



Quantum-chemical studies of Nb-doped CaTiO_3

F. ERAZO† and A. STASHANS

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

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ABSTRACT

There exists experimental evidence that several properties of the CaTiO_3 crystal, such as electrical conductivity and ferroelectricity, strongly depend on the Nb doping. In particular, if the concentration of Nb impurities is sufficiently high, a drastic increase in the electrical conductivity is observed. A supercell model and periodic quantum-chemical calculation scheme are used to study pure and Nb-doped crystals. The geometry optimization is carried out in order to find the equilibrium spatial structures of both cubic and orthorhombic phases, as well as to predict the most stable configurations of the Nb atom in these crystalline lattices. The obtained relaxation energies of 3.83 eV for the cubic phase and 15.04 eV for the orthorhombic phase are discussed, and their difference is explained. The composition of the electronic energy bands is analysed in comparison with the available experimental data. The increase in the electrical conductivity in the Nb-doped material for the orthorhombic phase is proved.

§1. INTRODUCTION

The increase in scientific research of the perovskite-type titanates since the discovery of ferroelectricity in BaTiO_3 crystal in the 1940s is astonishing. Because of their unusual properties the titanates have opened another alternative in the scientific investigation and industrial application of ceramic materials. The understanding of the chemical state of dopants and their spatial configurations is one of the most important subjects in the science and technology of these materials. The electronic state of dopants in oxide ceramics is considerably more complicated than those in semiconductors. The complex behaviour originates from various charged dopants in these oxides, which easily cause polarization as a result of lattice distortion. Despite the considerable efforts made to investigate titanates with perovskite structures such as CaTiO_3 (Kim *et al.* 1992, Ueda *et al.* 1997), SrTiO_3 (Choi *et al.* 1986, Komornichi *et al.* 1990) and BaTiO_3 (Chan *et al.* 1982, Motohira *et al.* 1996), the theoretical basis of carrier generation and behaviour in these materials has not been definitely elucidated so far.

The crystal structure of CaTiO_3 is not an ideal cubic perovskite type but has orthorhombic distortions because the ionic radius of a Ca ion is smaller than that of Sr and Ba ions. Because of its complicated structure and slightly less practical importance, only a few studies have been reported on the electronic structure of this material (Ueda *et al.* 1997, 1999). We have to note, however, that this crystal has some very important applications. CaTiO_3 is one of the important constituents

†Email: corp-ffa@yahoo.com

for the disposal of high-level radioactive waste materials (McCarthy 1977, Arita *et al.* 1997); it is also utilized in the construction of field devices and sensors for the study of the rheology of the interior mantles of the Earth (Li *et al.* 1996). Recently, little experimental work has been done to study carrier generation mechanisms in Y- and Nb-doped CaTiO_3 monocrystals (Ueda *et al.* 1997, 1999). These measurements indicate the drastic increase in the conductivity if the impurity concentration is very high. Furthermore, two broad bands were observed above the Fermi level using inverse photoemission spectroscopy and X-ray absorption spectroscopy (Ueda *et al.* 1998). These experimental results strongly motivated us to perform the present quantum-chemical computations of Nb impurities in CaTiO_3 crystal in order to calculate the equilibrium geometry and lattice distortion as well as to establish the influence of Nb impurities upon the electronic band structure of the crystal. The studies at a microscopic level might provide some answers on the unusual electrical properties of Nb-doped CaTiO_3 crystals.

§ 2. THEORETICAL METHOD

The quantum-chemical semiempirical method based on the intermediate neglect of differential overlap approach has been used in the present work. This approach is based on the molecular orbital theory (Pople and Beveridge 1970). The method as implemented in the CLUSTERD computer code (Stefanovich *et al.* 1990) has been developed especially for crystals, that is periodic system calculations. Owing to its semiempirical character and specific parametrization scheme (Shluger 1985), CLUSTERD is not cumbersome and time consuming in the treatment of the electronic and spatial structure of complex systems, especially with mixed ionic-covalent chemical bonding, such as in oxide crystals. The computer code allows one to study large systems which are not accessible by the periodic non-empirical methods. The method has been used successfully in recent years for defect calculations in oxide crystals, including SiO_2 (Shluger and Stefanovich 1990), $\alpha\text{-Al}_2\text{O}_3$ (Jacobs and Kotomin 1992, Jacobs *et al.* 1993), TiO_2 (Lunell *et al.* 1997) and WO_3 (Stashans and Lunell 1996).

In particular, the method has an important advantage of geometry predictions for crystals doped with point defects and impurity atoms (Jacobs *et al.* 1992, Stashans *et al.* 1994, Kotomin *et al.* 1995). Because of the very precise geometry reproduction some fundamental problems concerning Li intercalation in TiO_2 crystals were successfully resolved (Stashans *et al.* 1996a, Lunell *et al.* 1997). 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, that is it is obtained in the self-consistent field (SCF) manner. This leads to reliable information about the defect influence upon the electronic band-structure properties. The method also allows one to calculate with reasonable precision the excited state of the system, thus giving information about defect contribution into the absorption spectra of the crystal (ΔSCF method).

We have utilized the periodic large-unit-cell (LUC) model (Shluger and Stefanovich 1990). This model is free from the limitations of different cluster approaches applicable mainly to materials with a wide bandgap and having fully ionic chemical bonding. The basic idea of the LUC is in computing the electronic structure of the unit cell extended in a special manner at $\mathbf{k} = \mathbf{0}$ in the reduced Brillouin zone (BZ). This is equivalent to a band-structure calculation at those \mathbf{k}

points, which transform to the BZ centre on extending the unit cell (Evarestov and Lovchikov 1977). The total energy of the crystal is

$$E_{\text{LUC}} = \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}^{00}} + \frac{1}{2} \sum_{A \in \text{LUC}} E_C^A + \sum_j \varepsilon_j(0) + \frac{1}{2} \sum_{\mu, \nu \in \text{LUC}} \rho_{\mu, \nu}(0) Q_{\mu\nu}, \quad (1)$$

where $\varepsilon_j(\mathbf{k})$ are the eigenvalues of the Fock matrix occ is the number of occupied electronic states in the system, $\rho_{\mu, \nu}(\mathbf{k})$ are the density matrix elements in the basis of the Bloch combinations of atomic orbitals (AOs):

$$E_C^A = Z_A \sum_{l \neq 0} \sum_{B \in \text{LUC}} \left(\frac{Z_B}{R_{AB}^{01}} - \sum_{\mu \in B} \rho_{\mu\mu}(0) (\nu^{A0})_{\mu\mu}^{ll} \right), \quad (2)$$

$$Q_{\mu\nu} = T_{\mu\mu}^{00} - \sum_{A \in \text{LUC}} Z_A (\nu^{A0})_{\mu\mu}^{00} + \sum_{i \neq 0} H_{\mu\mu}^{01}, \quad \text{if } \mu = \nu, \quad (3)$$

$$Q_{\mu\nu} = \sum_i H_{\mu\nu}^{01}, \quad \text{if } \mu \neq \nu, \quad (4)$$

where $T_{\mu\mu}^{00}$ are the matrix elements of the kinetic energy operator, $(\nu^{A0})_{\mu\mu}^{ll}$ are those of the electron–core interaction operator, R_{AB}^{01} is the distance between the cores of atoms A and B, and Z_A and Z_B are the charges of these cores.

The total energy equation (1) is obtained after the introduction of the ‘cut-off function’

$$\omega(r_{\mu\nu}) = \frac{P_{\mu\nu}^{01}}{\rho_{\mu\nu}(0)}, \quad (5)$$

which is possible because of the fast decrease of the overlap integral $S_{\mu\nu}^{01}$ with the interatomic distance $r_{\mu\nu}$. We can also note that the Coulomb interaction is treated very precisely in the LUC model because of the theory of special \mathbf{k} points. Thus this model can be applied to any non-metallic crystal, including semiconductors (Moliver 1992, Stashans and Kitamura 1997). This theoretical model has been recently used with success also for point-defect computations in perovskite-type ceramics. Examples include the modelling of phase transition in KNbO₃ crystals (Eglitis *et al.* 1996) and impurity-doping studies in BaTiO₃ crystals (Pinto and Stashans 2000).

§ 3. RESULTS AND DISCUSSION

3.1. Advanced parametrization of a pure CaTiO₃ crystal and Nb atom

The parametrization procedure is of fundamental importance since it is the basis of success in semiempirical calculations. We have used the supercell model based on the LUC approach to parametrize the CaTiO₃ crystal and later to study Nb doping in this system. 80-atomic LUCs for both crystalline lattices were utilized, which were equivalent to a 16-times ($4 \times 2 \times 2$) extension of the primitive five-atom cubic unit cell and a four times ($2 \times 2 \times 1$) extension of the primitive 20-atom orthorhombic unit cell. The electronic energy bands were computed in the SCF manner including valence electrons only, that is the following AOs were taken: O 2s, O 2p, Ti 3d, Ti 4s, Ti 4p, Ca 4s and Ca 3p. We considered that it was essential to include the Ca 3p states as the basis AOs within the valence basis set since their overlap with AOs of the other atoms is not negligible. The semiempirical parameters of the Ca 4s and 3p AOs were

obtained in this work, while we used already existing parameters for O2s and 2p (Stefanovich *et al.* 1990) and Ti 3d, 4s and 4p AOs (Stashans *et al.* 1996b).

As a result for the cubic structure we obtained the lower valence band composed mainly of O2s AOs and the upper valence band (UVB) made up of O2p AOs. The subband of Ca 3p AOs was found just between these two valence bands. The lower part of the conduction band (CB) was mainly Ti 3d in nature with some admixture of Ca 4s states. Similar results were obtained for the orthorhombic structure, although in the latter case a noticeable admixture of Ti 3d AOs in the UVB and O2p AOs in the CB was observed. This indicates the hybridization between Ti 3d and O2p states, which is normal owing to the phase transition from cubic to orthorhombic. In general, our results on the electronic band structure are in very good agreement with the experimental data (Ueda *et al.* 1998, 1999), especially for the orthorhombic crystalline lattice. This is understandable since the majority of the experimental results are just for the orthorhombic structure, which is more stable and is observed only below approximately 1533 K (King-Smith and Vanderbilt 1994). It can be noted that, at temperatures between 4.2 and 300 K, CaTiO₃ has been classified as an incipient ferroelectric or a quantum paraelectric (Lemanov *et al.* 1999). During our periodic quantum-chemical parametrization we managed to reproduce completely the geometry of both crystalline lattices. The obtained lattice parameters $a = 3.78 \text{ \AA}$ for the cubic lattice and $a = 5.28 \text{ \AA}$, $b = 5.35 \text{ \AA}$ and $c = 7.51 \text{ \AA}$ for the orthorhombic lattice are very close to the experimental data (Wyckoff 1960): $a = 3.84 \text{ \AA}$ for the cubic lattice and $a = 5.37 \text{ \AA}$, $b = 5.44 \text{ \AA}$ and $c = 7.64 \text{ \AA}$ for the orthorhombic lattice.

In order to obtain the parameter set for the Nb atom, we reproduced the ground state and interatomic distance of the NbO molecule as well as the ground state and the first ionization potential of the Nb atom (table 1). The parameters thus obtained are shown in tables 2 and 3.

3.2. Geometry of cubic phase of CaTiO₃:Nb

In order to study the Nb atom impurity in the cubic lattice of the CaTiO₃ crystal we used the 80-atom LUC and in the central region of the LUC made the following substitution: Nb \rightarrow Ti. Since the Ti atom has four valence electrons and the Nb atom has five valence electrons, with this substitution we obtain one extra electron in the system. Owing to the impurity insertion, which is a considerable perturbation for the otherwise perfect crystalline lattice, one can anticipate atomic displacements, which would reduce the total energy of the LUC. Different kinds of atomic relaxation were considered, which included both symmetric and antisymmetric atomic displacements. As a result we obtained the spatial configuration, which in equilibrium

Table 1. Calculated properties of the Nb atom and the NbO molecule in comparison with the available experimental data. The experimental data are taken from Weast (1979) for the Nb atom and from Huber and Herzberg (1979) for the NbO molecule.

Property	Quantum-chemical calculations	Experimental data
Nb atom ground state	Kr ₃₆ , 4d ⁴ 5s ¹	Kr ₃₆ , 4d ⁴ 5s ¹
Nb atom first ionization potential (eV)	6.28	6.77
NbO molecule ground state	⁴ Σ ⁻	⁴ Σ ⁻
NbO molecule interatomic distance (Å)	1.71	1.69

Table 2. Semi-empirical parameter sets for Ca, Ti, O and Nb atoms.

Atom	AO	ζ (au)	E_{neg} (eV)	$-\beta$ (eV)	P^0 (e)
Ca	4s	1.48	14.0	0.4	0.15
	3p	2.80	42.5	3.0	2.00
Ti	4s	1.40	3.7	0.5	0.65
	4p	1.00	-15.0	0.5	0.04
	3d	1.93	7.2	9.0	0.55
O	2s	2.27	4.5	16.0	1.974
	2p	1.86	-12.6	16.0	1.96
Nb	5s	1.55	24.5	0.5	0.8
	5p	1.40	2.0	0.5	0.01
	4d	1.35	23.7	8.0	0.117

Table 3. Two-centre parameters $\alpha_{\mu B}$ where $\mu \in A$.

A	$\alpha_{\mu B}$ (au ⁻¹)			
	B \equiv Ca	B \equiv Ti	B \equiv O	B \equiv Nb
Ca	0.15	0.55	0.18	0.10
Ti	0.07	0.13	0.10	0.03
O	0.57	0.37	0.15	0.45
Nb	0.20	0.05	0.10	0.00

includes two kinds of impurity-surrounding atom movements. The six Nb-neighbouring O atoms approach the impurity by 0.23 Å along the $\langle 100 \rangle$ directions. This corresponds to a reduction in the initial interatomic distance (equal to 1.89 Å) by 12.4%. This geometry relaxation gives a 2.62 eV contribution to the total relaxation energy, which is equal to 3.83 eV (table 4). The eight Ca atoms closest to Nb move the impurity outwards along the directions $\langle 111 \rangle$ by 0.03 Å. This corresponds to an increase in the initial interatomic distance between Nb and Ca atoms (equal to 3.27 Å) by 1.0%. The contribution to the total relaxation energy of this kind of atomic movement is equal to 1.21 eV or 31.6% (see table 4). We intended to change the atomic positions in different asymmetric ways but did not succeed in reducing the system's total energy. Obviously, only a symmetric type of atomic displacement occurs in the cubic lattice of the Nb-doped CaTiO₃ crystal. It should be noted that, in general, atomic movements are in accordance to the Coulomb law since the Nb atom has a larger positive charge than the Ti atom for which it substitutes ($q(\text{Nb}) = 3.09e$; $q(\text{Ti}) = 2.18e$).

Table 4. Contributions to the relaxation energy by the O atoms, $E(\text{rel-O})$, and the Ca atoms, $E(\text{rel-Ca})$, in the Nb-doped CaTiO₃ cubic phase.

Type of relaxation energy	Value of partial relaxation energy (eV)	Contribution of the partial relaxation energy (%)
$E(\text{rel-O})$	2.62	68.4
$E(\text{rel-Ca})$	1.21	31.6

3.3. Geometry of the orthorhombic phase $\text{CaTiO}_3:\text{Nb}$

The atomic relaxation in the orthorhombic phase was carried out in a similar manner to that in the cubic phase. We substituted one of the Ti atoms situated in the middle of the 80-atom LUC by a Nb atom. Different kinds of relaxation were considered. As a result we came to the conclusion that three types of atomic displacement have a non-negligible contribution to the relaxation energy. Firstly, the O atoms closest to Nb (figure 1) move towards the impurity by 0.06 \AA , which is 3.4% if the initial distance and on average is equal to 1.89 \AA . These movements are along the $\langle 111 \rangle$ directions. Secondly, six Ca atoms closest to Nb move away from the impurity by 0.18 \AA . One of these atoms is considerably closer to the impurity than the others, although it moves in a similar manner to the others. This corresponds to an increase in the Nb–Ca distance by 5.7% of the initial distance (3.10 \AA). The displacements of the Ca atoms are along the $\langle 011 \rangle$ and $\langle 111 \rangle$ directions. Finally, the three Ti atoms closest to Nb located at an average initial distance of 3.75 \AA also move away from the impurity by 0.07 \AA , which corresponds to an increase in the Nb–Ti distance by 1.8%. The displacements of the Ti atoms are along the $\langle 110 \rangle$ and $\langle 001 \rangle$ directions. All three types of atomic relaxation occur in accordance with the Coulomb law, that is the negative O atoms move towards the positively charged Nb atom, and the positive Ca and Ti atoms move away from the impurity (see figure 1).

As follows from table 5, the total relaxation energy is equal to 15.04 eV , which is considerably greater than in the cubic lattice. The orthorhombic structure is more

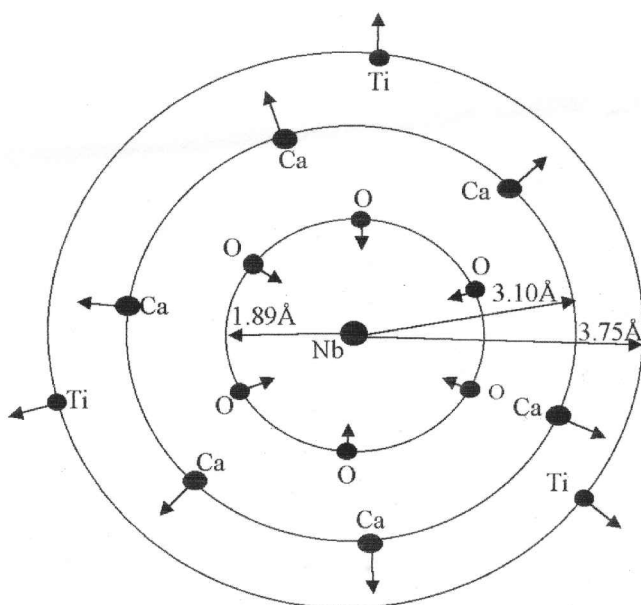


Figure 1. A schematic diagram of the atoms closest to Nb in the orthorhombic CaTiO_3 crystal. The impurity has six neighbouring O atoms at an average distance equal to 1.89 \AA , which showed as a first sphere of atoms. The next-neighbour Ca atoms are situated at average distance of 3.10 \AA . They are also six in number and are showed as a second atomic sphere. Finally, there are three Ti atoms located at average distance of 3.75 \AA ; they form the third atomic sphere. The O atoms move towards the Nb impurity while the Ca and Ti atoms move away from the Nb impurity, which has a positive effective charge with respect to the perfect crystalline lattice.

Table 5. Contributions to the relaxation energy by the O atoms, $E(\text{rel-O})$, the Ca atoms, $E(\text{rel-Ca})$, and the Ti atoms, $E(\text{rel-Ti})$, in the Nb-doped CaTiO₃ orthorhombic phase.

Type of relaxation energy	Value of partial relaxation energy (eV)	Contribution of the partial relaxation energy (%)
$E(\text{rel-O})$	3.67	24.4
$E(\text{rel-Ca})$	11.24	74.7
$E(\text{rel-Ti})$	0.13	0.9

densely packed than the cubic structure. Therefore, the insertion of the Nb impurity creates a larger perturbation in the orthorhombic phase and as a result a large magnitude of the relaxation energy. Additionally, one can see that Ca atoms contribute most to the relaxation energy. This is because of the electron transfer from the Nb atom to the conduction band and, in particular, to the Ca atoms of the second atomic sphere (see figure 1), which occurs only in the orthorhombic phase.

3.4. Effect of Nb doping upon the CaTiO₃ electronic band structure

The effects of the Nb atom upon the CaTiO₃ electronic band structure are without doubt very different for two crystalline lattices. In the case of the cubic lattice, we find the local one-electron energy level between the top of the UVB and the CB, which is mainly composed of the Nb 5s AO. During the geometry optimization this level tends to fall into the UVB.

In the case of the orthorhombic structure, we observe that the electron from this local energy level transfers to the CB. This can be deduced from the occurrence of the Ca 4s and Ti 3d states in the UVB. The extra electron mainly is ‘absorbed’ by 4s AOs of the Ca atoms of the second sphere, although some of it transfers to 3d AOs of Ti atoms from the third sphere (see figure 1). Obviously, this forced electron transfer from the Nb local energy level to the CB is connected with the crystal lattice symmetry since we do not observe this phenomenon in the cubic structure. The consequence of this effect is the occurrence of free electrons in the CB, which increases the electrical conductivity. This effect has indeed been observed in a number of experimental studies (Ueda *et al.* 1997, 1998), when the Nb impurity concentration is high. It can be noted that, in explaining the inverse photoemission spectroscopy results, Ueda *et al.* (1998) came to the conclusion that the origins of the two energy peaks are Ti 3d and Ca 4s. Our results confirm this explanation.

§4. CONCLUSIONS

The present periodic quantum-chemical calculation evaluate the structural and electronic properties of the Nb-doped CaTiO₃ crystal in two known phases, cubic and orthorhombic. The obtained equilibrium spatial configurations favour symmetric atomic movements in the defective region. The obtained relaxation energies are equal to 3.83 eV and 15.04 eV for the cubic and orthorhombic phases respectively. This indicates that the orthorhombic lattice is more compact and the Nb impurity presents a major perturbation there as in the case of the cubic lattice. This leads to a large magnitude of the relaxation energy.

There are also considerable differences in the way in which the Nb atom influences the band structure of the two phases. While for the cubic crystal we do not find

any unusual features, the transfer of an extra electron from the local energy level within the bandgap to the CB is found for the orthorhombic crystal. This explains the increase in the electrical conductivity observed in a number of experimental studies (Ueda *et al.* 1997, 1998).

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