

LETTER TO THE EDITOR

Quantum chemical modelling of electron polarons and excitons in ABO_3 perovskitesE A Kotomin^{†‡}, R I Eglitis^{†§} and G Borstel[†][†] Universität Osnabrück, Fachbereich Physik, D-49069 Osnabrück, Germany[‡] Institute of Solid State Physics, University of Latvia, Kengaraga str. 8, Riga LV-1063, Latvia

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Abstract. Quantum chemical calculations using the intermediate neglect of the differential overlap (INDO) method, combined with the large unit cell periodic model argue for an existence of the self-trapped electrons in $KNbO_3$ and $KTaO_3$ perovskite crystals. An electron in the ground state occupies predominantly t_{2g} orbital of a Nb^{4+} ion. Its orbital degeneracy is lifted by a combination of the breathing and Jahn-Teller modes where four nearest equatorial O atoms are displaced outwards and two oxygens shift inwards along the z axis. Triplet exciton is shown to be in a good approximation of a pair of nearest Jahn-Teller electron and hole polarons (a bipolaron) which is very likely responsible for the ‘green’ luminescence observed in these crystals.

The existence of small radius polarons in ionic solids was predicted theoretically by Landau in 1933 [1]. Strict experimental (ESR) proof of self-trapped *holes* was given for alkali halides by Känzig in 1957, a quarter of century later [1]. For a long time it was believed that the electron self-trapping is not energetically favourable in ionic solids due to the large energy loss necessary for an electron localization on a single cation, which is the first stage of the trapping process, and is not compensated by the energy gain due to crystal polarization, at the second stage of the self-trapping. However, in 1994 the first ESR evidence appeared [2] for the electron self-trapping in $LiNbO_3$ perovskite crystals, accompanied by the IR absorption band around 1 eV. In 1998 self-trapped electrons (STE) were also reported in another type of material— $PbCl_2$ crystals [3]. Lastly, very recently, existence of the STE in $KNbO_3$ was discussed in [4]. In this letter, we model theoretically the electron self-trapping in $KNbO_3$ and $KTaO_3$ perovskites. Many ABO_3 perovskites reveal photoluminescence in the visible range (‘green’ luminescence peaking around 2.2 eV in $KTaO_3$ and $KNbO_3$) [5–7]. The origin of this luminescence has been discussed more than once. Suggested mechanisms include donor-acceptor recombination [8], recombination of electron and hole polarons [6], charge transfer vibronic excitaton (CTVE) [9, 10], transitions in MeO_6 complexes [11], etc. Preliminary calculations presented in [10] supported the idea of the CTVE in $KTaO_3$. In this paper, we perform modelling of the triplet excitons in $KNbO_3$ and $KTaO_3$ and calculate their luminescence energies.

We have used the semi-empirical, quantum chemical method of the intermediate neglect of the differential overlap (INDO) [12]. The modification of the standard INDO method for ionic solids is described in detail in [13–15]. This method is based on the Hartree-Fock formalism and allows self-consistent calculations of the atomic and electronic structure of pure and defective crystals. In the last decade the INDO method has been used in the study of bulk

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solids and defects in many oxides [13–18] and semiconductors [19, 20]. This method has been earlier applied to the study of phase transitions and frozen phonons in pure KNbO_3 [21], pure and Li-doped KTaO_3 [22], point defects in KNbO_3 [23–25], and solid perovskite solutions $\text{KNb}_x\text{Ta}_{1-x}\text{O}_3$ [26, 27]. More details about the INDO method and relevant computer program CLUSTERD are given in references [12–15]. In the present calculations we use the periodic so-called large unit cell (LUC) model [28]. In this model the electronic structure calculations are performed for an extended unit cell at the wave vector $\mathbf{k} = 0$ in the narrowed Brillouin zone (BZ) which is equivalent to the band-structure calculations at several special points of the normal BZ, transforming to the narrow BZ centre after the corresponding extension of the primitive unit cell. In ABO_3 crystals under study with the unit cell containing five atoms the $2 \times 2 \times 2$ extended LUC used in our calculations consists of 40 atoms.

The detailed analysis of the development of the INDO parametrization for pure KNbO_3 and KTaO_3 is given in [21, 22]. The INDO method reproduced very well both the available experimental data and the results of *ab initio* LDA-type calculations. In particular, this method reproduces the effect of a ferroelectric instability of KNbO_3 due to off-centre displacement of Nb atoms from the regular lattice sites, as well as the relative magnitudes of the relevant energy gains for the [100], [110] and [111] Nb displacements. These are consistent with the order of the stability of the tetragonal, orthorhombic and rhombohedral ferroelectric phases, respectively, as the crystal's temperature decreases. This is a very non-trivial achievement since the typical energy gain due to the Nb off-centre displacement is of the order of several mRy per unit cell.

The calculated frequencies of the transverse-optic (TO) phonons at the Γ point in the BZ of cubic and rhombohedral KNbO_3 , and the atomic coordinates in the minimum energy configuration for the orthorhombic and rhombohedral phases of KNbO_3 , are also in good agreement with experiment, thus indicating that a highly successful INDO parametrization has been achieved. The frozen-phonon calculation for T_{1u} and T_{2u} modes of cubic KTaO_3 are also in good agreement with experiment. Appreciable covalency of the chemical bonding is seen from the calculated (static) effective charges on atoms (calculated using the Löwdin population analysis): $0.62e$ for K, $2.23e$ for Ta and $-0.95e$ for O in KTaO_3 , which are far from those expected in the purely ionic model ($+1e$, $+5e$ and $-2e$, respectively) often used. These charges show slightly higher ionicity in KTaO_3 as compared with the relevant effective charges calculated for KNbO_3 : $0.54e$ for K, $2.02e$ for Nb and $-0.85e$ for O.

Recently [25] we performed calculations for the hole polarons in KNbO_3 , and found that both one-site (atomic) and two-site (molecular) polarons bound to a K vacancy could co-exist. A hole is either localized by a single O atom displaced toward the vacancy, or is shared by a couple of nearest O atoms. The relevant absorption band was observed recently experimentally by means of the transient optical spectroscopy [29].

As an extension of the hole polaron study, we have modelled here the *electron* polaron. As before, we used the $2 \times 2 \times 2$ extended cubic cell with the LUC containing 40 atoms. We allowed six nearest oxygen atoms in the octahedron around a central Nb atom in KNbO_3 to relax, in order to find the energy minimum of the system (figure 1(a)). All other Nb and K atoms, as well as the rest of the O atoms were kept fixed at their perfect lattice sites. According to our INDO calculations (figure 1(b)), initially the ground state is three-fold degenerate (t_{2g}). This degeneracy is lifted as a result of the combination of the breathing mode and the Jahn-Teller (JT) effect: 1.4% a_o (a_o is lattice constant) outward displacement of the four nearest equatorial O atoms (with the energy gain of 0.12 eV) and an *inwards* 1% a_o relaxation of the two oxygens along the z direction (an additional gain of 0.09 eV) (figure 2). That is, the total lattice energy gain is 0.21 eV. A similar JT electron polaron was observed recently in BaTiO_3 [30].

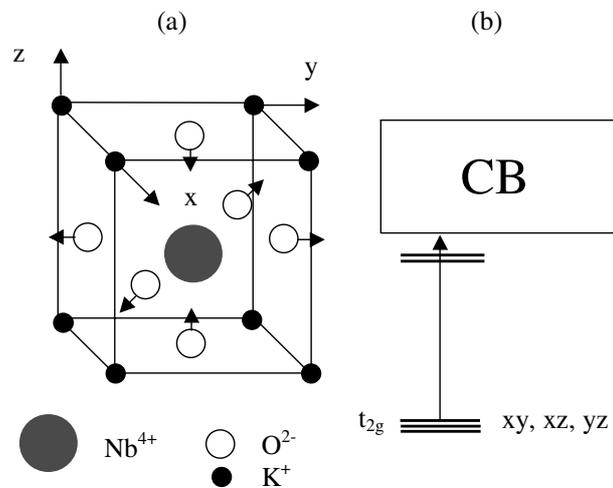


Figure 1. (a) Sketch of the asymmetric O atom relaxations around an electron localized on the central Nb atom in the self-trapped electron. (b) Local energy states within the gap.

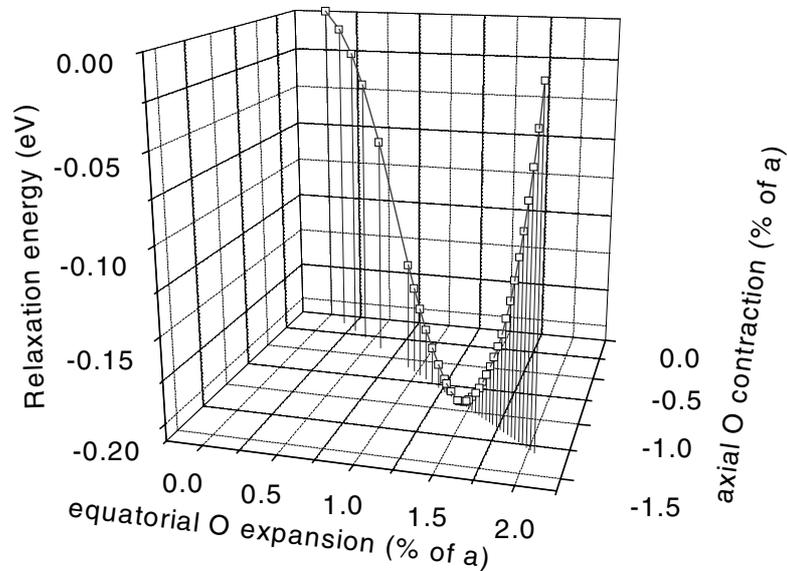


Figure 2. Lattice energy gain due to relaxation of four equatorial O atoms and axial O contraction of two oxygens along the z axis, around the electron polaron.

As a result, a considerable ($0.5e$) electron density is localized on the central Nb atom producing three closely spaced energy levels in the band gap. They consist mainly of the xy , xz and yz Nb 4d atomic orbitals (split t_{2g} energy level in an isolated ion) whereas two further empty levels are located close to the conduction band bottom. The electron polaron absorption energy was estimated by means of ΔSCF to be 0.78 eV. The relevant absorption process corresponds to an electron transfer to the nearest Nb atom. This absorption band has been recently observed under picosecond laser excitation [4].

As to the energetics of the self-trapped electron formation, previous *ab initio* LMTO calculations [21] have demonstrated that the bottom of the KNbO_3 conduction band has a narrow subband which probably permits the electron localization energy to be small enough for a positive total self-trapping energy balance.

In similar calculations for KTaO_3 we obtained optical absorption of 0.75 eV, with the following ground state relaxation: 1.7% a_0 for four O equatorial atoms and 1.2% a_0 inward displacement of two other O atoms along the z axis. This results in the total lattice relaxation energy of 0.27 eV. This is larger than in the KNbO_3 case because of higher KTaO_3 ionicity.

Next, we have calculated the triplet state of the excitons in the two crystals. Preliminary calculations for KTaO_3 [10] have demonstrated that the triplet exciton is a triad centre containing *one* active O atom (O1) and two Nb atoms located on the opposite sites from this O atom (see figure 3(a)). The total energy of the system is lowered by the combination of Coulomb attraction between electron and hole and the vibronic effect in this charge transfer

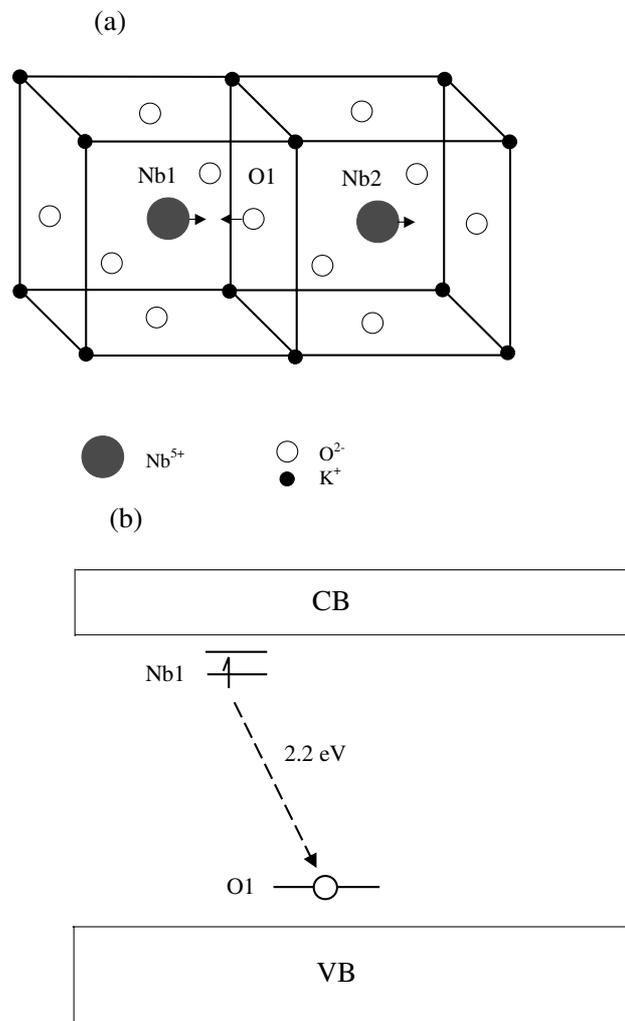


Figure 3. Schematic view of the charge transfer vibronic exciton (a) and its luminescence (b).

vibronic exciton (CTVE) [9, 10]. In order to find the CTVE energy minimum, we performed the self-consistent geometry optimization for 40 atom LUC (see figure 3(a)). According to our calculations, the oxygen ion O1 in KNbO₃ is displaced by 4.9% a_o towards the Nb1 ion (figure 3(a)) which is active in the CTVE formation. Simultaneously, this Nb1 ion reveals a displacement of 2.9% a_o towards the O1 ion, whereas another Nb2 ion (which is located on the other side from the oxygen ion O1 along the CTVE-axis) has a repulsion from the oxygen O1 and is displaced outwards by 4.3% a_o . We obtained that the total energy reduction in CTVE in KNbO₃ due to the lattice relaxation of O1, Nb1 and Nb2—three main atoms—is quite appreciable, -2.37 eV. The charge redistribution between ions is $-0.47e$ on the Nb1, $+0.65e$ on the O1, and $-0.1e$ on the Nb2.

A strong lattice distortion caused by the CTVE induces the local energy levels in KNbO₃ band gap. Namely, the O1 energy level with a hole is located 0.9 eV above the VB top, its wave function consists mainly of its $2p_x$ atomic orbital directed towards the Nb1 atom. On the other hand, two closely located Nb1 energy levels (one of them is two-fold degenerate) appear at 0.7 eV below the CB. They have t_{2g} symmetry and consists mainly of $4d_{xy}$ atomic orbitals of Nb1 and to a smaller extent Nb2 ions, with admixture of atomic orbitals of other nearest Nb atoms surrounding the CTVE (see figure 3(a)). The luminescence energy calculated using the Δ SCF method is very close to the experimentally observed 2.2 eV (table 1 and figure 3(b)). Results of the exciton calculations in KNbO₃ and KTaO₃ are collected in table 1. As one can see, the atomic displacements and relaxation energy in KTaO₃ is larger, due to more ionic nature of this crystal. However, this practically does not affect the luminescence energy.

Table 1. Calculated properties of excitons in the two crystals (see figure3(a) for atom labelling). Numbers in brackets give the experimental values.

| | E_{rel} (eV) | Displacement (% a_o) | Effective charge (e) | Charge transfer (e) | E_{lum} (eV) |
|-------------------|----------------|-------------------------|--------------------------|-------------------------|----------------|
| KNbO ₃ | 2.37 | | | | 2.17 (2.2) |
| Nb1 | | 2.9 | + 1.55 | -0.47 | |
| Nb2 | | 4.3 | + 1.92 | -0.1 | |
| O1 | | 4.9 | -0.20 | + 0.65 | |
| KTaO ₃ | 2.71 | | | | 2.14 (2.2) |
| Ta1 | | 3.1 | + 1.74 | -0.49 | |
| Ta2 | | 4.5 | + 2.12 | -0.11 | |
| O1 | | 5.2 | -0.24 | + 0.71 | |

In summary, we predict the existence of electron polarons in KNbO₃ and KTaO₃ perovskites with the optical absorption around 0.8 eV. Further experimental studies, especially ESR measurements and transient optical spectroscopy, are needed for a final identification of small-radius electron polarons. Our calculations give also a strong support to the ‘green’ luminescence in these crystals as a result of the recombination of the electrons and holes in the charge transfer vibronic exciton rather than due to the electron transitions in MeO₆ complex. Our results also demonstrate that well-parametrized quantum chemical methods are an efficient tool for the study of optical properties of advanced materials.

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Note added in proof. It should be noted that NB4⁺ polaron absorption band around 0.72 eV has been observed recently in strontium barium niobate [31].

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