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Magnetism driven by non-metal interstitials from first-principles prediction: The case of hydrogen- and fluorine-doped calcium monoxide with rock-salt structure

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ABSTRACT

Our first-principles calculations based on density functional theory confirmed the formation of *sp*-ferromagnetic states of calcium monoxide with interstitial nonmagnetic F or H atoms. *The hydrogen and fluorine interstitials in the oxides were found to be spin polarized and are more stable in the antiferromagnetic state and the ferromagnetic state, respectively.* For H-doped CaO, no considerable charge transfer takes place and the spin remains localized on the impurity. For F-doped oxide, the observation may be attributed to the *p*–*p* interaction and the charge transfer between the interstitial atom and the neighboring O atoms. We demonstrate that H-doped compound is a potential *n*-type antiferromagnet, while F-doped material is a potential *p*-type ferromagnet. The different dopants would induce different magnetic couplings, thus show different ground-state magnetic configurations. The mechanism for the magnetism should be useful for understanding d^0 magnetic semiconductors or insulators. The present potential d^0 diluted magnetic materials, at least some of them, may be useful in spintronics.

1. Introduction

Ferromagnetic semiconductors or insulators have been attracting intense interest for their potential applications in the field of spintronic devices. Over the past several years, there have been considerable possibilities of creating ferromagnetism in thin films of doped oxide materials. Several systems have been identified to be ferromagnetic at room temperature but all of these systems contain either a transition metal element or a rare earth metal element as a dopant. Magnetic transition metals such as V, Cr, Mn, Fe, Co, and Ni, rare earth metal such as Eu, Gd, Tb, Dy, Ho, and Er, are frequently used as magnetic dopants to fabricate magnetic materials. Nevertheless, in spite of accelerated interest in these materials, the exact mechanism responsible for the observed magnetic properties continues to be strongly debated in the literature. Since in such systems the formation of nonrandom alloys, secondary phases or clusters of intrinsic magnetic ion precipitates cannot be rule out, the origin of ferromagnetism is still controversial, while the technological applications of these materials would be detrimental due to non-intrinsic behaviors [1–7].

In addition, some of Mn-doped and Co-doped ZnO systems were reported to exhibit only paramagnetic rather than ferromagnetic states [8–10]. It is thought that additional charge doping may be needed to stabilize the ferromagnetic ground state in such systems [11,12]. In fact, charge-injection induced magnetism and half metallicity in some systems has been reported [13–15]. It is also found that additional charge would affect the magnetic properties significantly [16,17]. That simple substitution of Mn^{2+} and Co^{2+} for divalent Zn in ZnO, for instance, does not generate any extra carriers in itself. On the other hand, the strong Hund's rule coupling J_H that favors a high-spin configuration on the impurity site is another important factor. The large splitting between occupied majority spins and unoccupied minority spins in these transition metal impurities is only partially due to the Coulomb repulsion U which is actually strongly reduced in a solid [18]. Moreover, for group II–VI compounds, it is difficult to dope transition metal ions effectively to realize *p*- or *n*-type devices due to their intrinsic band gaps. A possible way to overcome this drawback is to use nonmetal elements to substitute magnetic transition metal elements to dope such compounds. The strong effective Hund's rule coupling between the carriers was proposed as another way to introduce magnetism in nonmagnetic semiconductors or insulators in recent years. The origin of such strong coupling in these cases comes from the kinetic energy and symmetry of the molecular orbitals rather than from local, on-site interactions.

Ferromagnetism in materials without magnetic impurities, which can be called intrinsic or d^0 ferromagnetism, has been reported in recent investigations [19–21]. Several unexpected

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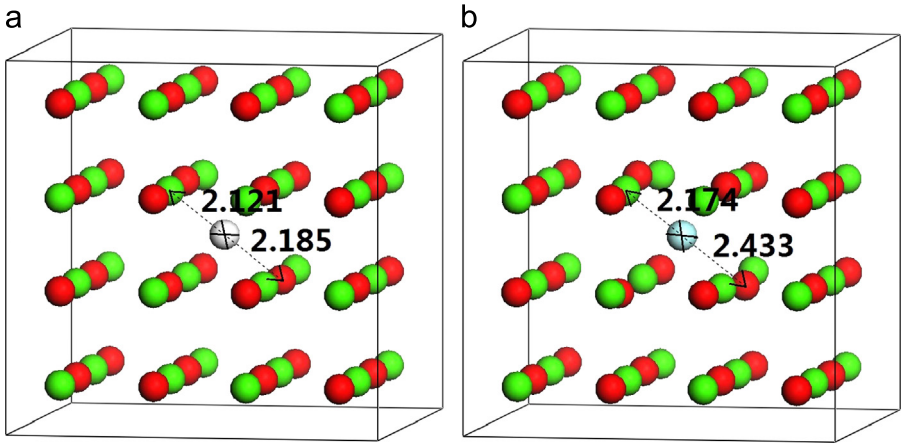

Fig. 1. (Color online) The description of the local structure near the impurity of (a) H- and (b) F-doped CaO, respectively.

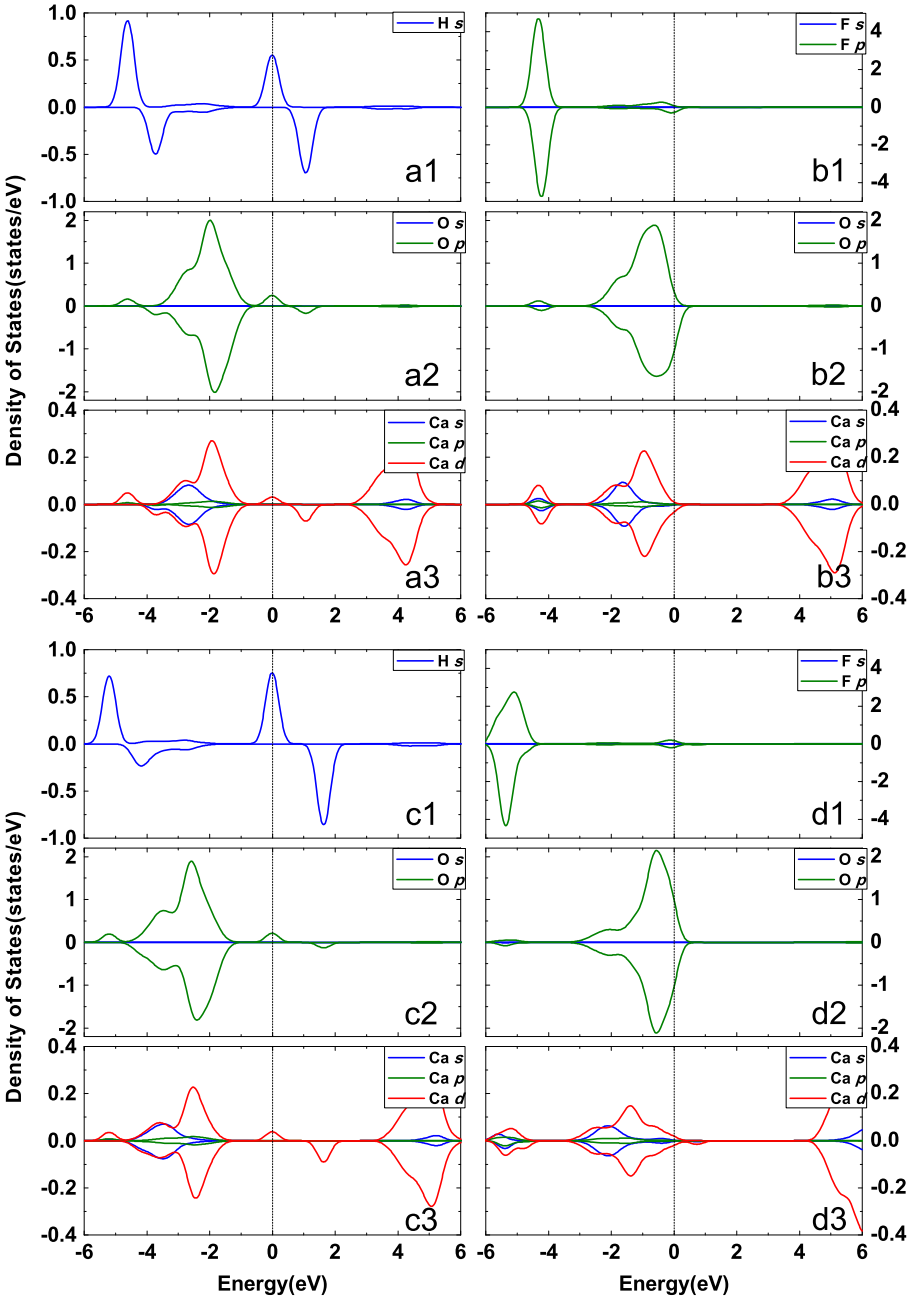

Fig. 2. (Color online) The spin-resolved partial density of states of [(a1)–(a3)] H-doped CaO from GGA calculation, [(b1)–(b3)] F-doped CaO from GGA calculation, [(c1)–(c3)] H-doped CaO from GGA + *U* calculation, and [(d1)–(d3)] F-doped CaO from GGA + *U* calculation, respectively. The zero of the energy scale is set at the Fermi energy. The black dotted line indicates the Fermi level.