

Quantum-chemical study of photo-excited states in tetragonal SrTiO₃ lattice

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ABSTRACT

The nature of photo-excited states in SrTiO₃ has been a topic of intense debate during the last few decades. Using a quantum-chemical method developed for crystals, we present a theoretical interpretation of the structural and electronic properties of triplet excitons in the tetragonal SrTiO₃ crystal. Our study demonstrates that the defect structure may correspond to the Mott-Wannier-type exciton having a considerable distance, 2.14 Å, between the hole and the electron parts of the defect. The geometry optimization leads to an extensive defective region containing up to five atoms. However, the obtained magnitudes of atomic movements do not exceed 0.15 Å. It is also observed that the self-trapped exciton polarizes the lattice around it. Using the so-called (Δ SCF method, the luminescence energy due to the exciton is found to be equal to 1.13 eV. As it corresponds to the infrared part of the spectrum, the experimentally detected green luminescence due to photo-excited states should be attributed to the singlet excitons.

§1. INTRODUCTION

The primitive unit cell of strontium titanate (SrTiO₃) contains five atoms (Wyckoff 1960) similar to other perovskite-type crystals. The structure of SrTiO₃ has simple cubic symmetry, which transforms to the tetragonal symmetry below 105 K. This corresponds to the transition from paraelectric phase to ferroelectric phase. The static dielectric constant increases extraordinarily when the temperature decreases, and it is stabilized at over 10⁴ below 10 K without a ferroelectric phase transition (Müller and Burkard 1979). This property is known as quantum paraelectricity (QPE). The nature of QPE has not yet been revealed (Hasegawa *et al.* 2000). Despite the fact that many studies have been carried out so far on this ferroelectric material, there is still not sufficient understanding of the nature of many properties and phenomena in SrTiO₃. On the other hand, it is well understood that point defects play an important role in many applications of the SrTiO₃ crystal and, therefore, further studies are necessary on this subject. One of the most common defects in non-metallic crystals is the so-called exciton. Hasegawa *et al.* (2000) conclude that the time-resolved luminescence spectra decay profile for SrTiO₃ corresponds to

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electron and hole hopping with various lifetimes and formation of self-trapped excitons.

The triplet-state exciton is a pair consisting of a hole and an electron, which is produced when photons of energy greater than the energy of the bandgap are absorbed in the crystal. The electron and hole produced in this way are free and may move independently through the crystal, giving rise to photoconductivity but, because an electron and hole have an attractive Coulomb interaction, it is possible for stable bound states of the two particles together to be formed, and then the photon energy required is smaller than the bandgap energy. As a result, the re-emission of excitation energy in form of luminescence might occur. It is possible to think of excitons in two different limiting approximations: one due to Frenkel, in which the exciton is considered as tightly bound, and the other approximation due to Mott and Wannier, in which the exciton is weakly bound, having an electron–hole interparticle distance, which is large in comparison with an atomic radius.

A long-term investigation of singlet and triplet excitons has been carried out in cubic alkali halide crystals (Rashba and Sturge 1982, Lushchik and Lushchik 1989, Song and Williams 1993, Lushchik *et al.* 1996), which led to the conclusion that intrinsic excitons undergo significant changes between the initial photon absorption and the process of exciton radiative annihilation. Free excitons created by exciting radiation undergo transformation into self-trapped excitons in singlet or triplet states. Later the recombination between electrons and trapped holes causes the appearance of the recombination luminescence of the self-trapped exciton. Some considerable efforts have been made to understand the nature of excitons in corundum (α -Al₂O₃) crystal using the methods of vacuum-ultraviolet spectroscopy as well as intrinsic and extrinsic luminescence excitation by synchrotron radiation (Wang *et al.* 1983, Kulis *et al.* 1991, Kirm *et al.* 1999), leading to the observation of luminescence. The adiabatic potential surface for triplet exciton self-trapping has also been studied in the crystalline SiO₂ crystal (Shluger and Stefanovich 1990) using the same computer code as we do. This computer code based on the Hartree–Fock formalism has been found to be very reliable in many applications on crystal studies. The results obtained by Shluger and Stefanovich interpreted in great detail the nature of self-trapped-exciton optical absorption and luminescence in the SiO₂ crystal.

There are not many studies of excitons in perovskites owing to the complexity of possible spatial configurations of the exciton in these materials and the necessity to take into consideration rather complex chemical bonding, which also includes a covalent component. However, recently quantum-chemical calculations on self-trapped excitons in KTaO₃ and KNbO₃ crystals have been performed (Eglitis *et al.* 2000) using again the same computer code. Thus it has been showed repeatedly that the CLUSTERD computer code (Stefanovich *et al.* 1990) is adequate for the exciton studies in different oxides. Additionally, we have tested the present method for a number of the other applications on SrTiO₃. Some examples include studies of hole self-trapping in SrTiO₃ cubic lattice (Stashans 2001, Stashans and Pinto 2001), and defect doping studies in the SrTiO₃ bulk (Stashans and Sánchez 2000, Sánchez and Stashans 2001, 2002), as well as quantum-chemical computations of defects on the SrTiO₃ surfaces (Stashans *et al.* 2001, Stashans and Serrano 2002).

The purpose of the present article is to obtain the equilibrium geometry and electronic structure of the triplet exciton in the SrTiO₃ tetragonal lattice. We also study the lattice distortion due to the exciton and possible luminescence due to the hole–electron pair annihilation.

§2. OUTLINE OF THE COMPUTATIONAL METHOD

The employed method of periodically repeated large unit cells (LUCs) (Shluger and Stefanovich 1990) is designed for the calculation of the total energy and electronic structure of crystals. The calculations are based on the Hartree–Fock formalism in the framework of the intermediate neglect of differential overlap (INDO) approach. We chose the LUC model because of its advantages compared with different cluster models, for example better treatment of the exchange interaction. Additionally, it is important to note that, from the viewpoint of simulating the exciton self-trapping, the original equivalency of the perfect lattice sites is essential. Only the periodic models meet this condition. A full discussion of the mathematical equations to calculate the total energy within the framework of the LUC approach has been given in numerous studies (Shluger and Stefanovich 1990, Stefanovich *et al.* 1990, Erazo and Stashans 2000) carried out previously. Here we shall only state that the method includes a number of the so-called semi-empirical parameters. The atomic parameter sets are optimized by calculating the following properties and comparing them with the experimental results:

- (i) the main features of a given crystal (width of the forbidden energy gap, widths of the upper and lower valence bands, and lattice constants of the crystal);
- (ii) the interatomic distances and ground states of some selected diatomic molecules;
- (iii) the ionization potentials of the host atoms of the crystal.

The numerical parameters for the SrTiO₃ crystal were obtained before reproducing the most important properties of this material and also in studies of other crystals. Specifically, parameters for the O 2s and 2p atomic orbitals (AOs) are taken from the work of Stefanovich *et al.* (1990), and the numerical values of parameters for the Ti 4s, 4p and 3d AOs as well as the Sr 5s and 4p AOs from the work of Stashans and Sánchez (2000). Thus, we have restricted ourselves to using the so-called valence basis set. The INDO parameters utilized in the present work are given in tables 1 and 2. Throughout the present work we have exploited a LUC of 135 atoms; that is, the 27 times (3 × 3 × 3) extended primitive unit cell of the SrTiO₃ has been used.

Table 1. Numerical parameter sets used in the present work: ζ , E_{neg} , P^0 and β .

Atom	AO	ζ (au)	E_{neg} (eV)	P^0 (electrons)	β (eV)
Sr	5s	1.59	11.15	0.18	-0.4
	4p	2.80	37.5	2.00	-4.5
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

Table 2. Electron–core interaction parameters $\alpha_{\mu B}$ for the tetragonal phase.

A	$\alpha_{\mu B}(\text{au}^{-1})$		
	B = Sr	B = Ti	B = O
Sr	0.15	0.55	0.25
Ti	0.10	0.16	0.14
O	0.59	0.362	0.15

§ 3. RESULTS AND DISCUSSION

3.1. Structural and electronic features of the exciton

A total spin density analysis is required in order to answer the question of the exciton's possible localization–delocalization configuration. As a result of the spin-density analysis for the 135-atom LUC, the electron part of the exciton is found to be well localized on the Ti(4) atom while the hole part settles down on the O(3) atom (figure 1). The elements of the self-consistent field (SCF) spin-density matrix for the atoms situated within the defective region are given in table 3. As follows from these data, 93% of the electron is localized on the $3d_{xy}$ AO of the Ti(4) atom while the hole

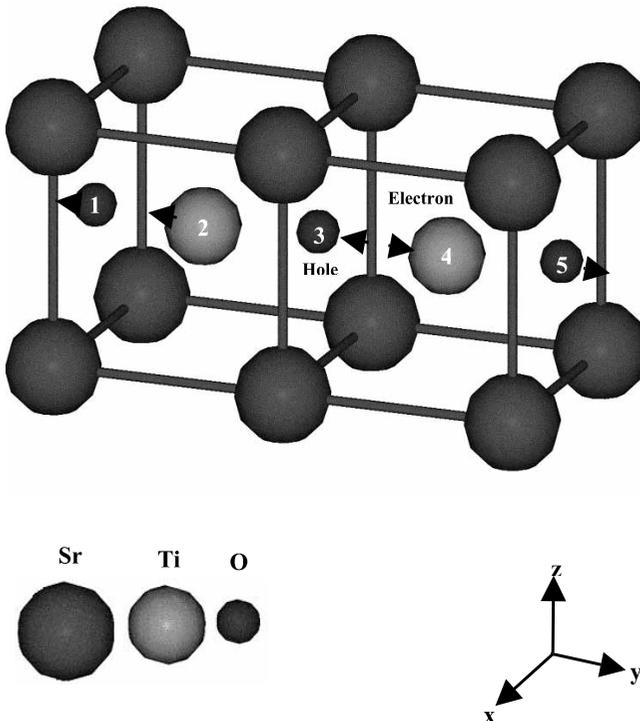


Figure 1. Spatial structure of the triplet exciton in the tetragonal SrTiO₃ lattice. The hole and the electron parts are localized on the O(3) and Ti(4) atoms respectively. The surrounding atoms move outwards the defect along the y axis, creating the crystalline lattice polarization along the same axis.

Table 3. SCF spin-density matrix elements for the atoms within the defective region. Predominantly, the electron part is localized on the 3d_{xy} AO of the Ti(4) atom while the hole part is found to be localized on the 2p_x and 2p_y AOs of the O(3) atom. The atomic numeration corresponds to that given in figure 1.

Electron	4s	4p _x	4p _y	4p _z	3d _{x²-y²}	3d _{xy}	3d _{xz}	3d _{yz}	3d _{z²}
Ti(2)	-0.0396	-0.0054	-0.0046	-0.0014	-0.0809	-0.0480	-0.0092	-0.0109	-0.0376
Ti(4)	0.0053	0.0016	0.0006	0.0003	0.0056	0.9307	0.0134	0.0103	0.0263
		Hole	2s	2p _x	2p _y	2p _z			
		O(1)	0.0006	0.0058	0.0649	0.0036			
		O(3)	0.0044	0.3868	0.4550	0.0090			
		O(5)	-0.0003	0.0000	0.0222	-0.0032			

part mainly (84% of localization) is found on the 2p_x (39%) and 2p_y (45%) AOs of the O(3) atom.

The performed geometry optimization as shown in table 4 leads to rather strong electron density redistribution. In general, it is found that the movements of five atoms in the defective region are non-negligible. Two of them move by up to 4% (0.15 Å) of the magnitude of the corresponding lattice parameter $a_0 = 3.88$ Å. It should be mentioned that, because all atomic movements are along the y axis, we express the lattice distortion in terms of the a_0 lattice parameter. The defect-nearest O(1), Ti(2) and O(5) atoms, situated along the y axis, move outwards from the defect (see figure 1). As one can see from the atomic charge analysis (table 4) and considering the above-mentioned particular atomic movements, there exists obvious lattice polarization due to the hole presence. This polarization occurs along the y direction and also leads to a weakening of the chemical bonding between the oxygen, which receives a hole and its surrounding cations. It is important to state that the polarization axis does not coincide with the ferroelectric z axis. Thus, the exciton presence in the ferroelectric tetragonal SrTiO₃ phase might reduce ferroelectric polarization in this material and can induce the loss of bulk ferroelectricity in the material.

The computed distance between the two centres (hole and electron) is found to be approximately 2.14 Å. This implies that the triplet-state exciton may correspond to the so-called Mott–Wannier-type exciton, which is weakly bound. We can state that this is adequate for a commonly accepted exciton model for ionic crystals. Finally,

Table 4. Atomic displacements Δr and changes Δq in atomic charge due to the triplet exciton self-localization in the tetragonal SrTiO₃ lattice. The atomic numeration and the direction of their movements correspond to those given in figure 1.

Atom	Δr (% a_0)	Δq (electrons)
O(1)	1.0	+0.096
Ti(2)	4.0	-0.280
O(3)	4.0	+0.450
Ti(4)	2.1	-0.500
O(5)	2.0	+0.097

the calculated relaxation energy as a difference between the total energies of relaxed and unrelaxed systems is found to be equal to 3.3 eV.

3.2. Luminescence due to the exciton

Annihilation of an exciton, that is electron and hole mutual recombination, gives rise to luminescence, which can be observed experimentally. In our study, the luminescence energy was obtained as a difference of total energies for the SCF ground and excited states for optimized triplet exciton geometry (called the Δ SCF method). That is, the potential energy curve was calculated for the triplet exciton, and then according to the Frank–Condon principle the de-excitation energy is that for the vertical transition from the minimum of the triplet exciton relaxed state to the SCF singlet state of the exciton for a fixed atomic arrangement. Thus the computed luminescence energy was found to be equal to 1.13 eV.

In this connection, some recent results reported for the triplet exciton state in the cubic phase of ABO_3 oxides (Eglitis *et al.* 2000, 2002) should be mentioned. These workers proposed the charge-transfer vibronic exciton (CTVE) approach to describe the electronic excitations in these systems. However, they use the electronic density matrix in their analysis of electron and hole polaron localization within the crystalline lattice, rather than the SCF spin-density matrix, which gives a more precise pattern for the exciton localization. Secondly, the geometry used in their papers apparently does not correspond to the equilibrium geometry, leading to incorrect values of calculated luminescence energies. Therefore, the CTVE existence in titanates is rather doubtful.

Our theoretical interpretation of the results obtained in the present work is given in figure 2. We consider that the experimentally observed green luminescence in a number of perovskites is due to singlet excitons in these materials. Since the triplet state of a given excited system normally lies lower than the singlet state, the luminescence energy due to the triplet exciton should be considerably smaller than the

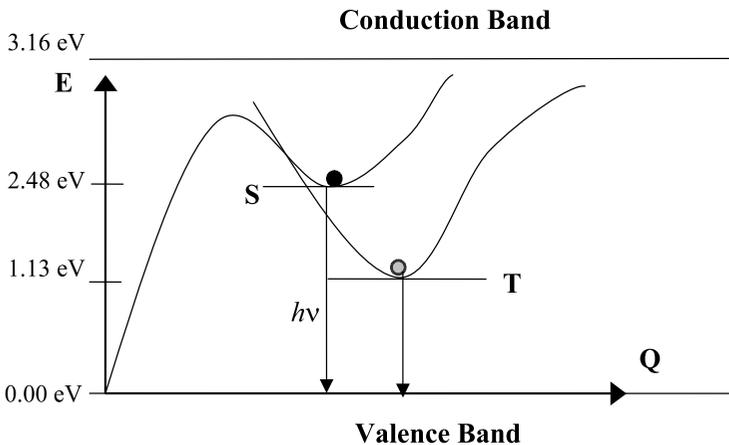


Figure 2. Total energy curve as a function of the generalized coordinate Q for the self-trapped exciton in the tetragonal $SrTiO_3$ lattice. The luminescence of the singlet state might be responsible for the experimentally detected green light, while the triplet exciton state lies considerably lower and as a result might participate in the photo-degradation of the material.

bandgap width. According to the experimental data, the bandgap width in the SrTiO₃ crystal is around 3.16 eV, and the observed green luminescence of 2.48 eV (Hasegawa *et al.* 2000) is very close to this magnitude. Therefore, we expect the green luminescence to occur owing to the singlet exciton annihilation, as shown in figure 2. Meanwhile, the triplet exciton may have a counterpart in the photodegradation process of the material rather than in the emission of green light since the magnitude of its luminescence energy, 1.13 eV, falls within the infrared spectrum.

§4. CONCLUSIONS

The quantum-chemical approach developed for crystals has been applied to study the triplet state of an exciton in the tetragonal SrTiO₃ crystal. The structural, electronic and optical properties of the triplet exciton are investigated in detail. The model of the so-called Mott–Wannier exciton, which normally occurs in ionic crystals, may describe our results on the exciton geometry. The hole and electron parts are well localized on oxygen and titanium atoms respectively, with the interparticle distance equal to 2.14 Å. The obtained atomic displacements within the defective region and electronic charge density redistribution point to a very strong crystalline lattice polarisation around the defect. The Δ SCF calculated luminescence energy, 1.13 eV, falls within the infrared spectrum. This implies that the experimentally determined luminescence energy of photo-excited state annihilation in the tetragonal SrTiO₃ crystal, 2.48 eV (Hasegawa *et al.* 2000), corresponds to the de-excitation of the singlet state of excitons in this material.

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