We present the results of a series of ab initio calculations on the ground states and the low lying excited states of the \( \text{F} \) and \( \text{F}^+ \) centers in bulk \( \text{ZnO} \). Both types of \( \text{F} \) centers are oxygen vacancies, causing rather strong distortions of the local geometries. The calculations were performed by means of wave function based methods, mostly at the CASSCF level. Dynamic correlation was included for the first two coordination shells of the \( \text{F} \) centers. The calculated absorption energy for the \( \text{F}^+ \) center (3.19 eV) is in excellent agreement with the experimental value of 3.03 eV. For the emission from the \( ^3\text{T}_2 \) state of the \( \text{F} \) center to the \( ^1\text{A}_1 \) ground state we obtained a transition energy of 2.73 eV. Experimentally, a green photoluminescence is observed at 2.38–2.45 eV. We estimated that the errors in our calculation should be even smaller in the latter case than for the \( \text{F}^+ \) state, where the calculated transition energy differs by less than 0.2 eV from the experimental value. Therefore, we assume that the \( ^3\text{T}_2 \) to \( ^1\text{A}_1 \) transition is not the origin of the green luminescence.

1. Introduction

Oxides and halides show often anion vacancies called \( \text{F} \) centers or colour centers because the local excitations at the oxygen vacancies are responsible for absorption or emission of visible light. In this paper we investigate an oxygen vacancy in bulk \( \text{ZnO} \) and perform high level ab initio calculations for the excitation energies of the electrons located at the vacancy.

The origin of the green photoluminescence of \( \text{ZnO} \) at about 2.43 eV (510 nm) is of special interest and is still discussed controversially. Several authors\(^1\)\(^-\)\(^5\) claim that the existence of either \( \text{F}^+ \) centers or \( \text{F} \) centers in \( \text{ZnO} \) is responsible for this photoluminescence. Leiter \(^1\)\(^-\)\(^4\) assume that the singlet ground state of the neutral \( \text{F} \) center is excited via photon absorption to an excited singlet state. This state decays non-radiatively by intersystem crossing to a paramagnetic emissive triplet state which is detectable by ODMR (optically detected magnetic resonance). The energy of the excited singlet state is extrapolated to be about 3.4 eV. In a different model\(^6\) it is assumed that the green luminescence is caused by the recombination of a photogenerated hole with the singly ionized oxygen vacancy. Xu \( \text{et al.}^8 \) performed LDA supercell calculations for different defects and interstitials and concluded from their DOS for the different point defects that the green luminescence is caused by an electronic transition from interstitial \( \text{Zn} \) or \( \text{O} \), or from interstitial \( \text{Zn} \) to a \( \text{Zn} \) vacancy as earlier proposed by Bylander.\(^7\) Kohan \( \text{et al.}^9 \) performed periodic DFT calculations (LDA) on the stability of different native point defects in \( \text{ZnO} \). They claim \( \text{Zn} \) defects to be responsible for the green emission.

In addition to the green photoluminescence, a broad blue absorption band is observed experimentally at about 410–420 nm (2.95–3.03 eV)\(^3\)\(^-\)\(^4,10\) which is attributed to the \( \text{F}^+ \) centers in \( \text{ZnO} \). The existence of the \( \text{F}^+ \) center is proven by EPR. The \( g \) values of the \( \text{F}^+ \) center are \( g_{||} = 1.9948 \) and \( g_{\perp} = 1.9963 \).\(^10\) Semiempirical calculations of Xanthakis \( \text{et al.}^11 \) for the \( \text{F}^+ \) center yield an excitation energy of 1.6 eV in total disagreement to the experimental value of 3.03 eV.

To our knowledge, no high level ab initio cluster calculations on the excitation energies of the \( \text{F} \) or \( \text{F}^+ \) centers in \( \text{ZnO} \) exist, while several investigations have been performed on other materials, e.g. on alkaline halides\(^12\)\(^-\)\(^15\) and on alkaline earth oxides,\(^16\)\(^-\)\(^20\) to give only some examples. A systematic study with respect to cluster size and basis sets on the accuracy of the optical excitations at \( \text{O} \) vacancies in \( \text{MgO} \) was performed by Sousa \( \text{et al.}^20 \). In their best calculations they achieved an accuracy of 0.4 eV for the excitation energies. A review of different methods to take care of long range polarization effects on the ionization potential of the \( \text{F} \) center was given by Pacchioni.\(^15\)

In this paper we report on a series of wave function based quantum chemical cluster calculations for the absorption and emission spectra of a neutral \( \text{F} \) center and a positively charged \( \text{F}^+ \) center in bulk \( \text{ZnO} \). We compare whether the transition energies are in agreement with the experimentally observed green luminescence (510 nm) and the blue absorption of the \( \text{F}^+ \) centers at 410 nm, respectively.

2. Embedded cluster model

\( \text{ZnO} \) crystallizes in a wurtzite structure, consisting of alternating hexagonal layers of zinc and oxygen ions. Both ions are tetrahedrally coordinated to each other. The structure is described by the lattice constants of the hexagonal unit cell, \( a = 3.2495 \text{ Å} \) and \( c = 5.2069 \text{ Å} \).\(^21\)\(^-\)\(^22\) The \( \text{Zn} \) layers are at the positions \( z = 0, c/2, c, \ldots \) and the oxygen ions at \( z = u^*c, c/2 + u^*c, c + u^*c, \ldots \). The distance between the oxygen and the zinc layers is given by \( u^*c \). A value of \( u = 0.375 \) is equivalent to an ideal tetrahedral surrounding of the zinc ions by the oxygen ions and vice versa.\(^22\)\(^-\)\(^25\) The last two values are in good agreement and are obtained by single crystal X-ray diffraction and neutron diffraction. Therefore, we used \( u = 0.3825 \) in all subsequent calculations.

In all our calculations we used an embedded cluster approach for the description of the \( \text{F} \) center. Only a small part of the \( \text{ZnO} \) crystal in the neighbourhood to the \( \text{F} \) center was treated by ab initio methods. The long range interaction with the crystal was included by an embedding point charge field generated for the experimental structure of bulk \( \text{ZnO} \). The