First-principles study of the magnetic properties of nitrogen-doped alkaline earth metal oxides

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ABSTRACT

We present a first-principles study of the magnetic properties of N-doped MgO, CaO and SrO, which have been proposed to constitute a new class of dilute magnetic semiconductors (DMSs) with no magnetic elements. In this study, it was found that under a homogeneously distributed condition, Curie temperatures could reach room temperature at sufficient N concentrations in the range of 20–30 at.%; however, an inhomogeneous N distribution in these DMSs is the favored configuration, which indicates that spinodal decomposition leads to a room-temperature blocking temperature at smaller N concentrations than those estimated for room-temperature ferromagnetism in the homogeneous distribution condition.

1. Introduction

Ferromagnetism that is induced by non-magnetic impurities has attracted significant interest in the field of spintronics [1–10]. This so called d^0 ferromagnetism has been referred to as a new class of magnetism, wherein the ferromagnets contain no magnetic elements with partially filled d or f shells [11]. The increasing interest is due to the unexpected finding that p bands can spontaneously polarize to provide a ferromagnetic state.

In our previous studies, we initially theoretically proposed that N-doped alkaline earth metal oxides could be potential candidates for the realization of d^0 ferromagnets [12,13]. Thereafter, it was experimentally reported that local magnetic moments can be formed in N-doped MgO [14] and SrO [15]. In these studies, these oxide materials were prepared via molecular beam epitaxy with reported maximum N doping concentrations of 13 at.% for MgO and 25–30 at.% for SrO.

A remaining question is whether these materials are magnetically ordered at room temperature. To elucidate this point, we present a first-principles study of the magnetic properties of N-doped alkaline earth metal oxides.

2. Calculation method

The electronic structures of O substituted by N in MgO, CaO and SrO were calculated using the Korringa–Kohn–Rostoker coherent potential approximation (KKR-CPA) [16,17] within the context of the pseudo-self-interaction-corrected (PSIC) local density approximation (LDA) [18,19]. In this system, N atoms randomly distribute at anion sites in the host material, which can be described as $XO_{1-c}N_c$, wherein X represents the anion atoms of the host materials (Mg, Ca or Sr) and c represents the N concentrations. To correct the error of the LDA, the self-interaction correction method (LDA+SIC) was proposed by Perdew and Zunger [18], and the pseudo-self-interaction correction method (LDA+PSIC) has been developed by Filippetti and Spaldin [19]. It has been shown that this method reasonably reproduces the electronic structures of ZnTe-, GaN- and ZnO-based dilute magnetic semiconductors (DMSs) [20]. To evaluate the percolation effect of ferromagnetic coupling, we calculated the effective exchange coupling constants J_{ij} between N atoms at sites i and j embedded in a CPA medium by using a classical Heisenberg model and Liechtenstein's formula [21]. Using the calculated exchange interactions, the Curie temperatures (T_C) of the DMSs were estimated using the mean field approximation (MFA) as $k_B T_C = (2/3)\sum_{i \neq 0} J_{0j}$, where k_B is Boltzmann's constant, and then were determined exactly, in principle, using a Monte Carlo simulation (MCS) [22]. It has been shown that this MCS provides a practical estimation accuracy for DMSs with homogenously distributed impurities, such as in (Ga,Mn)As [23] and (Zn,Cr)Te [24]. Thereafter, to evaluate the impurity distribution homogeneity, we compared the energies of X(O,N) with different impurity concentrations. Details of the calculation procedure

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employed in the present study [22] and calculated examples of d^0 ferromagnets [25] can be found in the previously reported studies. In the present calculations, we used MACHIKANEYAMA [26] for the KKR-CPA calculation in the context of the LDA and the package developed by Toyoda et al. [20], in addition to PSIC implemented in MACHIKANEYAMA for the LDA+PSIC calculation. The experimentally derived lattice constants of the MgO, CaO and SrO host materials, which have a rock-salt structure ($a=4.21$, 4.81 and 5.16 Å, respectively [27]), were used, and lattice relaxation was not taken into account. The form of the potential was restricted to the muffin-tin type.

It should be noted that our predictions regarding the stability of ferromagnetism and Curie temperature (T_C) in the previous studies [12,13] could be inaccurate because they were based on the local density approximation (LDA), the mean field approximation (MFA) and the assumption of a homogeneous impurity distribution. First, for a wide variety of materials, the LDA gives reasonable predictions; however, for strongly correlated systems, such as ZnO, it often fails to predict the electronic structure and band gap energy [28]. This error mostly comes from self-interaction, wherein this interaction is due to the LDA of the exchange-correlation potential, and refers to the fictitious interaction of an electron charge with the Coulombic and exchange-correlation potential generated by the same electron. Second, exchange interactions in many DMSs are very short ranged and the MFA often overestimates T_C because, due to the short-ranged interactions, the percolation of ferromagnetic coupling is difficult to achieve for small impurity concentrations. Third, it has been found that the assumption of homogeneity can be unrealistic in many magnetic element-doped DMSs because of the strong attractive interactions between the magnetic elements. For example, inhomogeneous impurity distributions have been observed in several DMS systems, such as (Ga,Cr)N and (Al, Cr)N [29]. In this study, these points are also discussed.

3. Results and discussion

To compare the density of states (DOS) that were calculated within the standard LDA and the LDA+PSIC, we plotted the DOS
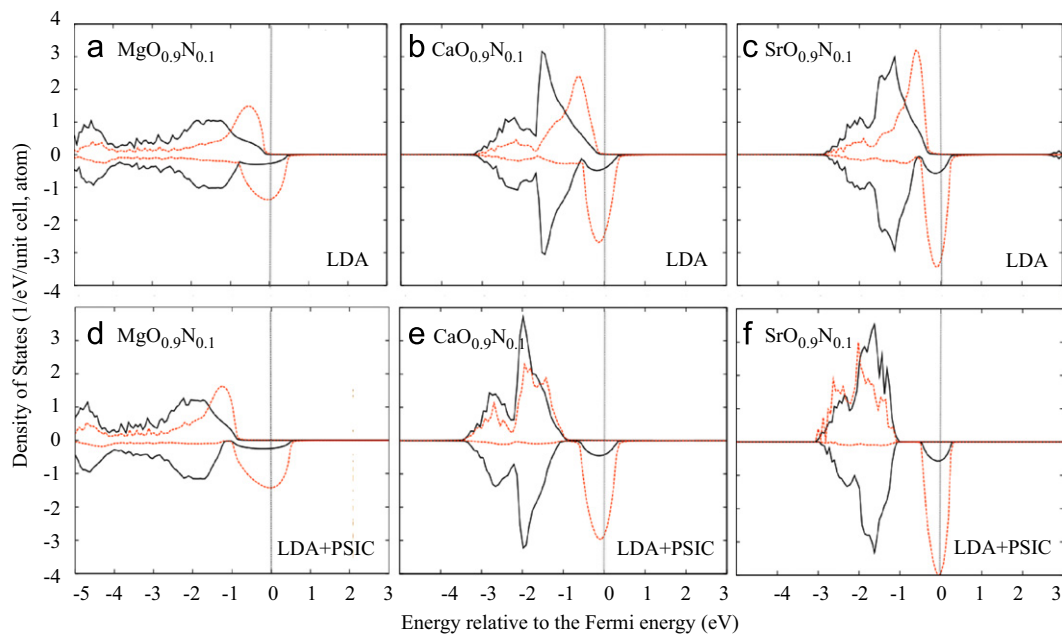
of 10 at.% N-doped MgO, CaO and SrO (Fig. 1). The LDA+PSIC calculation provided a larger exchange splitting and higher localization of local magnetic moments in comparison to that obtained using the LDA. Except for the band widths, the DOS among these DMSs in ferromagnetic states have similar structures, i.e., spin-polarized and half-metallic N impurity bands that are partially filled by electrons in the band gap.

Hereafter, we discuss the calculated results within the LDA+PSIC. The T_C values that were calculated with the MCS were much lower than those calculated with the MFA, and the MCS demonstrated that the T_C could reach room temperature at sufficient N impurity concentrations in the range of 20–30 at.% (Fig. 2). Most contributions of the effective magnetic interactions in these DMSs come from those of the first- or second-nearest neighbors (Fig. 3). Because of the exponential decay of the impurity wave function in the band gap, the exchange interaction is very short ranged, which results in the discrepancy in T_C estimated by the MFA and MCS.
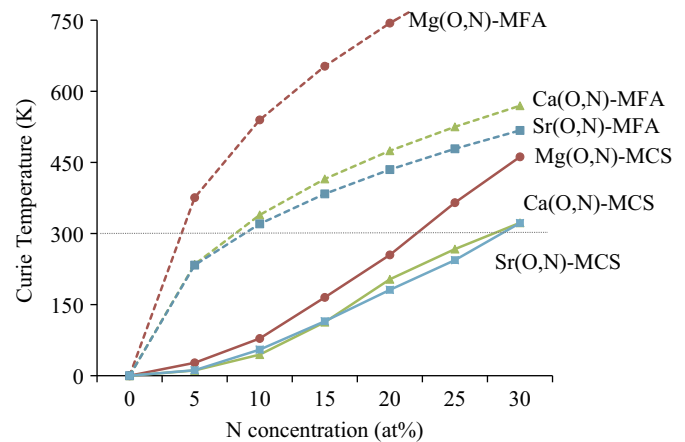
Fig. 2. (Color online) Doping concentration dependency on the calculated Curie temperatures. The circle, triangle and square symbols represent calculated values of Mg(O,N), Ca(O,N) and Sr(O,N), respectively. The solid lines and dotted lines represent values calculated with the MCS and MFA, respectively.

Fig. 1. (Color online) Total and partial densities of states (DOS) calculated by LDA (upper panel) and LDA+PSIC (lower panel). The solid lines and dotted lines represent total DOS and N-2p partial DOS, respectively. The positive and negative values of the density states represent those for up spin and down spin, respectively.