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Computational Studies and Comparison of Nb- and La-Doped $SrTiO_3$

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Motivated by the discovery of the superconductivity in strontium titanate doped with a small number of electron carriers, we have performed quantum-chemical Hartree–Fock calculations to study La- and Nb-doped $SrTiO_3$. The crystalline lattice distortion due to these impurities is obtained for both cubic and tetragonal structures, which shows considerable differences for atomic displacement in the defect-surrounding region for two crystallographic phases. La- and Nb-induced local energy levels are found in the gap between the upper valence band and the conduction band. Electron transfer effects from the local energy levels to the conduction band are observed when the tetragonal $SrTiO_3$ crystal is doped with the La impurity.

Introduction It is important to study matter at the nanometric scale for modern high-technology applications. Crystalline form of nanowires and nanotubes can be studied by both experimental and theoretical approaches. However, the importance of knowing the fundamental physics laws, which govern behaviour of the crystals used in the industry, cannot be neglected. So, the fundamental, quantum-mechanical methods are of primary significance. The perovskites are an extremely important class of ceramic materials and the strontium titanate ($SrTiO_3$) is one of the most widely used electronic ceramic materials, which has a perovskite-type structure. Its typical application is use as a grain-boundary barrier layer capacitor [1], oxygen-gas sensor [2], and epitaxial growth substrate for the high-temperature superconductor thin films [3] as well as catalytic material [4]. La- and Nb-doped $SrTiO_3$ not only is used as a substrate for thin-film deposition of high-T_c superconductors and ferroelectrics but also has a fundamental interest since stoichiometric $SrTiO_3$ is highly insulating, but a slightly reduced compound shows superconductivity.

Behaviour of the doping carriers has been long studied in the perovskites in order to understand rich variations in physical properties due to the impurity doping. $SrTiO_3$ is known to become superconducting when a small number of electron carriers are added by La substitution for a Sr atom [5], and Nb substitution for a Ti atom [6]. The better understanding of effects produced by the impurity doping in $SrTiO_3$ could be of help in high-technology applications of this material.

By means of the modified for crystals quantum-chemical method and using the periodic Large Unit Cell (LUC) model [7], we have modelled the La and Nb doping in the cubic and tetragonal crystalline lattices of $SrTiO_3$. The work has been carried out in a way to analyse the properties of the cubic (paraelectric) phase versus tetragonal (ferroelectric) phase that becomes superconducting after doping.

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Method The modified for crystals quantum-chemical method as it is implemented into the CLUSTERD computer code [7] is based on Molecular Orbital (MO) theory and uses a number of semi-empirical parameters, which approximate some two-centre integrals in the Hartree-Fock self-consistent-field procedure. We use a periodic supercell model based on the LUC approach. The LUC (i) takes into account explicitly the periodicity of a crystal under study, and (ii) considers completely the exchange interaction. The basic mathematical equations of the model are given in [7]. We have to note that the model has been proved to be a very powerful tool in a number of studies (see [8–11] and references therein) on perfect and defective crystals.

The parameter set for the O atom was taken from Ref. [7] whereas the one for the Ti atom was taken from Ref. [12]. The parameter set for the Sr atom was obtained by reproducing the electronic band structure and spatial properties of the $SrTiO_3$ crystal for both cubic and tetragonal phases, as well as the basic features of the Sr atom and the SrO molecule. The numerical parameters of the Sr atom as well as the La atom are described in detail in Ref. [12]. Finally, the parameter set for Nb was taken from Ref. [13].

Results and Discussion If one Nb atom in the LUCs of 40 and 135 atoms substitutes for one of the Ti atoms than the number of valence electrons increases by one. This produces charge redistribution in the defective region leading to the displacements of the Nb-surrounding O and Sr atoms. As it is known, the directions $\langle 100 \rangle$ and $\langle 010 \rangle$ are completely equivalent due to the symmetry of the cubic and tetragonal phases of the crystal. As a result for the tetragonal phase the atomic displacements were found to be the same, 0.06 Å for the Sr atoms in the *xy*-plane under the impurity and 0.11 Å for the Sr atoms in the plane above it. The calculated movements of O atoms are 0.05, 0.07 and 0.08 Å, respectively, depending on their relative position with respect to the impurity (see Fig. 1). The geometry optimisation was performed taking into account the fact that the tetragonal phase of the crystal presents a ferroelectric behaviour. This implies the presence of a spontaneous electric dipole along the *z*-axis, which might change due to the doping. As a consequence the ferroelectricity influences atomic movements along the *z*-axis for both kinds of atoms. We have found that the Sr and O atoms have opposite displacements along the ferroelectric axis, which evidences a local change in the electric dipole moment of the crystal due to the impurity presence. The calculated lattice relaxation in the cubic phase of Nb-doped $SrTiO_3$ shows a pattern of completely symmetric atomic movements.

In calculation of the La-doped $SrTiO_3$, the LUCs of 40, 80 and 160 were used and two La atoms producing two different system states substituted two of the Sr atoms. The singlet state corresponds to the case when two extra electrons occupy the same local energy level within the band gap and the triplet state is considered when two electrons occupy two different local energy levels.

Our studies of the La-doped cubic phase reveal that the inclusion of La causes a reduction in the symmetry of the system. Our studies also show that the singlet state is energetically more favourable than the triplet state. In the tetragonal phase we observe that the most favourable energy configuration for the singlet state is obtained when the La atoms are situated along the $\langle 011 \rangle$ direction [14]. The important outcome of our computations is the observation of the extra electron transfer from the local energy level within the band gap to the conduction band. This occurs only in the triplet state

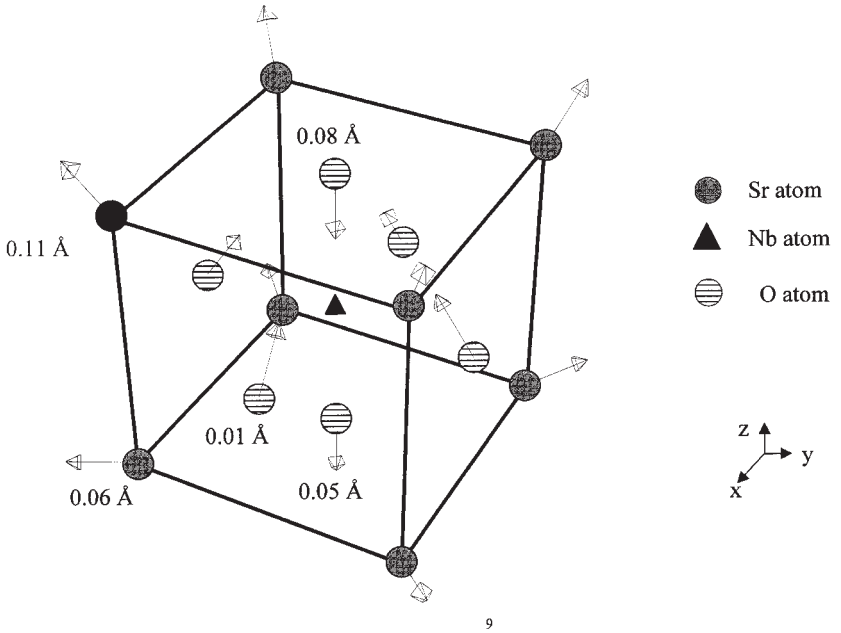

Fig. 1. Relaxation of the Nb-closest atoms in the tetragonal $SrTiO_3$ crystal. The numbers describe displacements of the same kind of atoms within the same plane

of the tetragonal phase. This indicates that just the triplet state of the system is responsible for producing free electrons in the conduction band of the material and promoting the superconductivity in accordance with the experimental data [5]. It is important to mention that the impurity concentration ($x = 0.0625$) in our studies is very close to the one used in the experiments ($x = 0.05$) [5].

Conclusions The results obtained by the advanced quantum-chemical method based on the Hartree-Fock theory show that the La impurity in the $SrTiO_3$ crystal promotes different lattice relaxation for the cubic and tetragonal phases, respectively. When two La atoms replace for two Sr atoms, two different system states occur resulting in two local energy peaks within the band gap in agreement with the available experimental data [5]. For some arrangements of the two La atoms in the triplet state of the tetragonal phase [14], the two extra electrons jump from the local energy level within the band gap to the conduction band contributing into the superconductivity of this material. The electrons, which transfer to the conduction band, are found to be related with the AOs of the Ti atoms that form Ti–O planes. So, we can conclude that superconductivity are mainly promoted within the Ti–O planes. In both cases, La- and Nb-doping, one can see peculiar atomic distortions along the z-axis pointing to the presence of the ferroelectricity in the tetragonal phase of this material.

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