Computational study of self-trapped hole polarons in tetragonal BaTiO₃

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We have used a quantum-chemical method developed for crystal calculations to investigate self-trapped hole polarons in technologically important BaTiO₃ perovskite-type crystal. The tetragonal structure of this material is considered in the present work. The computations are carried out in a self-consistent-field manner using the embedded molecular cluster model. The spatial configuration of a hole polaron and displacements of defect-surrounding atoms are obtained and analyzed. The probability of spontaneous hole self-trapping in a perfect crystal lattice is estimated by calculating the hole self-trapping energy as a difference of the atomic relaxation energy and the hole localization energy. This value is found to be negative, -0.87 eV, which demonstrates the preference of the self-trapped polaron state compared to a free hole state in the valence band. The computed polaron absorption energy, 0.4 eV is found to be in an excellent agreement with the available experimental data and independent estimations of the polaron theory.

I. INTRODUCTION

In spite of their simple crystallographic structure, perovskite-type crystals are fascinating materials having important optical and ferroelectric properties and a wide range of applications. In the 1940s Slater predicted[1] that, due to their simple perovskite-type structure, the main properties of BaTiO₃ would be understood in the near future. Nowadays, however, we have a better knowledge about only some of its physical properties, such as ferroelectricity and phase transition,[2–4] and this material still remains the focus of extensive study by both experimentalists and theoreticians. The reason for such an interest is the fact that the BaTiO₃ crystal has excellent photorefractive properties due to its large electro-optic coefficients and high photorefractive sensitivities. These features make BaTiO₃ a promising material in a number of important technological applications,[5] including self-pumped phase conjugation or holographic storage.[6] It is well known that photorefractive materials such as BaTiO₃ are sensitized, involving point defects.[7] It was also discovered that the photoconductivity of the BaTiO₃ crystal does not scale linearly with light intensity[8] ($\sigma_{ph} \sim I^x, x<1$), and in most cases this effect is caused by the presence of holes in the valence band.[9]

The present work is focused on the problem of the self-trapped hole (STH), the so-called hole polaron or Jahn-Teller (JT) hole polaron, occurrence in an otherwise pure BaTiO₃ tetragonal lattice. Our computational study suggests that some of the experimentally observed shallow levels in the tetragonal BaTiO₃ are related to the presence of the STH or JT hole, which could be trapped at regular O sites and can occur spontaneously in the BaTiO₃ crystal under radiation. Our research is important, considering the tremendous efforts made by experimentalists toward the fundamental understanding of the high-temperature superconductivity (HTSC) in cuprates[10] as well as colossal magnetoresistive (CMR) manganites,[11] which both have perovskite-type structures. The presence of JT polarons in the HTSC and CMR manganites and their strong coupling to lattice vibrations are well

known.[12–14] Another principal finding is that a fraction of the holes in the CuO₂ planes in the HTSC cuprates becomes localized.[15] This could form charge- and spin-ordered phases, which may compete with superconductivity in the cuprates.[16] Thus the study of JT hole polarons in a tetragonal BaTiO₃ crystal could contribute considerably to the fundamental knowledge of perovskite oxides.

Since the discovery of hole polarons in pure alkali halides,[17] they have been found in many ionic crystals, including alkaline-earth fluorides and crystals with KMgF₃ and PbFCl crystallographic structures, as well as in rare-gas crystals.[18–21] Theoretically, this kind of defect is well established.[22] The problem that arises when one studies the STH polarons in the BaTiO₃ crystal lies in the fact that they cannot be monitored directly using the EPR technique due to the zero nuclear spin on regular O atoms.

The aim of this paper is to clarify whether it is likely that STH polarons occur spontaneously in the tetragonal phase of pure BaTiO₃, and, thereafter, to calculate both structural and optical properties of this point defect. For this objective we choose to use a quantum-chemical method modified for crystal computations. The paper is structured as follows. In Sec. II we give details of the computational method and some results of pure crystal bulk calculations. In Sec. III we discuss how to determine the spontaneous formation of the STH polarons. Sections IV and V contain results of the microscopic structures of JT polarons in the tetragonal BaTiO₃ lattice as well as studies of the ground and excited states and a calculation of the absorption energy of this point defect. In Sec. VI we give our conclusions.

II. COMPUTATIONAL DETAILS AND CRYSTAL BULK PROPERTIES

The method used to solve the many-particle electron-ion problem is based on the advanced version of the Hartree-Fock theory modified for crystal calculations (CLUSTERD computer code[23]). Two different models are implemented into the code: (i) the periodic large unit cell (LUC) model,[24]

which calculates both the electronic structure and the total energy of the perfect crystal via molecular orbitals (MO's) as a linear combination of atomic orbitals (AO's), and (ii) the embedded molecular cluster (EMC) model,[25] which is also based on a strict treatment of the total energy of the whole crystal, accounting for the perturbation (polarization) that the remaining crystal has on the EMC region, thus leading to the so-called quantum cluster approach. The method of calculating the polarization of a crystal by a point defect is nothing but a direct generalization of the usual static-lattice method suggested by Stoneham.[26] This method is based on the following points: (i) the "classic" ideas of the polarization are based on rigorous quantum consideration, (ii) the classic region comprises only the rest of the crystal, and (iii) an exact consideration of nonlinear (higher-order) crystal response is done, and a method to avoid a weak convergence of the Born series for the response function is developed. Although electronic polarization is not taken into account directly within the EMC approach, the model applies the Tolpygo theory of polarizing shells[27] for finding the wave function of the residue part of the crystal. Such an approach permits one to describe the polarization of the crystal residue reliably within the framework of polarizing shells, and to take into account exchange interaction between the EMC and the rest of the crystal. This advantage of the EMC model is especially important for charged defect calculations, as in our case. In the present work we have used both models: the LUC model to study the perfect crystal bulk properties, and the EMC approach to calculate a hole and its possible trapping in the tetragonal crystalline lattice of barium titanate.

It is necessary to point out that our method has proved to be reliable in reproducing spatial and electronic structure of a wide variety of crystals. Actually it was tested upon more than 30 crystals, including oxide crystals. For instance, the computer code gave satisfactory results on defect studies in complex oxides such as α-Al_2O_3,[28–30] TiO_2,[31,32] and WO_3.[33] In the last five years the current method was also successfully applied to study perfect and defective perovskites. Some examples include calculations of point defects and a modeling of phase transition in the $KNbO_3$ crystal,[34,35] Nb doping in the $KTaO_3$ crystal,[36] studies of pure and defective $SrTiO_3$ crystals,[37,38] and impurity doping in $CaTiO_3$ cubic and orthorhombic lattices.[39] We also attempted to study free[40] and impurity-trapped[41] hole polarons in the cubic phase of the $BaTiO_3$ crystal, obtaining interesting outcomes.

A full account of the LUC framework is given in Refs. 23 and 24, while the parametrization scheme is described in detail in Ref. 42. The numerical parameters approximate some one- and two-center integrals in the Hartree-Fock theory, thus remarkably reducing the computational time, and making available the investigation of complex systems. These numerical parameters also compensate for the neglect of all three- and four-center integrals according to the so-called intermediate neglect of differential overlap approximation. Note that the method has so far reproduced surprisingly well both available experimental data and the results of other *ab initio* calculations in many complex systems including perovskite materials.[34,36]

In order to calculate the tetragonal $BaTiO_3$ crystal we

TABLE I. Numerical parameter sets used in the present work: ζ (a.u.), E_{neg} (eV), $P^0(e)$, and β (eV).

Atom	AO	ζ	E_{neg}	P^0	β
Ba	$6s$	1.65	11.34	0.2	−0.4
	$5p$	2.8	30.6	2.0	−4.0
Ti	$4s$	1.4	1.4	0.65	−0.5
	$4p$	1.1	−10.0	0.04	−0.5
	$3d$	1.93	−2.9	0.62	−9.0
O	$2s$	2.27	4.5	1.974	−16.0
	$2p$	1.86	−12.6	1.96	−16.0

have used an eight-times ($2\times2\times2$) extended LUC. The reduced Brillouin zone (BZ) corresponding to the LUC is thus eight times smaller than the BZ constructed for the primitive unit cell, and each **k** point in the reduced BZ corresponds to a family of eight points of the full BZ. Therefore, one can be sure that the eight-times-extended LUC reliably describes the band structure of the perfect barium titanate, since it simulates eight **k** points in the full BZ. However, in order to justify our choice, charges in atoms and density of the states for eight-times-extended and 27-times ($3\times3\times3$) extended LUC's were calculated, and it was found that their magnitudes are practically equivalent. Additionally, the phonon frequencies were calculated for the tetragonal $BaTiO_3$ crystal,[43] showing the reliability of the eight-times-extended LUC model. It is important to note that similar studies for different LUC sizes were carried out recently on the $KNbO_3$ crystal,[44] proving the sufficiency of the eight-times extension of a primitive unit cell for perovskite-type crystals. The numerical parameter sets for the Ba, O, and Ti atoms used in the present work were taken from Ref. 40. Their values are given in Tables I and II. The results of our quantum-chemical calculations of the perfect $BaTiO_3$ crystal are presented in Table III. The obtained lattice constants $a=4.01$ Å and $c=4.04$ Å are in a good agreement with the experimental values.[45] The fully reproduced tetragonal structure of the $BaTiO_3$ crystal is shown in Fig. 1. The widths and compositions of the valence bands are also in accordance with the available experimental measurements.[46] The upper valence band is composed mainly of O $2p$ states, with a considerable admixture of Ti $3d$ states. This indicates a Ti $3d$–O $2p$ hybridization, and thus our model considers the so-called ferroelectric instability as suggested in previous studies.[2] We con-

TABLE II. Numerical two-center parameters α_{mB} (a.u.$^{-1}$) optimized during the calculations; the mth AO belongs to atom A, where $A \neq B$.

A	B		
	Ba	Ti	O
Ba	0.20	0.52	0.33
Ti	0.11	0.13	0.10
O	0.52	0.36	0.15

TABLE III. Basic properties of a tetragonal BaTiO$_3$ crystal obtained computationally in comparison to the available experimental results: ΔE_g, the width of the forbidden energy gap (in eV); E_{v1}, the upper valence-band-width (in eV); E_{v2}, the lower valence-band-width (in eV); a and c, lattice constants (in Å); $q(\text{Ba})$, and $q(\text{Ti})$, and $q(\text{O}_{1,2})$, charges on the Ba, Ti and O atoms, (in e), respectively (see Fig. 1).

Property	Our results	Expt. data[a]
ΔE_g	6.1[b]	3.2
E_{v1}	4.2	4.8
E_{v2}	3.2	2.8
a	4.01	3.99
c	4.05	4.03
$q(\text{Ba})$	1.73	
$q(\text{Ti})$	2.45	
$q(\text{O1})$	−1.359	
$q(\text{O2})$	−1.358	

[a]The experimental values of ΔE_g, E_{v1}, and E_{v2} are taken from Ref. 46, the experimental values of lattice constants a and c are taken from Ref. 45.

[b]Calculated as a difference between the highest occupied and lowest unoccupied MO's, i.e., only short-range correlation effects have been taken into account through the computations while the long-range effects are not included.

sidered it essential to include Ba $5p$ states as the basis AO's within the valence basis set, since their overlap with AO's of other atoms is not negligible. It is important to underline that our method reproduced differences between the two phases. In particular, comparing with the DOS of the cubic phase,[38] the corresponding DOS for the tetragonal phase points to the considerable Ti $3d$ amount in the upper valence band and O $2p$ states at the bottom of the conduction band. This implies a hybridization effect between the Ti $3d$ and O $2p$ states, which is required for the ferroelectricity phenomenon to occur in the titanates, as indicated in Refs. 47 and 48. It is also important to analyze the effective charges of the atoms for both phases. The following charges were obtained: $q(\text{Ti}) = 2.65e$, $q(\text{Ba}) = 1.73e$, and $q(\text{O}) = -1.46e$ for the cubic phase and $q(\text{Ti}) = 2.45e$, $q(\text{Ba}) = 1.73e$, and $q(\text{O}) = -1.36e$ for the tetragonal phase, respectively. As one can see, we have considerably more covalent chemical bonding for the tetragonal phase in accordance with expectations. In order to calculate the effective charges on atoms we have used the so-called Löwdin population analysis,[49] which, in our mind, is more precise when compared to the Mulliken method used to calculate static charges on atoms. In the Löwdin population analysis the effective charge on a given atom is obtained as

$$q_A = Z_A - \sum_a^{(A)} \sum_i n_i C_{ai}^2, \qquad (1)$$

where C_{ai} are coefficients of the Löwdin AO's, Z_A is the number of valence electrons of atom A, and n_i are population numbers of the ith MO.
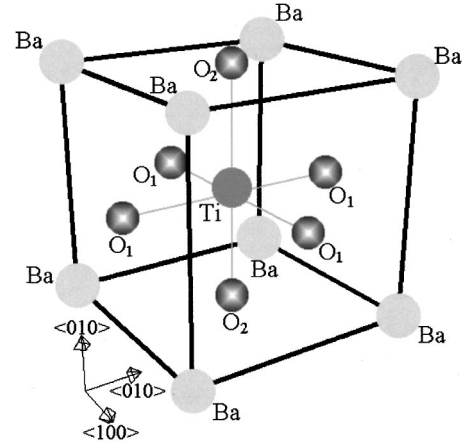

FIG. 1. Sketch of the tetragonal structure of a pure BaTiO$_3$ crystal.

III. RESULTS AND DISCUSSION

A. Prediction of the STH polaron creation

A hole is a *charged* intrinsic defect, and its simulation by periodic models is problematic without the inclusion of some compensating charge.[50] That is why we chose to use the EMC model[25] with a cluster consisting of 135 atoms. The size of the $[\text{Ba}_{27}\text{Ti}_{27}\text{O}_{81}]^0$ cluster was considered to be sufficient to reproduce satisfactory the defective and the chemical bonding of the BaTiO$_3$ crystal. Also, by exploiting the 135-atom molecular cluster, we preserved the symmetry of the crystal, which was important to obtain reliable electronic band structure of defective cluster and to calculate polaron absorption energy.

In order to estimate the hole self-trapping energy one has to compute E_{loc} and E_{rel}. A competition between the positive localization energy E_{loc} and the negative relaxation energy E_{rel} is decisive to make a final conclusion about the possibility of finding stable polarons in a given crystal.

It was found that when a hole is inserted into a molecular cluster, its spin density is mainly localized on one of the O atoms. For a one-site Wannier-type localized state of the hole one can use the Fowler estimate[51] for E_{loc}, being equal to the half-width of the upper valence band. However, this approximation is valid only for very diffuse and smooth energy bands, which is not our case because we have a considerable admixture of Ti $3d$ states in the O $2p$ valence band. In other words, the "center of gravity" of the O $2p$ band is not located at the exact middle of the band. According to Ref. 52, E_{loc} can be found using the expression

$$E_{\text{loc}} = \varepsilon(h) + \varepsilon_j(k) + (E_{\text{pol}}^1 + E_{\text{pol}}^2), \qquad (2)$$

where $\varepsilon(h)$ is the hole internal energy; $\varepsilon_j(k)$ is the hole energy in the free or delocalized state, whose value is obtained using the LUC method; E_{pol}^1 and E_{pol}^2 are two contributions to the polarization energy discussed below. In order to estimate the hole energy $\varepsilon(h)$, one can proceed in the following manner. If a hole is localized on one atom, it is convenient to use Wannier functions, which lead to the following form of the hole wave function:

$$\phi_h(r) = \sum_{Lj} c_{kj}^{(W)} W_{Lj}(r) = W_{0j}(r), \qquad (3)$$

where the hole is considered in the zeroth cell ($L=0$) of the LUC in the valence band j. We can denote $\varepsilon(h)$ as $\varepsilon^w(h)$ in order to describe the hole energy using the Wannier representation, which gives us the following expression:

$$\varepsilon^{(w)}(h) = -\langle W_{0j}|F^f|W_{0j}\rangle = -\varepsilon_j^{(W)}(0) \quad (L=0), \qquad (4)$$

Here F^f is the Fock matrix of a pure crystal obtained by the LUC computations. For $L=0$, it is known that

$$\varepsilon_j^{(W)}(L=0) = \frac{1}{N}\sum_j \varepsilon_j(k). \qquad (5)$$

The second term in Eq. (5) is related to the DOS of the energy band j in the following manner:

$$\frac{1}{N}\sum_k \varepsilon_j(k) = \int_{\text{Band-width}} \varepsilon N_j(\varepsilon)d\varepsilon. \qquad (6)$$

Consequently, if one compares Eqs. (4) and (6),

$$\varepsilon^{(W)}(h) = -\int_{\text{Band-width}} \varepsilon N_j(\varepsilon)d\varepsilon, \qquad (7)$$

which means that the hole energy is the ''center of gravity'' of the valence band j. Thus we have obtained for E_{loc} [$\varepsilon(h)+\varepsilon_j(\mathbf{k}=0)$] a value of 2.01 eV. This value is calculated in the Γ point ($\mathbf{k}=0$), because the upper valence band has its maximum just at this point.

In order to estimate the relaxation energy term E_{rel} we made displacements to 38 atoms situated in the defective region. It is necessary to bear in mind that before we relax these 38 atoms, we must optimize the geometry of the atoms situated in the cluster boundary in order to minimize the boundary effects. E_{rel} was calculated as a difference of the total energies of the molecular cluster in the relaxed and unrelaxed states, giving a value of 2.88 eV, which is a negative magnitude as explained above. Then using the simple equation

$$\Delta E_{\text{ST}} = E_{\text{loc}} + E_{\text{rel}}, \qquad (8)$$

we obtain -0.87 eV as a value of the hole self-trapping (ST) energy. Since $\Delta E_{\text{ST}}<0$, self-trapping is favored with respect to a free delocalized hole state in the valence band, and we predict the spontaneous occurrence of polarons in the tetragonal lattice of a pure barium titanate. It is important to mention that recently, using the so-called Fröhlich electron-phonon interaction, the polaron self-trapping or binding energy was explicitly expressed[53] through well-defined experimental values, i.e., lattice constants and dielectric constants. Using this independent estimate, ΔE_{ST} was found to be equal to 0.842 eV,[53] which practically matches our calculated value.

B. Structural properties of a STH polaron

An analysis of the electron-spin-density distribution shows that 76% of the hole spin is localized on the O(17)
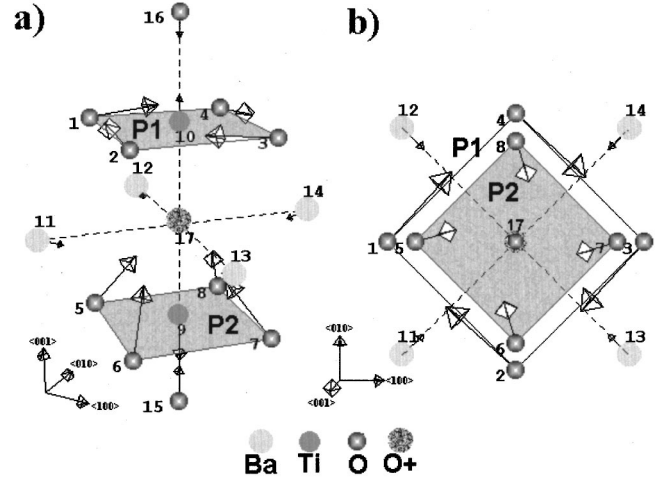

FIG. 2. Atomic structure details of the hole polaron surrounding region in the tetragonal lattice of the BaTiO$_3$ crystal. (a) Differences between the radial displacements of the O atoms belonging to the different planes, $P1$ and $P2$, respectively. (b) A view from the $\langle001\rangle$ direction showing the rotation of oxygens in the $P1$ and $P2$ planes.

atom (see Fig. 2), while the remaining 24% are shared by the defect-surrounding Ti and O atoms. The O(17) atom is situated practically in the middle of the cluster, and, taking into account our initial relaxation of the cluster boundary atoms, the artifact introduced by the boundary broken-bonds is totally eliminated. In crystals such as BaTiO$_3$, the crystalline lattice is quite rigid, and it seems that the strictness increases when the temperature decreases. Due to this fact and also because of the partially covalent character of the Ti-O bonding along the $\langle001\rangle$ direction, we performed two subsequent geometry relaxations. In the first stage we permitted 38 atoms situated within a radius of 2.1 Å to move freely from their regular sites from the O(17) atom. Thereafter we allowed 64 atoms in total to relax, including the above-mentioned 38 atoms, and in this way we obtained the best possible defect structural configuration. The automated geometry optimization using the downhill simplex method in multidimensions[54] was also used to achieve our goal.

Finally it was found that only 16 atoms have non-negligible displacement as can be seen from Table IV and Fig. 2, while the rest of the atoms in the defective region practically remain static, i.e., their displacements do not exceed 0.01 Å. The oxygens in the defective region have a non trivial relaxation if we compare their movements with the corresponding displacements in the cubic phase of the BaTiO$_3$ crystal containing the STH.[40] In the case of a tetragonal lattice we have two planes with four O atoms in each plane. In plane $P1$ (Fig. 2) the O atoms undergo a rotation of 2.05° around the vertical $\langle001\rangle$ axis, which passes through the O(17) atom [see Figs. 2(a) and 2(b)], without any radial displacements toward the O(17) atom. On the other hand, the O atoms that belong to plane $P2$ have a rotation of 1.83° around the $\langle001\rangle$ direction, with an additional radial displacement toward the O(17) atom (see Fig. 2). We believe that these peculiar rotations could be attributed mainly to the so-called Jahn-Teller effect. This effect was already observed in studies of O$^-$ holes associated with alkali acceptors in the BaTiO$_3$ crystal.[55]

TABLE IV. Atomic displacements Δr (in Å) and rotational angles α (in degrees) in the polaron-surrounding defective region obtained by the automated geometry optimization. A "$-$" sign denotes displacements of atoms outwards the defect situated on O(17). The rotation of both $P1$ and $P2$ planes are in the same sense. The atomic numeration corresponds to the one in Fig. 2.

	Atom	Δr	α
$P1$	O(1)	0.110	+2.051
	O(2)	0.110	
	O(3)	0.110	
	O(4)	0.110	
$P2$	O(5)	0.107	+1.83
	O(6)	0.107	
	O(7)	0.107	
	O(8)	0.107	
	Ti(9)	-0.053	
	Ti(10)	-0.013	
	Ba(11)	0.013	0.0
	Ba(12)	0.013	
	Ba(13)	0.013	
	Ba(14)	0.013	
	O(15)	0.035	
	O(16)	0.012	

It is important to stress that the LUC is elongated along the $\langle 001 \rangle$ direction, i.e., the produced dipole moment is along this direction. As follows from our output, it is possible to suggest that the defect enhances the electronic hybridization between the p-type AO of the O(9) and d_z-type AO of the Ti(15), and thus augments the covalent character in the chemical bonding within the defective region. The movements of the two defect-closest Ti atoms are outward from the O(17) atom [see Fig. 2(a)]. This is in accordance with expectations, since the effective charge of the O(17) atom becomes more positive with respect to the perfect crystal lattice. Another peculiar result is that the Ti(9) atom moves five times more than the Ti(10) atom along the $\langle 001 \rangle$ direction. This can be explained by considering the perfect tetragonal lattice symmetry. The hybridization between the O(15) and Ti(9) atoms as well as between O(17) and Ti(10) atoms is considerably stronger than between O(17) and Ti(9) atoms due to the shorter interatomic distance. This leads to the observed asymmetry in the lattice relaxation. The movements of the four Ba atoms are quite small [see Fig. 2(b)], and reflect the tiny role that Ba atoms play in the chemical bonding of the crystal.

C. Optical properties of the polaron

The ground state of the hole polaron is composed of either the $2p_x$ or $2p_y$ AO's of the O(17) atom (there is no distinction between these two states), and additionally has a considerable admixture of p and d states of the Ti(9) and Ti(10) atoms. This points to the interesting and rather rare fact that the STH in the BaTiO$_3$ tetragonal lattice has two ground states. The manner to calculate the excited state of the po-

laron is as follows: we take an electron from the occupied state in the upper valence band related to the O(17) atom, and excite it to the unoccupied state of the hole located within the band gap. Then, according to the Frank-Condon principle, the absorption energy is a difference between the self-consistent field (SCF) total energies of the cluster in its ground and excited states the (ΔSCF method). The excited state of the hole polaron is made up of the $2p_z$ AO of the O(17) atom with some contribution of the $2p_y$ AO of the O(17) atom as well as $4s$ and $3d_{z^2}$ states of the Ti(9) and Ti(10) atoms. Thus the calculated absorption energy is found to be equal to 0.4 eV. This result could be an indirect proof of the STH polaron presence in the tetragonal BaTiO$_3$ crystal when it is exposed to radiation. This suggestion follows from the agreement between our calculated value and a number of experimental measurements[5,8,56] of absorption energy made on the undoped tetragonal BaTiO$_3$ crystal.

It is quite interesting to compare our results with those obtained previously,[53] where the authors, applying the Frank-Condon principle, found an expression for the small Fröhlich polaron absorption energy ν_p in oxides,

$$\nu_p = 2\gamma E_p, \qquad (9)$$

where γ is the electron-phonon coupling coefficient, and E_p is a value of the hole self-trapping energy $\Delta E_{\rm ST}$ using our notations. The magnitude of this coefficient depends strongly on the radius of the interaction.[53] In the case of the Fröhlich interaction it is known[57] that the value of γ is between ~ 0.2 and ~ 0.4. So, if we use Eq. (9) and values of our calculated self-trapping and absorption energies, the evaluation of the γ coefficient gives us 0.23, in very good agreement with the polaron theory. This remarkable result permits us to suggest with more confidence that the presence of STH polarons or small polarons is associated with the JT effect in the pure tetragonal BaTiO$_3$ crystal.

IV. CONCLUSIONS

In the present work we have studied the possibility of spontaneous STH occurrence in the tetragonal lattice of pure BaTiO$_3$. In order to solve the problem, we have modified for crystals a quantum-chemical method based on the Hartree-Fock theory. The main result achieved is that we predict a spontaneous occurrence of STH polarons localized on regular oxygen sites in the tetragonal lattice of barium titanate. The ground state of this point defect is mainly due to the O $2p_x$ state, with some contribution of the Ti $3d$ and $4p$ states. In the excited state the hole is composed of an O $2p_z$ state, mainly with some admixture of the Ti $4s$ and $3d_{z^2}$ states. The rotations that undergo two oxygen planes, $P1$ and $P2$ (Fig. 2), could be due to the Jahn-Teller effect. We support this conclusion by experimental measurements carried out on O$^-$ holes related with alkali acceptors in barium titanate. Monitoring of the STH polarons is not possible by direct EPR measurements, but some experimental data[5,8,56] could be understood better if one considers the possibility of STH occurrence in this material. Additionally, our study is in an excellent agreement with other high-precision calculations[53]

of polaron self-trapping energy in the $BaTiO_3$ crystal using the so-called Fröhlich electron-phonon interaction and the polaron theory. The computed hole self-trapping energy $\Delta E_{ST} = -0.87$ eV and electron-phonon coupling coefficient $\gamma = 0.23$ agree very well with the polaron theory calculations.[53,57]

Our present work, and other our group studies on a La-doped $SrTiO_3$ crystal[58] and a Nb-doped $BaTiO_3$ crystal,[59]

imply the important role of charge carriers upon different properties of these crystals having a perovskite-type structure. Similar studies of charge carriers in the HTSC cuprates and CMR manganites,[14,53,57] based on polaron theory, arrive at the same ideas. This allows us to draw a unified conclusion concerning deep similarities at the fundamental level between the HTSC cuprates, titanates, and other crystals having a perovskite-type structure.

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