Quantum-chemical simulation of Al- and Sc-bound hole polarons in BaTiO$_3$ crystal

Henry Pinto and Arvids Stashans

Centro de Investigación en Física de la Materia Condensada, Corporación de Física Fundamental y Aplicada, Apartado 17-12-637, Quito, Ecuador

Abstract

Quantum-chemical modelling of impurity-bound hole polarons in BaTiO$_3$ crystal was carried out employing the semi-empirical method of intermediate neglect of differential overlap (INDO) modified for crystals. Two-site hole has been found to be the most common configuration in the BaTiO$_3$ crystal doped with Al or Sc atoms. The automated geometry optimisation was carried out to obtain the polaron spatial configuration and atomic displacements in the defective region. The ΔSCF calculated absorption energy for the aluminium-bound polaron was found to be equal to 0.27 eV and the corresponding absorption energies for scandium-bound polaron were computed to be 1.92 eV and 0.62 eV.

1. Introduction

Impurity-doped titanates having perovskite-type structure have important technological applications, e.g., are used in gas sensors and resistors [1]. Because of their unique ferroelectric and piezoelectric properties these ceramics have been found increasing processibility as an active element in advanced microelectronic devices [2]. In particular, barium titanate is of special interest because it is used as optical sensor due to its large electro-optic coefficients and high photorefractive sensitivity [3-6]. Additionally, $BaTiO_3$ is a promising material for the holographic storage [7,8] and compact solid state laser diodes in the near infrared wavelengths [6].

It is known that the optical properties of $BaTiO_3$ are strongly influenced by the presence of impurity-induced local energy levels within the band-gap of the material [6]. The crystal has a feature of non-linear photoconductivity [4,5], which is due to the presence of hole polarons contributing into the shallow energy levels in the band-gap. That is why the investigation of impurity-bound hole polarons in $BaTiO_3$ crystal could be useful to understand the basic mechanisms of the process of photoconductivity.

In the present study, quantum-chemical simulation of Al- and Sc-bound polarons in $BaTiO_3$ is done. In order to carry out this investigation, we have used the semi-empirical INDO method modified for crystal calculations and the periodic large unit cell (LUC) model as it is implemented in the CLUSTERD computer code [9]. Due to its semi-empirical character the CLUSTERD is not cumbersome and time consuming in the treatment of the electronic and spatial structure of complex

systems, especially with partially covalent chemical bonding, like oxide crystals. This is not the case of non-empirical (*ab initio*) methods. The CLUSTERD computer code has been successfully employed to investigate a number of perfect and defective oxides and materials with simpler electronic band structure. In particular, the method has an important advantage of geometry predictions for crystals doped with impurity atoms [10-12] as it was proved in free and impurity-trapped polaron studies in α-Al_2O_3 crystal (see corresponding experimental data [13,14]. Thanks to the very precise geometry reproduction some fundamental problems concerning Li intercalation in TiO_2 crystals were successfully resolved [15,16]. We have to note that within our method no *a priori* assumption is made about the pattern of the electronic density distribution in the vicinity of the defect under study, i.e., it is obtained in the self-consistent-field (SCF) manner. This leads to a reliable information about the defect influence upon the electronic band structure properties. The method also allows one to calculate with the reasonable precision the excited state of the system thus giving the data about defect contribution into the absorption spectra of the crystal (ΔSCF method).

The CLUSTERD computer code and in particular, the LUC model has been successfully exploited for the point defect computations and modelling of phase transition in $KNbO_3$ crystal [17,18]. This material has identical properties to the $BaTiO_3$ crystal like non-linear photoconductivity due to the hole polarons, large electro-optic coefficients and high photorefractive sensitivity. This proves the usefulness of the method in the present work.

In the present work we propose a new semi-empirical parameters in order to reproduce more precisely the conduction band structure of barium titanate, which now is in a good agreement with the available experimental data [19]. As a result of

our computations we have found that the hole localises on two oxygens situated along the z-direction for the case of the Al-impurity doping and along the x-direction for the barium titanate containing Sc-impurity. The calculated absorption energies are 0.27 eV for polaron in the Al-doped crystal, and 0.62 eV and 1.92 eV for polaron in the Sc-doped crystal, respectively.

2. Computational Details and Parameterisation

The modified INDO method is based on Molecular Orbital (MO) theory [20]. In the present work we have made use of the periodic supercell model based on the LUC approach [21]. The LUC model considers very accurately the interactions within the crystal and calculates both the electronic structure and the total energy of the crystal using MOs as a linear combination of atomic orbitals (AOs). This model is very powerful for perfect crystal studies but has a limitation for defect studies in crystals. The problem arises due to the mutual interaction between defects arranged periodically. However, this problem can be overcome using a large enough unit cell, so the distance between the neighbouring point defects are sufficiently large to neglect the mutual interaction between them.

This method has been proved to be powerful and reliable tool in the study of a number of perfect and defective oxides [22-25] with complex spatial and electronic band structure. The use of the INDO method allows us to perform self-consistent-field (SCF) calculations of the perovskites doped with Al and Sc impurities, which substitute for a Ti atom. We have exploited a LUC of 40-atom (extension 2x2x2) as a supercell. In order to estimate the possible mutual impurity-impurity interaction, we have computed the overlap integrals for Al 3p and Sc 4s AOs. The obtained absolute values of these

integrals are equal to 1.566 x 10^{-8} and 1.932 x 10^{-8} for Al 3p and Sc 4s AOs, respectively. This points out to the fact that the overlap is negligible and mutual impurity-impurity interaction do not exist. It is important to point out that we substituted an Al or Sc impurity atom for one of the Ti atoms located in the middle of the supercell (Fig. 1). The valence basis set was used which included 3s, 3p AOs for the Al atom, 4s, 3p and 3d AOs for the Sc atom, 6s and 5p AOs for the Ba atom, 4s, 4p and 3d AOs for the Ti atom and 2s and 2p AOs for the O atom.

The basic idea of the LUC method is referred to the **k**=0 approximation. The information about the computational equations of the total energy within the LUC model is given in [20,21]. Here we shall only briefly outline the main ideas of the method. In this approximation the Fock matrix elements are made self-consistent through:

$$\frac{1}{N} \sum_{k} P_{pq}(\bar{k}) \exp(i\bar{k} \cdot R_{v}) \tag{1}$$

where the summation is carried out over all the **k** values in the reduced Brillouin zone (RBZ) of the large unit cell. Thus we obtain information of the density matrix $P_{pq}(\mathbf{k})$ only in the point **k**=0. However, it has been demonstrated that the **k**-points in the RBZ contain several **K** points of Brillouin zone (BZ) of the primitive unit cell [26,27]. Therefore, the calculation of band structure in the **k**=0 of the RBZ are equivalent to the calculation of several **K** points in the BZ of the primitive unit cell. As it was shown in many recent studies, an eigthfold-symmetric extension of the primitive unit cell proves to be sufficient to reproduce almost exactly the electronic band structure of a given crystal [26].

We have used 40-atom LUC to parameterise the BaTiO$_3$ crystal. In the modified INDO method the Fock matrix elements [20] contain a number of semi-empirical

parameters. The orbital exponent ζ enters the radial part of the Slater-type AO. The diagonal matrix elements that consider the interaction of an electron on the ith valence AO of the atom A with its own core are taken in the following form:

$$U_{ii}{}^{A} = -E_{neg}{}^{A}(i) - \sum_{m}\left(P_{mm}{}^{(0)A}\gamma_{im} - \tfrac{1}{2}P_{mm}{}^{(0)A}K_{im}\right) \tag{2}$$

where P_{mm} are the diagonal elements of the density matrix, $E_{neg}(i)$ is the electronegativity of the ith AO, γ_{im} and K_{im} are one-center Coulomb and exchange integrals, respectively. The interaction of an electron in the ith AO belonging to the atom A with the core of another atom B takes the following form:

$$V_{iB} = Z_{B}\left[\frac{1}{R_{AB}} + \left(\langle ii|mm\rangle - \frac{1}{R_{AB}}\right)\exp(-\alpha_{iB}R_{AB})\right] \tag{3}$$

where α_{iB} is the parameter which considers the non-point character of the core B and diffuseness of the ith AO. The distance between the atoms A and B is represented by R_{AB} and the $\langle ii|mm\rangle$ are two-centre Coulomb integrals. The non-diagonal elements of Fock matrix contain the resonant integral parameter β_{AB}:

$$F_{im}{}^{\mu} = \beta_{AB}S_{im} - P_{im}{}^{\mu}\langle ii|mm\rangle \tag{4}$$

where ith AO belongs to the atom A and mth AO belongs to the atom B, μ means α or β spin, S_{im} is the overlap integral matrix and $P_{im}{}^{\mu}$ is the spin density matrix. Thus the parameterisation scheme contains five parameters: ζ, E_{neg}, $P^{(0)}$, α and β.

Our proposed parameter set for the $BaTiO_3$ crystal is given in the Tables 1 and 2. The parameterisation was made by reproducing the following magnitudes: width of the forbidden energy gap, widths of the upper and lower valence bands, density of states (DOS) of both valence and conduction bands (Fig. 2) and cubic lattice constant of the crystal. The INDO parameter set for the Al atom was taken from [10] and the parameters for the Sc atom were obtained reproducing the first two ionisation potentials

(IPs) of the Sc atom as well as the ground state and the inter-atomic distance of the ScO molecule (Table 3).

The calculated density of states (DOS) for the $BaTiO_3$ crystal is shown in Fig. 2, and it is in very good accordance with the X-ray photoelectron spectra measurements [19]. As it can be seen from the Fig. 2, the widths and compositions of the valence and conduction bands are reproduced very well. The chemical character of the lower valence band is mainly O 2s in nature while the upper valence band is predominantly O 2p in nature with a small admixture of Ti 3d AOs. The bottom of the conduction band is composed of Ti 3d states mainly with a small contribution of Ba 5s states.

In order to parameterise the Sc atom, we attempted to reproduce values for the IPs of the Sc atom and the inter-atomic distance in the ScO molecule. The results are presented in Table 3. The first ionisation potentials are in good agreement with the experimental data [27]. The INDO calculated bond length of the ScO molecule is 1.6682 Å in coincidence with the experimental data [28]. Besides, we managed to reproduce correctly the ground state of the ScO molecule: $^2\Sigma^+$.

3. Results and Discussion

3.1 Polaron configurations and lattice distortion in Al-doped crystal

When we substitute an Al atom for one of the Ti atoms, we find that the hole is trapped by two oxygens, O(1) and O(2) (Fig. 1a), situated at both sides of Al atom along the z-direction. This result is in accordance with the expectations since, as it was mentioned above, the Al-impurity has a negative effective charge with respect to the perfect crystal and acts as a trap for a positively charged hole. Therefore, the hole localisation on these two oxygen atoms has mainly electrostatic (Madelung) origin. It

is important to point out that O(1) and O(2) atoms are situated along the z-direction and the Al(7) atom is just between them. These results are in some accordance with another studies of Al-bound polaron [29], where the author found that the hole is trapped by two Al-closest oxygens. However, we do not observe two different ground state configurations of the polaron discussed in [29].

The automated geometry relaxation was carried out using the down hill simplex method in multidimentions as it is implemented in the AMOEBA subroutine [30]. Up to 32 atoms, situated around the impurity-atom, were allowed to move from their regular lattice sites but it resulted that only six Al-nearest O atoms change their position by non-negligible magnitude (Table 4). The details of the relaxation were the following: the O atoms lying in the x-y plane move towards the Al atom shifting at the same time slightly downwards with respect to the Al(7) atom by a small magnitude. The two oxygens situated along the z-axis move towards the Al(7) maintaining their original orientation. The atomic displacements are depicted in Fig. 1a. Finally, the Ti(8) atom is displaced outwards of the defective region by some negligible magnitude in comparison to the displacements of the six oxygens mentioned above. As it can be seen from the Table 4, the average magnitude of atomic relaxation is 1-2 % of the original inter-atomic distances in the perfect crystalline lattice. This result can be attributed to the relatively rigid lattice of the $BaTiO_3$ crystal.

3.2 Polaron configurations and lattice distortion in Sc-doped crystal

The results obtained for the $BaTiO_3$ crystal doped with one Sc atom were not very different from those obtained for the case of Al impurity. Similarly, the hole is

trapped by two oxygens, O(5) and O(6) (Fig. 1b), situated along the x-direction. The automated geometry relaxation was carried out for the six Sc-nearest O atoms and the Sc atom itself. We found that the O(1) and O(2) atoms move by 0.028 Å towards the impurity atom along the z-direction. Additionally, we observed a small rotation of four oxygens, O(3), O(4), O(5) and O(6), situated in the x-y plane by 0.8° (see Fig. 1b). However, it has to be noted that these atoms preserved their original distances with respect to the Sc atom. The rotation can be attributed to the Jahn-Teller effect [31], which reduces the total energy of the system by asymmetric displacements. This effect has already been observed in another polaron studies [32]. Finally, we have found a small outward shift of the Sc atom along the z-direction with respect to its original position in the perfect lattice, as it can be seen from the Table 5 and Fig. 1b.

3.3 Calculation of polaron absorption energy

The wave function of the ground state of Al-bound polaron is principally due to the $2p_z$ AO of O(1) and $2p_z$ AO of O(2) atoms, while in the case of Sc-bound polaron ground state we have the wave function composed of $2p_x$ AO of O(5) and $2p_x$ AO of O(6) atoms. The absorption energies of the polarons were studied using the ΔSCF method. This method works in the following way: we take one electron from one of the upper valence band states related to the oxygens which receive the hole and put it to an unoccupied one, which is the ground state of the polaron. Then the complete SCF solution is obtained using the density matrix of the ground state of the polaron as an initial guess. Finally, the absorption energy is computed as a difference of total energies of the system in the ground and excited states.

The ΔSCF calculations for the Al-bound polaron gave us the absorption energy of 0.27 eV for the transition to the exited state described by the wave function having contributions of $2p_y$ AO of O(2) and $2p_z$ AO of O(1) atoms mainly. This exited state was found to be degenerated, i.e., the computations show us that there is another excited state with the same energy but different AO coefficients (wave function): $2p_x$ AO of the O(2) and $2p_z$ AO of the O(1) atoms. In the case of the Sc-bound polaron, the absorption energies were the following: 0.62 eV if the wave function of the excited state is $2p_z$ AO of O(5) and $2p_z$ AO of O(6) atoms and 1.92 eV corresponding to the wave function of the excited state having contribution of $2p_y$ AO of O(5) and $2p_y$ AO of O(6) atoms.

4. Conclusions

We have carried out the theoretical quantum-chemical simulation of the BaTiO$_3$ crystal doped with Al and Sc impurity atoms. The modified for crystal investigation INDO method and the periodic LUC model was utilised. It was found for both type of impurities that the hole is trapped by two oxygens situated along a specific direction with the impurity atom being just between these two oxygens. The ASCF computed absorption energies were found to be 0.27 eV for the Al-bound polaron and 0.62 eV and 1.92 eV for the Sc-bound polaron, respectively. The excited state of the Al-bound hole polaron was found to be degenerated.

References

[1] K. Ueda, H. Yanagi, H. Honoso and H. Kawazoe, Phys. Rev. B 56 (1997) 12998.

[2] A. Sternberg, A. Spule, L. Shebanovs, E. Birks, H.W. Weber, H. Klima and F. Sauerzopf, Key Eng. Mater. 5 (1997) 132.

[3] U. van Stevendaal, K. Buse, S. Kämpar, H. Hesse and E. Krätzig, Appl. Phys. B 63 (1996) 315.

[4] H. Song, S.X. Dou, M. Chi, H. Gao, Y. Zhu and P. Ye, J. Opt. Soc. Am. B 15 (1998) 1329.

[5] D. Mahgerefteh and J. Feinberg, Modern Phys. Lett. B 5 (1991) 693.

[6] G. Rass, G. Montemezzani, P. Bernasconi and M. Zgonik, J. Appl. Phys. 79 (1996) 3665.

[7] J. Feinberg, D. Heiman, A. R. Tanguay Jr. and R.W. Hellwarth, J. Appl. Phys. 51 (1980) 1297.

[8] J. Feinberg, J. Opt. Soc. Am. 72 (1982) 46.

[9] E.V. Stefanovich, E.K. Shidlovskaya, A.L. Shluger and M.A. Zakharov, Phys. Status Solidi B 160 (1990) 529.

[10] P. W. M. Jacobs, E. A. Kotomin, A. Stashans, E. V. Stefanovich and I. Tale, J. Phys.: Condens. Matter 4 (1992) 7531.

[11] Yu.F. Zhukovskii, E.A. Kotomin, R.M. Nieminen and A. Stashans, Comput. Mater. Sci. 7 (1997) 285.

[12] L. Kantorovich, A. Stashans, E. Kotomin and P. W. M. Jacobs, Int. J. Quant. Chem. 52 (1994) 1177.

[13] E. A. Kotomin, I. Tale, V. Tale, P. Butlers and P. Kulis, J. Phys.: Condens.

Matter 1 (1989) 6777.

[14] P. Kulis, Z. Rachko, M. Springis, I. Tale and J. Jansons, Rad. Eff. Defects Solids 119-121 (1991) 963.

[15] A. Stashans, S. Lunell, R. Bergström, A. Hagfeldt and S.-E. Lindquist, Phys. Rev. B 53 (1996) 159.

[16] S. Lunell, A. Stashans, L. Ojamäe, H. Lindström and A. Hagfeldt, J. Am. Chem. Soc. 119 (1997) 7374.

[17] R. I. Eglitis, A. V. Postnikov and G. Borstel, Phys. Rev. B 54 (1996) 2421.

[18] E. A. Kotomin, N. E. Christensen, R. I. Eglitis and G. Borstel, Comput. Mater. Sc. 10 (1998) 339.

[19] P. Pertosa and F.M. Michel-Calendini, Phys. Rev. B 17 (1978) 2011.

[20] J. Pople and D. Beveridge, Approximate MO Theories (McGraw-Hill, New York, 1970).

[21] A. Shluger and N. Itoh, J. Phys.: Condens. Matter 2 (1990) 4119.

[22] A. Stashans, E. Kotomin and J.-L. Calais, Phys. Rev. B 49 (1994) 14854.

[23] E.A. Kotomin, A. Stashans, L.N. Kantorovich, A.I. Lifshitz, A.I. Popov and I.A. Tale, Phys. Rev. B 51 (1995) 8770.

[24] A. Stashans, S. Lunell and R.W.Grimes, J. Phys. Chem. Solids 57 (1996) 1293.

[25] R.A. Evarestov, Quantum-Chemical Methods of Solid State Theory (Leningrad State University Press, Leningrad, 1982).

[26] A. Shluger and V. Stefanovich, Phys. Rev. B 42 (1990) 9664.

[27] CRC Handbook of Chemistry and Physics, R. C. Weast, Ed. (CRC Press, Boca Raton, Florida, 1979).

[28] K.P. Huber, G. Herzberg, Molecular Spectra and Molecular Structure, Constants of Diatomic Molecules (Van Nostrand, Princeton, 1979).

[29] H. Donnerberg, Mater. Sci. Forum 239-241 (1997) 341.

[30] W.H.Press, B.P. Flannery, S.A. Teukolsky and T. Vetterling, Numerical

Recipes: The Art of Scientific Computing (Cambridge University Press, New

York, 1986).

[31] R. Englman, Jahn-Teller Effect in Molecules and Crystals (Wiley, New York,

1972).

[32] Yu.F. Zhukovskii, E.A. Kotomin, R.M. Nieminen and A. Stashans, Comput.

Mater. Sci. 7 (1997) 285.

Table 1

Semi-empirical INDO parameter sets used in the present work: ζ (au), E_{neg} (eV), P^0 (*e*) and β (eV).

Atom	AO	ζ	E_{neg}	P^0	β
Ba	6s	1.65	6.2	0.2	-0.4
	5p	2.8	34.6	2.0	-4.0
Ti	4s	1.4	3.7	0.65	-0.5
	4p	1.1	-15.0	0.04	-0.5
	3d	1.93	7.2	0.55	-9.0
O	2s	2.27	4.5	1.974	-16.0
	2p	1.86	-12.6	1.96	-16.0
Al	3s	1.6	17.15	0.71	-1.5
	3p	1.5	12.5	0.39	-1.5
Sc	4s	1.03	14.1	0.04	-1.0
	3p	2.8	36.8	2.0	-0.5
	3d	1.95	13.9	0.14	-8.0

Table 2

Semi-empirical INDO two-centre parameters α_{mB} (au^{-1}) optimised during the calculations, mth AO belongs to the atom A, where A≠B.

A	B				
	Ba	Ti	O	Al	Sc
Ba	0.20	0.1	0.57	0.0	0.0
Ti	0.53	0.13	0.38	0.0	0.0
O	0.36	0.10	0.15	0.0	0.05
Al	0.0	0.0	0.3	0.05	0.0
Sc	0.0	0.0	0.89	0.0	0.0

Table 3

Calculated Sc ionisation potentials (in eV) in comparison to the experimental data [28].

	INDO results	Exp. data
1st IP	6.48	6.54
2nd IP	15.66	12.8

Table 4

Atomic coordinates and displacements, Δr, (in Å) for the Al-bound polaron in the defective region obtained by the automated geometry optimisation. A "+" sign denotes displacements of the atoms towards the polaron while a "-" sign means displacements in the opposite direction. The atomic numeration corresponds to the one in the Fig. 1a.

Atom	Coordinate	Perfect crystal	Defective crystal	Δr
O(1)	x	2.005	2.005	-0.072
	y	2.005	2.005	
	z	4.017	3.945	
O(2)	x	2.005	2.005	-0.072
	y	2.005	2.005	
	z	0.000	0.071	
O(3)	x	2.005	2.005	-0.073
	y	4.017	3.943	
	z	2.005	2.005	
O(4)	x	2.005	2.005	-0.073
	y	0.000	0.073	
	z	2.005	2.005	
O(5)	x	0.000	0.073	-0.073
	y	2.005	2.005	
	z	2.005	2.005	
O(6)	x	4.017	3.943	-0.073
	y	2.005	2.005	
	z	2.005	2.005	
Al(7)	x	2.005	2.005	+0.004
	y	2.005	2.005	
	z	2.005	2.000	
Ti(8)	x	2.005	2.005	+0.012
	y	2.005	2.005	
	z	6.026	6.038	

Table 5

Atomic coordinates, displacements, Δr, (in Å) and rotational angles, α, (in degrees) for the Sc-bound polaron in the defective region obtained by the automated geometry optimisation. A "+" sign denotes displacements of the atoms towards the polaron while a "-" sign means displacements in the opposite direction. The atomic numeration corresponds to the one in the Fig. 1b.

Atom	Coordinate	Perfect crystal	Defective crystal	Δr	α
O(1)	x	2.005	2.005	-0.028	0.0
	y	2.005	2.005		
	z	4.017	3.988		
O(2)	x	2.005	2.005	-0.028	0.0
	y	2.005	2.005		
	z	0.000	0.028		
O(3)	x	2.005	2.036	0.000	0.8
	y	4.017	4.017		
	z	2.005	2.005		
O(4)	x	2.005	1.980	0.000	0.8
	y	0.000	0.000		
	z	2.005	2.005		
O(5)	x	0.000	0.000	0.000	0.8
	y	2.005	2.036		
	z	2.005	2.005		
O(6)	x	4.017	4.017	0.000	0.8
	y	2.005	1.980		
	z	2.005	2.005		
Sc(7)	x	2.005	2.005	+0.004	0.0
	y	2.005	2.005		
	z	2.005	2.001		

Figure captions

Fig. 1. The atomic displacements in the 40-atom LUC around the polaron: a) Al-bound polaron structure, six Al-nearest O atoms and one Ti(8) atom are allowed to move, the hole is localised on the O(1) and O(2) atoms along the z-direction; b) Sc-bound polaron structure, the rotations of O(3), O(4), O(5) and O(6) atoms situated in the x-y plane are shown, the O(1) and O(2) atoms move towards the Sc atom position, the hole is localised on O(5) and O(6) atoms along the x-direction.

Fig. 2. The total density of states (DOS) for the $BaTiO_3$ crystal obtained by the LUC computations.