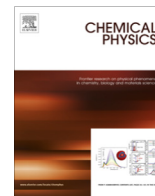




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Off-centre motion in doped cubic oxides: A general view on the instability

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ABSTRACT

The existence of an off-centre distortion for impurities in cubic oxides is explored by Density Functional Theory calculations. We find that models based on ionic radii are inadequate to explain the off-centre instability. By contrast, increase of the nominal impurity charge or decrease of the host lattice constant act against the off-centre distortion. This explains why the motion of just the Ni²⁺ impurity can happen in SrO, in agreement with experimental data, while not for smaller Cr³⁺ or Ti⁴⁺ ions in the same lattice. Moreover, the different electronic structure and coupling to the host lattice are shown to be behind a small but positive force constant for Na⁺ and Mn²⁺ in SrO. Our results indicate that an off-centre motion in MgO:Ni²⁺ is rather unlikely and that the local contributions to the instability in pure BaTiO₃ are not enough to induce ferroelectricity if just the movement of Ti⁴⁺ ion is considered.

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1. Introduction

When an insulating material is slightly doped, the impurities replace a small fraction of host cations. Nevertheless, the position occupied by an impurity in the lattice is not necessarily that of the replaced host ion as, in some cases, the impurity actually moves from the ideal substitutional site [1,2]. In cubic insulating lattices, this off-centre motion gives rise to a local symmetry lowering which, in turn, can induce deep changes into the physical and chemical properties associated with the impurity. As an example, the off-centre motion of Fe⁺ impurities in SrCl₂ [3–5] or KTaO₃ [6,7] induces a huge magnetic anisotropy associated to the spin of the impurity [8,9]. Aside from this reason, the study of this kind of structural instability in slightly doped materials is also attractive due to its partial relationship [10–12] with the ferroelectric distortions in pure insulating materials like BaTiO₃ or PbTiO₃, where, apart from a local component which *could* favour the off-centre motion, a cooperative component may also be present.

Thus, as indicated above, determining whether a transition metal impurity remains on-centre or experiences an off-centre distortion is a key element to understand its properties. In cubic lattices, partial information on this important issue can be obtained experimentally either by studying the symmetry of the spin-Hamiltonian associated with Electron Paramagnetic Resonance (EPR) data or by finding the temperature dependence of the

oscillator strength of *d–d* transitions [2,13,14]. However, in many cases these techniques provide very little insight on whether the off-centre motion is spontaneous or induced by the presence of another defect in the vicinity of the impurity, such as a vacancy or an unwanted ion, which triggers the symmetry-breaking distortion. An efficient way to answer this question is provided by modern first-principles calculations. For example, Density Functional Theory (DFT) calculations undoubtedly prove that the symmetry lowering observed by EPR in SrCl₂:M (M = Fe⁺, Cu²⁺) [3,5,15], SrF₂:Cu²⁺ [16] or CaF₂:Ni⁺ [17] obeys to a *spontaneous* off-centre motion of impurities *without* the need of any associated defect [4,18,19].

The present work explores, by means of first principles DFT calculations, the possible off-centre instabilities taking place in MO cubic oxides (M = Mg, Ca and Sr) doped with various ions like Na⁺, Ni²⁺, Mn²⁺, Cr³⁺ or Ti⁴⁺. This research is partially motivated by some Extended X-ray Absorption Fine Structure (EXAFS) and optical works suggesting that Ni²⁺ impurities in MgO move off-centre [20–22] in the same way as in SrO:Ni²⁺ [23,24]. In the latter case EPR experiments [24] reveal the existence of a very large zero-field splitting constant, $D = 20 \text{ cm}^{-1}$, ascribed to a motion of Ni²⁺ along a $\langle 111 \rangle$ direction. Nevertheless, that conclusion on Ni²⁺ in MgO contrasts with other EXAFS and EPR works indicating that Ni²⁺ remains on-centre in this lattice [25–28]. While shedding some light on this particular set of experimental results will be the focus of the first part of our work, our broader aim is to provide some insight in the trends favouring or preventing an off-centre motion in an isolated impurity. At the same time we will discuss

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whether these conditions are compatible with those discussed in the literature on ferroelectrics. For example, in the perovskites it is sometimes considered that a highly charged ion is more likely to trigger ferroelectricity and an associated off-centre movement than one with a small nominal charge due to the enhanced covalency these ions display [29]. On the other hand, a usual concept employed to explain the off-centre motion in both localised (impurities) and crystalline (ferroelectrics) systems is the association of the distortion to the small size of the displacing ion. More precisely, the simple comparison of the ionic radius of a cation with that of the cavity it occupies within the host lattice [30] is widely claimed as a sensible argument to understand an off-centre distortion. Moreover, this is also the main argument behind the widespread use of the tolerance factor in perovskite lattices to find whether octahedral rotations or ferroelectricity would be favoured in a particular crystal. Nevertheless this argument, widely used in the literature, has been shown not to be correct for explaining experimental data [31].

In order to study this problem in more detail we will carry out accurate DFT calculations on a large set of impurities with varying ionic radius, from the relatively large presented by Na^+ to the much smaller displayed by Ti^{4+} . Our findings indicate that approaches based on simplistic concepts like the ionic radius are too crude to describe the subtle properties of off-centre movement that requires a high-level modeling of the bonding of the central metal with its close neighbours using, for example, the pseudo Jahn–Teller effect [1].

This article is organised as follows. In Section 2 we provide a short account of computational tools employed in this work while main results are collected in Section 3. In the last section a general discussion on the conditions favouring the off-centre instability is reported.

2. Computational details

Periodic *ab initio* calculations based on DFT have been carried out by means of the CRYSTAL14 package that employs localised gaussian basis-sets to represent the Bloch orbitals [32]. All ions have been described using all-electron triple-zeta with polarisation (TZVP) basis-sets of reasonably high quality [33], except Sr where core electrons were described by means of a pseudopotential taken from the CRYSTAL data base [34]. We have used the hybrid exchange–correlation functional PW1PW, with 20% of exact exchange, that has shown to provide with highly reliable structural and electronic predictions [35]. This combination results in high-accuracy and the ability to treat magnetic transition metal impurities without resorting to semiempirical corrections depending on the particular ions present in the system as it occurs, for example, when employing LDA + U. Other technical details include a $4 \times 4 \times 4$ sampling of the reciprocal lattice, a selection of the ITOL integration parameters as 9, 9, 9, 36, 50 in order to avoid flat adiabatic potential surface problems, and a convergence threshold in energy of 10^{-8} hartree that leads to high accuracy.

Firstly, we have computed the equilibrium geometry of pure MO cubic oxides ($M = \text{Mg}, \text{Ca}$ and Sr) allowing to relax all atomic positions. The computed cell parameters differ, in all cases, less than 0.5% from the experimental values measured by X-ray diffraction at very low temperatures. Then, we have carried out geometry optimizations for the same lattices doped with several of impurities like Na^+ , Ni^{2+} , Mn^{2+} , Cr^{3+} or Ti^{4+} at low temperatures using supercells containing 64 and 128 ions where one of the cations was replaced by an impurity. In particular, we have fully relaxed the atomic positions for cells with the impurity in an on-centre configuration (O_h local symmetry around the impurity) and also in an off-centre configuration along a $\langle 111 \rangle$ direction allowing

distortions of local C_{3v} symmetry. Charged impurity centres like Cr^{3+} or Ti^{4+} replacing a divalent cation like Mg^{2+} , Ca^{2+} or Sr^{2+} were calculated imposing a homogeneous charge background over the cell that compensates for the impurity charge and renders the whole supercell neutral.

We have verified that, in the present systems, when the impurity actually goes off-centre the energy minimum is always reached for a $\langle 111 \rangle$ distortion. This kind of distortion is usually found for impurities in crystals with a rock salt structure and has been observed for $\text{KCl}:\text{Li}^+$, $\text{RbCl}:\text{Cu}^+$, $\text{RbI}:\text{Ag}^+$ or $\text{KCl}:\text{Mn}^+$ [4,12–14]. Also the ferroelectric distortion observed at low temperatures in BaTiO_3 (rhombohedral phase) involves a cooperative motion of Ti^{4+} ions along $\langle 111 \rangle$. A description of a $\langle 111 \rangle$ off-centre motion of an impurity in a crystal with rock salt structure is depicted in Fig. 1. If the impurity moves a quantity η along $\langle 111 \rangle$ there are three ligands at a short distance, R_S , and three other lying at a longer distance, R_L . The three η , R_S and R_L quantities have been derived for Ni^{2+} in MgO , CaO or SrO and also for Na^+ , Mn^{2+} , Cr^{3+} or Ti^{4+} in the same lattices by means of first principles calculations.

3. Results for impurities in cubic oxides: comparison with experimental data

In Table 1, we present the main results of our DFT calculations both for the on-centre cubic case and the trigonal (C_{3v}) off-centre optimization. The first case is simply characterised by the metal–ligand distance R that splits into well differentiated R_S and R_L quantities if the off-centre motion is energetically favourable (see Fig. 1).

As a first highlight, we would like to note that according to the present results Ni^{2+} in MgO remains on-centre and the $\text{Ni}^{2+}-\text{O}^{2-}$ distance, R , is equal to 2.114 Å. This figure is close to $R_0 = 2.106$ Å corresponding to the $\text{Mg}^{2+}-\text{O}^{2-}$ distance in pure MgO and consistent with the similar ionic radii of Ni^{2+} and Mg^{2+} . Moreover, the value $R = 2.114$ Å derived in the present calculations is in agreement with EXAFS measurements [25–27] carried out on $\text{MgO}:\text{Ni}^{2+}$. In particular, accurate data [27] reported for $\text{Mg}_{0.985}\text{Ni}_{0.015}\text{O}$ give $R = 2.105 \pm 0.005$ Å.

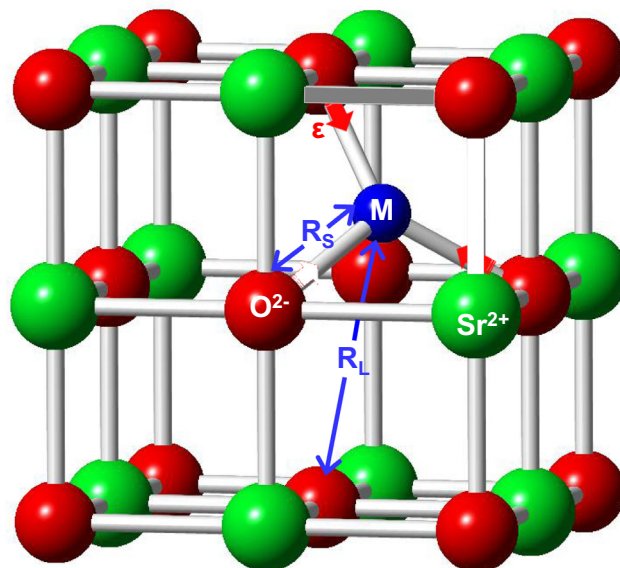


Fig. 1. Illustration of the MO_6 complex for the off-centre C_{3v} configuration showing the meaning of the metal–oxygen distances, R_L and R_S , and the inwards displacements ϵ of three oxygen ligands towards the off-centre impurity, M .

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