{aligned} \hat{g}(\varepsilon\hat{I}-\hat{H}_0)\hat{g}=&(\varepsilon-\varepsilon_d)\sum_{\tau\mathbf{k}}\sum_{\kappa}\sum_{i}\frac{|\kappa\mathbf{k}\rangle C_{di}^{\kappa}C_{di}^{\tau*}|\tau\,\mathbf{k}\rangle}{[\varepsilon-\varepsilon_\tau(\mathbf{k})][\varepsilon-\varepsilon_\kappa(\mathbf{k})]},\\ &+(\varepsilon-\varepsilon_p)\sum_{\tau\mathbf{k}}\sum_{\kappa}\sum_{i}\frac{|\kappa\mathbf{k}\rangle C_{pi}^{\kappa}C_{pi}^{\tau*}|\tau\,\mathbf{k}\rangle}{[\varepsilon-\varepsilon_\tau(\mathbf{k})][\varepsilon-\varepsilon_\kappa(\mathbf{k})]}. \end{aligned} \tag{79}$$

Here in the lattice sum we have separated summation over the transition elements from summation over the oxygen sites. By employing (63) we can simplify the result, leaving only the terms with $\kappa=\tau$. This yields

$$\begin{aligned} &\left[(\varepsilon-\varepsilon_d)\frac{\varepsilon-\varepsilon_p}{2(\varepsilon-\varepsilon_0)}+(\varepsilon-\varepsilon_p)\frac{\varepsilon-\varepsilon_d}{2(\varepsilon-\varepsilon_0)}\right]\\ &\quad\times{\sum_{\tau\mathbf{k}}}'\frac{|\tau\,\mathbf{k}\rangle\langle\tau\,\mathbf{k}|}{[\varepsilon-\varepsilon_\tau(\mathbf{k})]^2}+{\sum_{\tau\mathbf{k}}}''\frac{|\tau\,\mathbf{k}\rangle\langle\tau\,\mathbf{k}|}{\varepsilon-\varepsilon_p}. \end{aligned} \tag{80}$$

The first sum is only over the bands of bonding and antibonding states (61), while the second is over the bands of nonbonding states. If we need only the projection of this expression on the d-states, then the sum over the nonbonding $2p$-states vanishes and we are left with (49).

8. DISCUSSION AND CONCLUSION

This paper has presented a systematic study of the possibility of the symmetry of the one-electron wave function near V_O^+ in KTaO$_3$ breaking because of the interaction of the electron and the lattice polarization. In agreement with the experimental data we found that the lattice polarization can lower the energy of the asymmetric electron state so that the electron will stay in such a metastable state for a long time. In time the electron will hop to a similar state with an opposite orientation of the dipole moment vector.

The relative ease with which repolarization occurs explains the results of experiments on the variation of the width of EPR lines in external fields. Previously the results of these experiments seemed to suggest that V_O^+ plays no role in forming dipole centers, since the time it takes to reorientate a complex containing V_O seemed to be too great, especially at low temperatures. It is now clear, however, that the reorientation of the dipole moment is related not to oxygen diffusion but to electron transfer between the Ta^{5+}V$_O$Ta^{4+} and Ta^{4+}V$_O$Ta^{5+} states. This requires less energy and considerably smaller time intervals.

We have also established that the asymptotic behavior of the electric fields generated by the microscopic charged impurities differs from the field specified by the Coulomb formula written for a uniform polarized medium. Modifications of this formula lead to new results in the continuum approximation. Within this approach we found that at large values of ε the symmetric defect state is energetically preferable, while if the difference between the local field and the mean field are taken into account, the dipole state of V_O^+ is preferable. The correct asymptotic behavior of the electric field for a simple cubic lattice agrees with the data of other researchers.[9–11]

In the present work we suggested a new method for calculating the lattice polarization energy that combines all the merits of the Mott–Littleton model but allows for the correct asymptotic behavior of the electric fields. This asymptotic form assumes that at large distances the electric field of the microscopic impurities is much stronger than is usually assumed in the continuum approximation, which facilitates the formation of polar regions in polar lattices. Such a situation occurs in the $KTaO_3$:Li system,[16] where a small admixture of Li leads to a ferroelectric state. The sharp rise in the field strength of microscopic impurities in ferroelectric materials can also explain the existence of currents that are even in the field. Such currents manifest themselves in the familiar anisotropic scattering of thermal electrons by impurities. Previously it was assumed that because of ε in the denominator of the Coulomb formula, dipole moments could not effectively scatter thermal electrons. The effective increase in the impurity dipole moment by a factor of $\gamma(\varepsilon+2)/3$ for large ε makes the impurity potential virtually independent of ε. Thus, in calculation, not only of the polarization energy but also of the probability of the scattering of electrons by impurities, one must take into account the correct asymptotic behavior of the electric fields and potentials of microscopic impurities.

We were also able to obtain a compact expression convenient for estimates that makes it possible to calculate the covalent contribution of the impurity to the total energy of a defect. This proved possible because of the special properties of the band structure of crystals with a chemical bond of intermediate nature. In this crystal the dispersion in the bands of allowed states results from the covalent bond between the transition element and oxygen. Here the direct covalent interaction between the transition elements can be ignored. It appears that in this case, as in the case of alternant hydrocarbons, the electron states are described by simple analytic functions, just as they are in the two-level model. The square of the effective hopping integral (dependent on the wave vector in the Brillouin zone) can easily be found as the eigenvalue of the operator T^+T (see Ref. 23). In view of this the electron Green's functions also have a fairly simple form, and calculating them is reduced to calculating universal functions in the single-band model. Using these simplifying assumptions, we estimated the covalent contribution to the energy of an electron on V_O^+ and found that it is much lower than the polarization energy. This suggests that the state of V_O^+ with broken symmetry has a lower energy than the symmetric state.

Note that the very existence of V_O^+ in a crystal serves as an indication of a fine balance between donors and acceptors. At first glance such a state is difficult to attain and easy to lose. But earlier experimental work on reduced oxides of the perovskite family[3,4] has shown that such a state can be reliably observed. More than that, often it difficult to take the crystal out of such a state (say, to transform it to a state of the p-type). We believe that there are mechanisms for compensating the resulting perturbations based on the relative ease with which oxygen vacancies can be created.

The ground state of V_O^+ can be destroyed by means other than changing the relative concentration of donors and acceptors. A rise in temperature may thermally excite an electron in V_O^+ into the conduction state. The traps can be destroyed by flooding the crystal with light. It is interesting that notwithstanding the relatively low thermal activation energy (~ 0.2 eV), the peak in the spectrum of optical excitation of V_O^+ lies in the range of highly excited states with $\hbar\omega = 1.5-2.0$ eV (see Ref. 7).

A final remark is in order. The symmetry of the one-electron wave function near an oxygen vacancy can be broken not only because of the interaction between the electron and the polarization but also because of the Jahn–Teller effect. For instance, the electrostatic interaction of a V_O^+ electron with the valence electrons of the crystal in the event of a strong Hubbard interaction on the site of the transition elements also facilitates preferential electron localization on one of the cations closest to V_O (see Refs. 13 and 14). But one must bear in mind that the interaction with the polarization in virtual ferroelectric materials is a much more powerful factor. The displacement of the cations closest to V_O^+ is also asymmetric and facilitates electron localization, but we believe that this factor is of secondary importance.

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