Breaking of symmetry of one-electron orbitals at oxygen vacancies in perovskite-type oxides

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Abstract. Some general relationships have been derived in terms of the unrestricted Hartree–Fock method that define the conditions leading to the breaking of symmetry of one-electron orbitals at oxygen vacancies in oxides of the perovskite family. Numerical calculations of the critical values of relevant parameters have been carried out. Experimental data are discussed in the light of the results obtained.

1. Introduction

AMO_3-type oxides of the perovskite family can fairly readily be reduced and oxidized, which is usually associated with the presence in them of oxygen vacancies. This circumstance affects dramatically their electrical, optical and other physical properties. For that reason alone, the study of the electronic structure of the chief point defects in these crystals, namely, the oxygen vacancies, is deserving of attention.

When an oxygen vacancy develops in an oxygen site, a donor level arises in the forbidden gap. So as to calculate its energy and wavefunction, customarily the so-called restricted Hartree–Fock (HF) method is invoked, i.e. it is assumed that the one-electron wavefunction is transformed with respect to one of the representations of a defect's point symmetry group [1–3].

Yet it is known that often more exact results may be obtained by using the unrestricted HF method in which no symmetry restrictions are imposed on the one-electron wavefunctions. If the one-electron wavefunctions have a lower symmetry than the point symmetry of the defect, it may so happen that this method will yield a lower energy for the given system of electrons. The breaking of symmetry may be caused by a strong electrostatic repulsion of electrons in transition elements, the polarization of the medium, etc. In the present work, general conditions are ascertained within the framework of the unrestricted HF method conducive to the breaking of symmetry of one-electron orbitals near oxygen vacancies in the oxides under discussion, critical parameters are calculated, and the effect of the localization of electrons on the electronic polarization is discussed.

2. Unrestricted Hartree–Fock method

In the present work we wish merely to illustrate the effect of electron localization. For simplicity we make use of the tight-binding method with the minimal basis and neglect the overlap integrals as well as all three- and four-centre integrals. The electrostatic interaction

of electrons will be taken into account only for transition elements. In this case, the HF method equation can be written in the following simplest form

$$\epsilon_{i\alpha\sigma} + V_{i\alpha\sigma,i\alpha\sigma} - \epsilon C_{i\alpha\sigma} + \sum_{j\beta} t_{i\alpha,j\beta} C_{j\beta\sigma} = 0 \tag{1}$$

where $C_{i\alpha\sigma}$ are the components of the electron state vector in the site representation (i is the number of the atom, α is the number of the atomic orbital, σ is the spin index that may assume values of 1 or 2), t is the matrix of hopping integrals, $\epsilon_{i\alpha\sigma}$ are the energies of orbitals in an ideal crystal and $V_{i\alpha\sigma,i\alpha\sigma}$ are the diagonal matrix elements of the defect potential. The latter can, in the case of the transition elements, be represented as

$$V_{i\alpha\sigma,i\alpha\sigma} = W_{i\alpha\sigma} + U \sum_{\beta\mu \neq \alpha\sigma} q_{i\beta\mu}. \tag{2}$$

Here U is the Hubbard parameter (energy of the electrostatic interaction between two electrons in the same atom), $W_{i\alpha\sigma}$ are the constants determinable from the assumption that the perturbing potential is zero in the absence of a defect and $q_{i\beta\mu}$ are the charges contributed by various orbitals to the ith centre

$$q_{i\beta\mu} = \int^{\epsilon_F} N_{i\beta\mu}(\epsilon)\, d\epsilon \tag{3}$$

where $N_{i\beta\mu}$ is the partial density of electron states and ϵ_F is the Fermi energy.

3. Green functions method

In the Green functions method, the density of electron states is given by

$$N_{i\beta\mu} = -(1/\pi)\, \text{Im}\, G_{i\beta\mu,i\beta\mu} \tag{4}$$

where the Green function $\mathbf{G}$ may be found from the solution to the Dyson equation

$$\mathbf{G} = \mathbf{g} + \mathbf{g}\mathbf{V}\mathbf{G}. \tag{5}$$

Here $\mathbf{g}$ is the Green function of the ideal crystal, $\mathbf{V}$ is, as above, the defect potential matrix. Since the defect potential exists in a limited area of the crystal, the Green functions may, in that region, be found from the solution of a usually small number of linear inhomogeneous equations

$$(\mathbf{1} - \mathbf{g}\mathbf{V})\mathbf{G} = \mathbf{g}. \tag{6}$$

Formally this system may be solved by means of the Kramer rule

$$G_{i\beta\mu,i\beta\mu} = D_{i\beta\mu,i\beta\mu}/D \tag{7}$$

where D is the determinant of the homogeneous part of system (6)

$$D(\epsilon) = \|\mathbf{1} - \mathbf{g}\mathbf{V}\| \tag{8}$$

while $D_{i\beta\mu,i\beta\mu}$ is the determinant of the homogeneous part in which the corresponding column is replaced by a column of free terms.

A special situation arises when the denominator in (7) goes to zero

$$D(\epsilon) = 0. \tag{9}$$

The solutions of equation (9) yield the level energies ϵ in the forbidden gap. Near these energies the determinant (8) can be expanded in a Taylor series, which, with (9) included, gives

$$D(\epsilon) = D'(\epsilon_l)(\epsilon - \epsilon_l + i0) + \dots. \tag{10}$$

The integration in equation (3) may, in the vicinity of the energies ϵ_l, be carried out analytically. The result is

$$q_{i\beta\mu} = \sum_l n_{l\mu} \frac{D_{i\beta\mu,i\beta\mu}(\epsilon_l)}{D'(\epsilon_l)} - \frac{1}{\pi} \operatorname{Im} \int_{\text{band}} \frac{D_{i\beta\mu,i\beta\mu}(\epsilon)}{D(\epsilon)} \, d\epsilon \tag{11}$$

where $n_{l\mu}$ is the occupation number of the lth level, and the integration is performed over the band of filled states.

The total density of states can be obtained by analytical summation of partial densities (4), which yields

$$N(\epsilon) = N^0(\epsilon) - (1/\pi) \operatorname{Im}(D'/D) \tag{12}$$

where $N^0(\epsilon)$ is the density of states of the unperturbed crystal. The electron energy of the cell can, in the HF method, be estimated from the formula

$$E = \int^{\epsilon_F} \epsilon N(\epsilon) \, d\epsilon - \sum_{\substack{i\beta\mu \\ j\alpha\sigma}}^{l} q_{i\beta\mu} q_{j\alpha\sigma} F_{i\beta\mu,j\alpha\sigma} \tag{13}$$

where F are the Slater integrals of the electrostatic interaction between electrons and the prime on the summation sign denotes elimination of self-interaction between the charges.

In the particular case when the basis includes at each atom only one orbital and the electrostatic interaction is taken into account at transition elements only we have

$$E = \int^{\epsilon_F} \epsilon N(\epsilon) \, d\epsilon - U \sum_{\substack{i \in M \\ \mu \neq \sigma}} q_{i\mu} q_{i\sigma}. \tag{14}$$

Note that the integral in (14) can be represented as the sum over the numbers of the local levels and the integral over the band of allowed states

$$E = \sum_{l\mu} n_{l\mu} \epsilon_{l\mu} + \int_{\text{band}} \epsilon N(\epsilon) \, d\epsilon - U \sum_{\substack{i \in M \\ \mu \neq \sigma}} q_{i\mu} q_{i\sigma}. \tag{15}$$

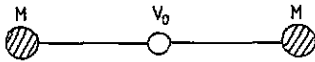The energy of local levels in (15) is found from (9), the density of states from (12), and the charges from (11).

Figure 1. Atoms nearest the oxygen vacancy in the AMO₃ oxides of the perovskite family.

4. Defect potential

Usually the dielectric constant ϵ_0 in perovskite-type oxides is very great, ranging from 100 to 1000, which is why the defect radius r_0 is very small. Actually, the defect consists of few atoms nearest the vacancy. Let us set $r_0 = a$ where a is the lattice constant. In this case, the defect will comprise the vacancy site and two nearest transition elements (1 and 2 in figure 1).

To simplify the model as much as possible only one state at each atom will be included in the basis, namely the low-lying d_π state at the transition element and the $p\pi$ state at oxygen. Subsequently, after elucidating the nature of a possible electronic instability, the model may easily be generalized.

Unfortunately we do not know the values of the displacement of transition elements near the oxygen vacancy, which did not allow us to determine correctly the non-diagonal elements of matrix **V**. In view of this fact, at the first stage we set these elements equal to zero. In the case of the site from which the oxygen atom is removed, the electronic states of this atom will have to be eliminated from the basis—for that purpose the potential V_0 is made to go to infinity [4]. The diagonal elements of matrix **V** at the transition elements can be found by solving the following equations

$$V_{11} = W_{11} + U q_{12} \qquad V_{12} = W_{12} + U q_{11}$$
$$V_{21} = W_{21} + U q_{22} \qquad V_{22} = W_{22} + U q_{21}. \tag{16}$$

The dependence of the charges in (16) on the potential can be derived from formula (11). The determinants necessary for the calculation have in this formula the following form

$$D = V_0 \begin{vmatrix} 1 - g_{11}V_1 & -g_{10} & -g_{12}V_2 \\ -g_{01}V_1 & -g_{00} & -g_{02}V_2 \\ -g_{21}V_1 & -g_{20} & 1 - g_{22}V_2 \end{vmatrix} \tag{17}$$

$$D_{1,1} = V_0 \begin{vmatrix} g_{11} & -g_{10} & -g_{12}V_2 \\ g_{01} & -g_{00} & -g_{02}V_2 \\ g_{21} & -g_{20} & 1 - g_{22}V_2 \end{vmatrix} \tag{18}$$

$$D_{2,2} = V_0 \begin{vmatrix} 1 - g_{11}V_1 & -g_{10} & g_{12} \\ -g_{01}V_1 & -g_{00} & g_{02} \\ -g_{21}V_1 & -g_{20} & g_{22} \end{vmatrix}. \tag{19}$$

For brevity the spin index is omitted here.

5. Green functions of the ideal crystal

A detailed study of the electronic structure of perovskite-type oxides [5] has shown that the inclusion into the basis of the tight-binding method of only the d states of transition elements

and p states of oxygen is quite sufficient for a fairly good approximation of augmented plane-wave (APW) calculations. In this case the Hamiltonian matrix is factorized into blocks that correspond to the π and σ bands; furthermore, for the π bands it is additionally factorized into three equivalent submatrices. The Green function matrix is factorized likewise. For simplicity we included in the basis the electron states that correspond to one submatrix only of the π bands (figure 2):

$$\mathbf{h} = \begin{pmatrix} \epsilon_d & V_\pi[1 - \exp(-ik_xa)] & V_\pi[1 - \exp(-ik_ya)] \\ V_\pi[1 - \exp(ik_xa)] & \epsilon_p & 0 \\ V_\pi[1 - \exp(ik_ya)] & 0 & \epsilon_p \end{pmatrix}. \tag{20}$$

Here V_π is the integral of the (pdπ) interaction, a is the lattice constant and ϵ_d, ϵ_p are the diagonal matrix elements of the Hamiltonian for the atoms M and O, respectively.
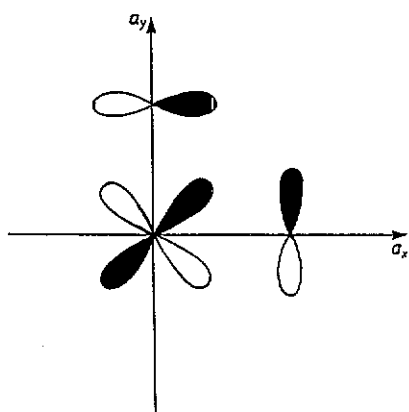

Figure 2. The electron states included in the basis.

Matrix (16) has one eigenvalue $\epsilon = \epsilon_p$ that does not depend on the wavevector (dispersionless band of non-binding states) and two more eigenvalues

$$\epsilon^\nu = \epsilon_0 + (-1)^\nu \{\Delta^2 + 2V_\pi^2[2 - \cos(k_xa) - \cos(k_ya)]\}^{1/2} \tag{21}$$

which may be termed the bands of the binding ($\nu = 1$) and the loosening ($\nu = 2$) states. Here ϵ_0 is the half-sum and Δ is the half-difference between the energies ϵ_p and ϵ_d. The vectors of the electron states for bands (21) may be determined from the following formulae

$$C_{px} = \{V_\pi[1 - \exp(ik_xa)]/(\epsilon - \epsilon_p)\}C_d$$
$$C_{py} = \{V_\pi[1 - \exp(ik_ya)]/(\epsilon - \epsilon_p)\}C_d \tag{22}$$
$$C_d = [(\epsilon - \epsilon_p)/(2\epsilon - \epsilon_p - \epsilon_d)]^{1/2}.$$

For the band of non-binding states they are

$$C_{px} = -\exp\left(\frac{ik_xa}{2}\right)\left(\frac{1 - \cos(k_ya)}{2 - \cos(k_xa) - \cos(k_ya)}\right)^{1/2}$$
$$C_{py} = \exp\left(\frac{ik_ya}{2}\right)\left(\frac{1 - \cos(k_xa)}{2 - \cos(k_xa) - \cos(k_ya)}\right)^{1/2}. \tag{23}$$

When the energies and vectors of electron states are known, the Green functions may be calculated by means of the following well known formula

$$g_{i\alpha\sigma,j\beta\sigma} = \frac{1}{\Omega} \sum_{\tau} \int_{BZ} d^3k \frac{C^{\tau*}_{i\alpha\sigma} C^{\tau}_{j\beta\sigma}}{\epsilon - \epsilon^{\tau}(k)} \tag{24}$$

where the integration is carried out over the Brillouin zone with Ω being its volume; the summation is done over the electron state bands. For the case in hand, the integrals (24) may be reduced to the elliptical form. The result of this operation is $(e > 1)$

$$g_{11} = g_{22} = -\frac{\epsilon - \epsilon_p}{2\pi V_\pi^2 e} K\left(\frac{1}{e}\right)$$

$$g_{00} = -\frac{\epsilon - \epsilon_d}{4\pi V_\pi^2 e} K\left(\frac{1}{e}\right) + \frac{1}{2(\epsilon - \epsilon_p)}$$

$$g_{01} = -g_{02} = -\frac{(\epsilon - \epsilon_p)(\epsilon - \epsilon_d)}{8\pi V_\pi^3 e} K\left(\frac{1}{e}\right) - \frac{1}{4V_\pi} \tag{25}$$

$$g_{12} = \frac{\epsilon - \epsilon_p}{4V_\pi^2} - \frac{\epsilon - \epsilon_p}{2\pi V_\pi^2} K\left(\frac{1}{e}\right)$$

where

$$e = 1 - \frac{(\epsilon - \epsilon_0)^2 - \Delta^2}{4V_\pi^2} \tag{26}$$

while $K(k)$ is the complete elliptical integral

$$K(k) = \int_0^1 \frac{dx}{(1 - x^2)^{1/2}(1 - k^2 x^2)^{1/2}}. \tag{27}$$

The obtained Green functions of electrons can easily be calculated since there are in the literature excellent analytical representations of total elliptic integrals.

6. Neutral oxygen vacancy

A neutral oxygen vacancy has at its donor level two electrons. They can either have delocalized wavefunctions adapted to the defect symmetry or be localized at different transition elements. In any case, the following symmetry restrictions can be placed on atomic potentials and charges in (16)

$$V_1 \equiv V_{11} = V_{22} \qquad V_2 \equiv V_{12} = V_{21}$$

$$q_1 \equiv q_{11} = q_{22} \qquad q_2 \equiv q_{12} = q_{21}. \tag{28}$$

In the light of the restrictions (28), equations (16) can be rewritten as

$$V_1 = W + Uq_2 \qquad V_2 = W + Uq_1 \tag{29}$$

where

$$W = W_{11} = W_{22} = W_{12} = W_{21}.$$

One may now conveniently switch to new variables

$$x = V_1 - V_2 \qquad y = V_1 + V_2. \tag{30}$$

Equations (16) in these variables take the form

$$x = U(q_2 - q_1) \tag{31}$$

$$y = 2W + U(q_1 + q_2). \tag{32}$$

Note that the explicit form of the determinants (17)–(19) by which the charges q_1 and q_2 are given is such that

$$q_1 = A - Bx \qquad q_2 = A + Bx \tag{33}$$

where A and B are functions of x^2 and y. By substituting (33) into (31) we obtain

$$x = 2UBx. \tag{34}$$

Evidently, a solution $x = 0$ exists for any parameter values of the problem and it will correspond to the delocalized state. A new (localized) solution is possible only when the following condition is met

$$2UB = 1. \tag{35}$$

Making use of the above Green functions we have calculated the dependencies $B(x)$ for definite values of the parameter y. The results are given in figure 3. At $x = 0$, $B(x)$ has a finite value falling off sharply with increasing x (quadratically for small x). Figure 3 shows also a graphical solution to equation (35) for various U. For $U < U_c$ this equation is seen to have no solutions, while in the case of $U > U_c$ it does have two symmetrically lying solutions. Here

$$U_c = 1/[2B(0)]. \tag{36}$$

Figure 4 depicts the dependence of U_c on the position of the level in the forbidden gap. The value of y was found from the equation $D = 0$ into which $x = 0$ was substituted. As expected, for shallow levels with strongly delocalized wavefunctions U_c has been found to be relatively great, while for deep levels it is relatively small.

Note that, as the level approaches the valence band, U_c starts rising again. This can be explained as follows. First, in this energy region the impurity state possesses mainly the character of the 2p states of oxygen, rather than the d states of the transition elements, as is the case in the upper part of the gap. This situation lowers the electrostatic interaction of electrons because of the comparatively big radius of oxygen's 2p orbitals. Secondly, near the top of the valence band the radius of the impurity state gets greater, which also decreases the electrostatic interaction. Both factors promote the delocalization of the electron's wavefunction.
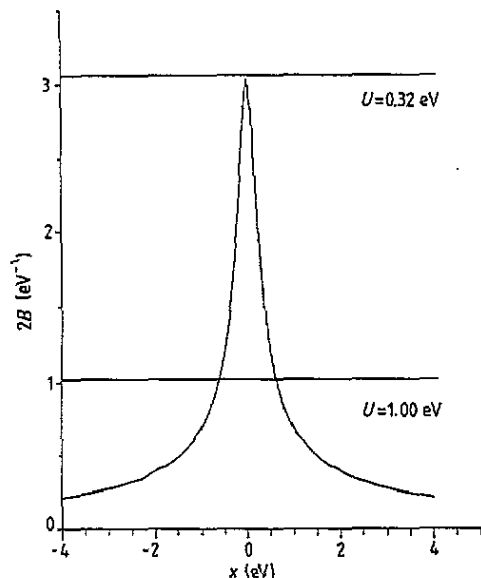
Figure 3. The dependence $B(x)$ for SrTiO$_3$ ($y = 2$ eV) and graphical solution to equation (35) for $U = 0.3$ eV and $U = 1$ eV
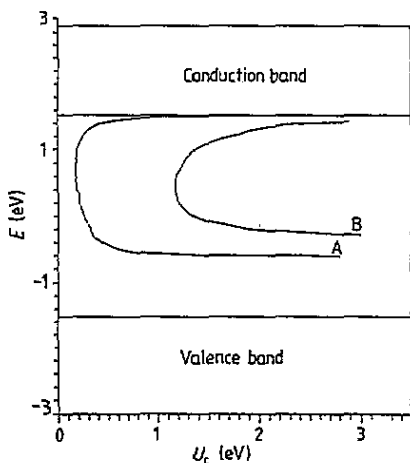

Figure 4. The dependence of U_c on the energy level position in the forbidden gap for neutral (A) and charged (B) oxygen vacancy.

Let us discuss the nature of the localized solution. For this purpose, the model under consideration will be compared with the well known study on the H$_2$ molecule (see e.g. [6]). The simplest model describing the spectrum of the H$_2$ molecule in terms of the HF method is as follows.

For each of the hydrogen atoms, only two one-electron states $\chi_{i\sigma}$ ($i = 1, 2$; $\sigma = 1, 2$) are included in the bases, which differ from each other in their spin projection. The molecular orbitals will be constructed in the form of their superposition

$$\varphi_1 = \chi_{11} \cos \vartheta + \chi_{21} \sin \vartheta$$
$$\varphi_2 = \chi_{22} \cos \vartheta + \chi_{12} \sin \vartheta. \tag{37}$$

The normalization conditions are here included automatically. The electron energy will be written with the electrostatic interaction of electrons at hydrogen atoms and the covalent component of chemical bonding taken into account

$$E = 2\epsilon_0 + 2t \sin(2\vartheta) + \tfrac{1}{8}[1 - \cos(4\vartheta)]U. \tag{38}$$

Here t is the hopping integral (on assumption that $t < 0$), and ϵ_0 is a certain constant. From the necessary condition of the extremum of function (38) it follows that under the equilibrium conditions

$$8t \cos(2\vartheta) + U \sin(4\vartheta) = 0. \tag{39}$$

The sufficient condition for the minimum of the function (38) has the form

$$- 4t \sin(2\vartheta) + U \cos(4\vartheta) > 0. \tag{40}$$

It may be seen from inequality (40) that a delocalized solution $\vartheta = \pi/4$ exists at any value of the model parameters. However, for

$$U > -4t \tag{41}$$

it grows unstable and the electrons are in this case preferably localized near different hydrogen atoms.

At first sight the two models described above are similar. Indeed, in both of them, when the Hubbard parameter U exceeds a certain critical value, the two electrons are localized at different atoms. However, there are also some essential differences. First, the wavefunctions of the two cations closest to the vacancy do not overlap and, accordingly, the hopping integral between the states of these two atoms equals zero. Here we may speak only about an indirect interaction between the atoms via the M–O–M–O... chains. Since the oxygen atom is not present in the vacancy site, these chains are quite long and the resulting indirect interaction proves to be relatively weak for deep states. Secondly, in our model the two electrons at the vacancy levels cannot be examined independently of the rest of the electrons because that would lead to physically wrong results. The point is that the charges contained in equations (13)–(15) must be formed by all the electron states of the crystal that include both the discrete and the continuum spectrum. Moreover, in our model the charge at the atom is dependent on the depth of the impurity state, while in the H_2 molecule this charge is a constant value equal to unity.

As has been noted above, one aspect that is common to both models is that there is in them a sharp transition (phase transition of second kind) between the localized and delocalized states. However, as has been demonstrated in a number of publications [6,7], this transition is for the H_2 molecule a consequence of approximations adopted within the framework of the HF method. When going beyond the limits of this method, the sharp transition does not occur. This may be accounted for by the consideration that in the absence of long-range order the sharp transition is not possible in principle. Consequently, it is equally impossible for a single oxygen vacancy. One may infer from this that the

inclusion of electron correlations must in this case, similarly to the H_2 molecule, result in a smoothed transition.

It should be emphasized in this connection that the ground state of the crystal under consideration is not magnetic and judging from the formal valency of the transition elements, it cannot be magnetic. Therefore, it is the oxygen vacancy that causes the instability of the electron system. When there is such a vacancy, two occupied electron states preferably localized at cations arise in the system. The localization of electrons at different atoms results from the electrostatic interaction between the electrons.

Now, as a counterexample, we consider the magnetic system L_2CuO_4 in the dielectric phase. The ground state of this crystal is antiferromagnetic, which is quite well reproduced in terms of the unrestricted HF method [8]. When an oxygen vacancy is created in the antiferromagnetic CuO_2 layer of this system, the electrons in the impurity states are localized at different cations nearest to the vacancy [8]. It is hard to identify in this case the principal cause of such a localization for the following reason. As the magnitude of the Hubbard parameter decreases, the width of the forbidden gap in which the impurity levels are present grows smaller, and at a certain critical value this gap vanishes altogether. In this case the antiferromagnetism disappears and the crystal acquires metallic properties.

7. Single-charge oxygen vacancy

This vacancy has at its donor level only one electron. In this case the sole symmetry restriction in equation (16) has the form

$$W_1 \equiv W_{11} = W_{21} \qquad W_1 \equiv W_{11} = W_{21}. \tag{42}$$

Otherwise the four values of the potential have to be determined independently.

Let us now go to new variables

$$x_1 = V_{11} - V_{21} \qquad x_2 = V_{22} - V_{12}$$
$$y_1 = V_{11} - V_{21} \qquad y_2 = V_{22} - V_{12} \tag{43}$$

Equations (16) take in these variables the form

$$x_1 = U(q_{12} - q_{22}) \qquad x_1 = U(q_{12} - q_{22}) \tag{44}$$

$$y_1 = 2W_1 + U(q_{12} + q_{22}) \qquad y_2 = 2W_2 + U(q_{21} + q_{11}). \tag{45}$$

From the explicit form of the determinants (17)–(19) through which the atomic charges are expressed in (11), it follows that

$$q_{12} = A_2 + B_2 x_2 \qquad q_{22} = A_2 - B_2 x_2$$
$$q_{21} = A_1 + B_1 x_1 \qquad q_{11} = A_1 - B_1 x_1. \tag{46}$$

Here the functions A_2 and B_2 depend only on x_2 and y_2 while A_1 and B_1 are dependent on x_1^2 and y_1.

With (42) taken into account equations (46) assume the form

$$x_1 = 2U B_2 x_2 \qquad x_2 = 2U B_1 x_1. \tag{47}$$

After eliminating x_2 from these equations we have

$$x_1 = 4U^2 B_1 B_2 x_1. \tag{48}$$

This implies that a delocalized solution $x_1 = x_2 = 0$ exists for any parameter value of the model. A new, localized solution arises when

$$4U^2 B_1 B_2 = 1. \tag{49}$$

The dependencies of B_1 on x_1 and B_2 on x_2 at predetermined y_1 and y_2 are similar to those obtained in the preceding section for the function $B(x)$. From the condition (49) it follows that there exists a critical value of the Hubbard parameter

$$U_c = 1/\{2[B_1(0) B_2(0)]^{1/2}\} \tag{50}$$

above which the electron is preferably localized at one of the transition elements.

The dependence of U_c on the donor level position in the forbidden gap is shown in figure 4. We assumed that the level energy is independent of the electron spin projection. So as to determine the value of $y \equiv y_1 \equiv y_2$, equation (9) was used into which $x \equiv x_1 \equiv x_2$ was substituted. We see that, similarly to the case of the neutral vacancy, U_c are relatively great for shallow levels, while for deep ones they are small. At the same time, for the single-charge vacancy U_c are appreciably greater compared to the neutral vacancy.

Figure 5 lists calculated self-consistent values of potentials obtained by means of equations (16). These results show that, in the case of the deep levels, as U grows the electron rapidly localizes at one of the atoms and thus a dipole moment arises in the system. These findings confirm that for $U > U_c$ the electron ground state has a broken symmetry.
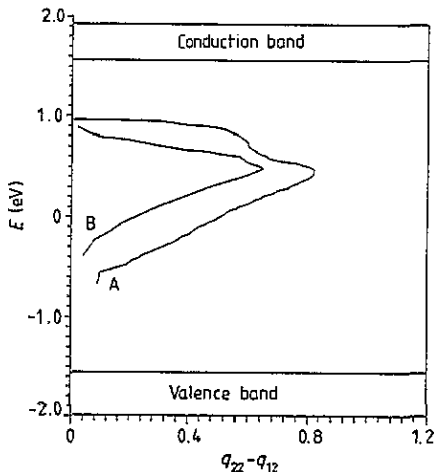

Figure 5. The dependence of the degree of electron localization on the energy level position in the forbidden gap for charged oxygen vacancy: $U = 2$ eV (A) and $U = 1$ eV (B).

At the same time, a self-consistent calculation has shown that a solution with a broken symmetry exists even at $U = 1$ eV, despite the fact that, as may be seen from figure 4, $U_c > 1$ eV for any position of the level in the forbidden gap. The point is that

when evaluating U_c we made use of the condition $x_1 = x_2$, which can be satisfied only approximately, whereas actually these quantities are related in a more complicated manner; see equation (42). The results of the self-consistent calculation may be regarded as more exact, so the critical values of U_c given in figure 4 are, apparently, slightly overestimated.

Let us now consider possible causes of the electron localization at the one-charge vacancy. First of all, we wish to point out that the model of H_2 described in section 6 can no longer be applied seeing that there is only one electron at the impurity level. Evidently, the localization of this electron can result either from non-symmetrical distortions of wavefunctions of valence electrons and/or from the lattice deformation. Consider in some detail the former cause (the latter will be dealt with in section 8).

Let us assume that the electron at the impurity level is preferably localized at the first cation. In this case, the wavefunctions of the valence electrons are constructed in such a manner as to be localized to a greater degree at the second cation. This involves the lowering of the potential energy of the electrostatic interaction between electrons. However, the one-particle portion of the energy grows with the electron localization because the covalent component of chemical bonding is decreased in this event. At large U the change in the potential energy becomes predominant and the electrons are localized, while at small U the change in the kinetic energy is prevalent and the electron's wavefunctions turn out to be delocalized.

A simple graphical model illustrating the foregoing is represented by a two-centre construct with two electrons at different orbitals. Let the two equal centres have two states each $\chi_{i\sigma}^{(n)}$ differing in the average radius and the spin projection. The molecular orbitals are written as their superpositions.

$$
\begin{aligned}
\varphi_1 &= \chi_{11}^{(1)} \cos \vartheta_1 + \chi_{11}^{(2)} \sin \vartheta_1 \\
\varphi_2 &= \chi_{22}^{(1)} \sin \vartheta_2 + \chi_{22}^{(2)} \cos \vartheta_2.
\end{aligned}
\tag{51}
$$

The electron energy is found with the Hubbard electron rejection and the covalent mixing of orbitals is taken into account

$$
E = \epsilon_0 + 2t_1 \cos \vartheta_1 \sin \vartheta_1 + 2t_2 \cos \vartheta_2 \sin \vartheta_2 + \tfrac{1}{2}(\cos^2 \vartheta_1 \sin^2 \vartheta_2 + \sin^2 \vartheta_1 \cos^2 \vartheta_2)U
\tag{52}
$$

where ϵ_0 is a constant and t_1, t_2 are the hopping integrals for the first and second state. The necessary condition for the extremum of function (52) is

$$
\begin{aligned}
4t_1 \cos(2\vartheta_1) + U \sin(2\vartheta_1) \cos(2\vartheta_2) &= 0 \\
4t_2 \cos(2\vartheta_2) + U \sin(2\vartheta_2) \cos(2\vartheta_1) &= 0
\end{aligned}
\tag{53}
$$

while the sufficient condition for the minimum of function (52) at $\vartheta_1 = \vartheta_2 = \pi/4$ leads to the following inequality ($t_1 < 0$, $t_2 < 0$)

$$
U > 4(t_1 t_2)^{1/2}.
\tag{54}
$$

When this condition is violated, new solutions are stabilized that are localized at different atoms for which we may obtain from (53)

$$
\cos^2(2\vartheta_1) = \frac{U^4 - 16^2 t_1^2 t_2^2}{U^2(16t_1^2 + U^2)} \qquad \cos^2(2\vartheta_2) = \frac{U^4 - 16^2 t_1^2 t_2^2}{U^2(16t_2^2 + U^2)}.
\tag{55}
$$

It follows from the formulae derived that the greater is U compared to t_1 and t_2, the higher is the degree of electron localization. Note that even when one electron is completely localized at one of the atoms (which is, for example, possible when $t_1/U = 0$), the second electron is generally localized at the second atom only partially, and its localization is the greater, the less is t_2/U.

Thus, owing to the electrostatic interaction, the valence electrons are ejected from the region in which the impurity state is localized and, at large U, this leads to a lowering of the system's energy and, as a consequence, to the stabilization of the localized impurity state.

As noted in section 6, a sharp boundary between the states with the localized and delocalized electrons at the vacancy exists only within the framework of the unrestricted HF method. When the electron correlations are included, this boundary must vanish. In other words, there can exist no stationary multi-electron state with broken symmetry in the one-impurity system (on condition that the host lattice is stable with respect to the breaking of its symmetry). Consequently, the average dipole moment of the F centre must be zero. Of course, the time which the electron spends near one of the centres may, in terms of certain experiments, be quite large. The measurement time in such experiments must be less than the time of electron fluctuation between two potential wells. Eventually, the electron does create a stationary dipole moment, in case two cations near to the vacancy prove for some reason non-equivalent. This may occur if one of them is replaced by the impurity element or if the system as a whole is placed in a uniform electric field.

Thus, the state of the oxygen vacancy with broken symmetry is not, strictly speaking, the eigenstate of the isotropic Hamiltonian. The electron can exist in such a state for a limited time, hopping then to the same state but with the opposite direction of the dipole moment. At the same time, when possible non-symmetrical displacements of the ions nearest to the vacancy are taken into account, such a state may stabilize or, rather, the time of its existence can grow appreciably. This may invalidate our assertion that the state with broken symmetry is quasistationary.

8. Two-impurity model

In the foregoing we examined the electron structure of an oxygen vacancy near which there are two equivalent transition elements (belonging to the main crystal lattice). The potentials at these elements were different from the potentials at the atoms of the main lattice on account of the electrostatic field of the oxygen vacancy. Having analysed that model, we have found that there is a critical value of the Hubbard parameter U above which the one-electron wavefunction lowers its symmetry in the unrestricted HF method. A similar situation is equally conceivable in the event when the lattice contains two closely positioned equivalent impurity elements in the absence of any oxygen vacancies. In this case the difference of the potential at the foreign atoms from that at the host crystal atoms can be accounted for by the fact alone that here we have to do with different chemical elements, which, accordingly, possess dissimilar orbital electron energies.

The above-derived formulae remain valid for the two-impurities model provided that the determinants (17)–(19) are replaced with the following ones:

$$D = \begin{vmatrix} 1 - g_{11}V_1 & -g_{12}V_2 \\ -g_{21}V_1 & 1 - g_{22}V_2 \end{vmatrix} \tag{56}$$

$$D_{1,1} = \begin{vmatrix} g_{11} & -g_{12}V_2 \\ g_{21} & 1 - g_{22}V_2 \end{vmatrix} \tag{57}$$

$$D_{2,2} = \begin{vmatrix} 1 - g_{11}V_1 & g_{12} \\ -g_{21}V_1 & g_{22} \end{vmatrix}. \tag{58}$$

If there are two electrons at the donor level, they can either have delocalized wavefunctions adapted to the given symmetry ($U < U_c$) or be localized at different impurity elements ($U > U_c$). One electron at the donor level can have a delocalized orbital ($U < U_c$) or be localized at one of the impurities and form a dipole moment ($U > U_c$).

9. Instability caused by polarization of the medium

Earlier we reasoned from the assumption that the instability of the delocalized HF state results from the electrostatic electron interaction. However, in polar dielectrics the polarization of the medium may be a factor equally effective in bring on the instability. To illustrate this point, let us consider the following simple model. Surround both of the two transition elements with spheres of radius r_0 and assume that inside these spheres the dielectric constant of the medium is ϵ_∞ while outside them it is ϵ_0 (letting $\epsilon_0 \gg \epsilon_\infty$). When interference effects are neglected, the addition to the electron energy stemming from the polarization of the medium will be given by the sum of the electron charges squared in the first and the second spheres

$$\Delta E_p = -\frac{e^2}{2\epsilon_\infty r_0}(Q_1^2 + Q_2^2). \tag{59}$$

The product of the multiplication of charges in (59) appears only with the inclusion of the interference of the fields induced by the first and second charges. Neglect of this contribution is similar to the assumption used above when the inter-centre electrostatic interaction was not taken into account.

On condition of the complete localization of the electron in both spheres

$$Q_1 + Q_2 = 1. \tag{60}$$

Evidently, under the additional condition (60) the minimum of the function (59) is attained in the event of the complete localization of the electron in one of the two spheres. An increase in the electron's kinetic energy is a factor counteracting this development. If this increase is smaller than the lowering of the potential energy, the HF solution delocalized over the two atoms will be unstable.

10. Discussion of experimental data

The determination of the depth of oxygen vacancy levels was done by electrical [9] and optical [10] methods. It has been found that the energy of the maximum in the optical absorption spectrum of the oxygen vacancy in $SrTiO_3$ ($\sim$ 1.7 eV) appreciably exceeds the thermal activation energy (0.35 eV) obtained from the temperature dependence of the electrical conductivity. Calculations carried out in [3, 8] have shown that this can be explained by the low probability of the optical excitation of an electron to near-bottom

conduction-band states. Thus the depth of the level of a single-charge oxygen vacancy is 0.35 eV for $SrTiO_3$. For other oxides of this family it lies in the 0.2–0.7 eV range [9]. Our calculations show that this result corresponds to $U_c = 1$ to 2 eV. As to the zero-charge vacancies, their levels are very shallow—of the order of some hundredths of an eV with U_c being in this case 2 eV. So the breaking of symmetry of one-electron orbitals is more probable at single-charge vacancies than in the zero-charge case.

The specificity of the state characterized by disturbed symmetry of one-electron orbitals lies in the fact that a great dipole moment is associated with it. Indeed, the maximal estimate of the dipole moment of an electron localized at one of the transition elements amounts to $p = ea/2$ where a is the lattice constant and e is the electronic charge. Hence, one may argue that the loss of symmetry of one-electron wavefunctions at oxygen vacancies could be experimentally detected from the electron polarization. Let us examine this assumption.

First we estimate the electron polarization in a two-well two-level model in which

$$P_i = (np/3) \tanh(eE_i a/kT) \tag{61}$$

where n is the concentration of vacancies and E is the electric field vector. Usually $eEa \ll kT$ and in this case formula (61) simplifies to

$$P_i = (npea/6kT)E_i. \tag{62}$$

Accordingly, the contribution of vacancies to the polarizability looks as follows

$$\alpha = npea/6kT. \tag{63}$$

After substituting into (63) the maximal estimate for p at $T = 300$ K and $a = 4$ Å we come to $\alpha = 1$ at $n = 10^{21}$ cm^{-3}. In weakly reduced oxides of the perovskite family $n = 10^{17}$ to 10^{18} cm^{-3}.

It follows from the above-presented data that the thermal polarization is negligible in the case under examination. Another situation arises when an oxygen vacancy develops at the Curie temperature. In this case even a small amount of defects can lead to macroscopic changes of crystal parameters. So, it is known that oxides increase the perovskite's polarization. This can be explained by the presence at the oxygen vacancy of a dipole moment, which arises owing to the breaking of symmetry of the one-electron wavefunction. Point dipoles can influence the crystal parameters similarly to an external electric field. A like effect may be obtained by substituting a smaller atom for another one (e.g. in $KTaO_3$:Li, Li is substituted for K). In the latter case the smaller atom is shifted and creates the dipole moment. In contrast to this, a vacancy without the dipole moment leads to the decrease in the polarization like in the case with the external pressure (e.g. V_A in the ferroelectric $ATiO_3$). Note that the asymmetry of the oxygen vacancy in perovskites and corresponding asymmetric scattering of the carriers by this defect can give contributions to field-even and photovoltaic currents in ferroelectrics observed in various experiments.

Experimental research into polarization processes gives only indirect information about symmetry of one-electron orbitals near oxygen vacancies. Apparently, spectral methods could be more productive, in the first place, electron paramagnetic resonance (EPR) spectroscopy. So far it is only known [12] that, upon reduction of $SrTiO_3$, the EPR spectra exhibit strengthening of the signal that corresponds to Ti^{3+}. This points indirectly to the localization of the oxygen vacancy electron at one of the Ti atoms nearest to this vacancy. Such a development transforms this atom from the tetravalent state (in $SrTiO_3$, Ti atom's valency is 4) into the trivalent one (obviously, formal valency is implied).

Some additional evidence could be obtained by measuring the frequency and temperature dependencies of the loss angle tangent. Presently, only for some systems are there indications of the existence of the corresponding relaxational maxima. However, their dependence on the oxidation and reduction degree of the samples has not so far been experimentally studied.

11. Conclusion

The present study has shown that in the unrestricted HF method the one-electron orbitals located in the vicinity of an oxygen vacancy in perovskite-type oxides can at $U > U_c$ (U is the Hubbard parameter) have a lower symmetry than the symmetry of the defect. Calculations in terms of a simple model in which the basis included only one atomic orbital at each atom indicate the following.

In the case of a neutral vacancy, U_c is, for deep levels, of the order of some tenths of an eV while for shallow levels it grows and may exceed 1 eV; as regards the single-charge vacancy, there in the case of deep levels to 1–2 eV and for shallow levels it may attain even greater values. Experimental data as well as results of numerical calculations [9] show that neutral vacancies have in perovskites relatively shallow levels of the order of some hundredths of an eV whereas levels of the single-charge vacancies are deep, viz. 0.2–0.6 eV. This evidence, apparently, justifies the conclusion that the localization of electrons is hardly possible at a neutral vacancy, the less so in view of the fact that at room temperature they are strongly ionized. In our judgment, the localization of the electron at the single-charge oxygen vacancy is a more realistic assumption; moreover, the polarization of the medium may promote such a localization. However, numerical estimates have shown that the experimental determination of the degree of electron localization near oxygen vacancies from data on the crystal polarizability is not effective—rather, detailed spectroscopic investigation is needed for that purpose.

Unfortunately, it is impossible, in terms of the HF method, to elucidate the question as to how the inclusion of electron correlations may alter the results obtained. But calculations carried out earlier, for finite clusters with cyclic boundary condition [8], have shown that the value of the total electron energy found by unrestricted HF method is substantially closer to the exact value derived by means of the direct diagonalization of the Hamiltonian than that obtained in the restricted version of the method. In other words, the use of orbitals with broken symmetry is a convenient means to improve the standard restricted HF method. This is also evidenced by the results of a calculation on the dispersion of the model Hamiltonian [8] which show that this dispersion is substantially decreased when switching from the restricted to the unrestricted HF method. We may therefore argue that the results derived in the present work can essentially improve the model of the electronic structure of oxygen vacancies in perovskite-family oxides which was previously developed on the basis of the restricted HF method. Next we describe some principle features of our model and compare it with other existing models of atomic vacancies.

In the conventional theory of the F centres it is assumed that an atomic vacancy gives rise to a local potential well that binds the electron. For example, in alkaline-haloid crystals the anion vacancy has high barriers near cations owing to the fact that the wavefunction of the F centre must be orthogonal to the lower-lying states (for example in KCl to the 3s states of K). This leads to the ejection of the electron from the area where the cations are located. In addition to that, the Madelung potential lowers the potential in the defect centre, which is consistent with the orthogonalization of the states at cations and binds the electron at the F centre.

In contrast, the theory of the electronic structure of atomic vacancies in covalent crystals considers that the local state in the forbidden gap arises already at the stage of the breaking of chemical bonds. According to this theory, the atomic vacancy, for example, in Si has local states that arise simply because the states of the atom being removed from the lattice are eliminated from the basis of the atomic states. Formally, this is achieved by localizing the vacancy potential at only one defect site and by letting the matrix element of this potential go to infinity [4].

A more complex situation occurs in crystals with the intermediate character of chemical bonding to which the perovskite family oxides belong. It has been shown that in this case the rupture of chemical bonds does not lead to the appearance of local states in the forbidden gap. At the same time, the localization of the electron in the well created by the atomic vacancy does not take place either (rather, there is no well in this event). Indeed, on account of the presence in ionocovalent crystals of relatively low-lying empty electron states of cations and the covalency of chemical bonding, the electron is drawn from the centre to the cations. One may, of course, imagine a peculiar situation when the defect centre state is not mixed by the Hamiltonian with the low-lying cation states, but such a state can be a ground state only in the case of weak covalency of chemical bonding characteristic of ionic crystals.

Thus, unlike ionic crystals, the electron at the F centre in oxides is drawn to the cations nearest to the vacancy. The stabilization of that state occurs on account of the potential at cations brought on by the vacancy and the medium polarization. The deeper this potential, the greater is the electron's binding energy.

Next we turn to the question concerning the form of the wavefunction of the electron at the neutral and charged oxygen vacancies. In [1–3] it was asserted that in these cases the one-electron wavefunction is delocalized with respect to two cations nearest to the vacancy, and at these has equal weights. Here a certain analogy may be found with the well known study of the electron structure of the H_2 molecule, where it was shown that, with increasing distance between the nuclei, the delocalized one-electron state becomes unstable and, after exceeding a certain critical distance, the electrons are localized near different atoms. We have shown in the present work that an analogous localization of electrons occurs near different cations closest to the oxygen vacancy. Moreover, owing to non-symmetrical distortions of the wavefunctions of valence electrons, such a localization takes places even at the F centre. However, in the physical interpretation of these results one has to bear in mind that a state with a broken symmetry of the point defect is not, strictly speaking, stationary.

Acknowledgments

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