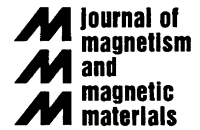




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First-principles investigations of the magnetocrystalline anisotropy in strained Co-substituted magnetite (CoFe_2O_4)[☆]

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Abstract

The magnetocrystalline anisotropy energy of CoFe_2O_4 under uniaxial strain along [00 1] direction has been studied by using the linear muffin-tin orbital method within the density functional theory. The calculated uniaxial anisotropy constant K_{out} is positive for extensive in-plane (00 1) strains and is negative for compressive in-plane strains. The positive value of K_{out} indicates that a CoFe_2O_4 film under an extensive in-plane strain would show the out-of-plane [00 1] magnetization. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ferrite; Magnetic anisotropy energy; Electronic structure

Magnetite (Fe_3O_4) is an inverse cubic spinel oxide with one iron atom on the tetrahedral A-site and two Fe atoms on the octahedral B-site per formula unit (fu) above the Verwey transition temperature (120 K) [1]. The high temperature phase of magnetite is a half-metallic ferrimagnet with magnetic moment on A-site antiparallel to moment on B-site, resulting in a saturation moment of $4 \mu_{\text{B}}/\text{fu}$. At the Verwey temperature, Fe_3O_4 undergoes a metal–insulator transition, accompanied by a structure transition from cubic to monoclinic [2]. The mechanism of the Verwey transition is still a challenging problem to be solved. In the meantime, because of the attractive electronic and magnetic properties as well as the potential industrial applications in magnetic multilayer devices, the magnetism of Fe_3O_4 remains to be one of the most interesting areas of research.

In the past decade, investigations of Co substitution were carried out to gain insight into the electronic, magnetic, and anisotropic properties of magnetite. Cobalt ferrite (CoFe_2O_4) is also a half-metallic material with a smaller saturation magnetic moment of $3.7 \mu_{\text{B}}/\text{fu}$ [3]. CoFe_2O_4 crystallizes in the same spinel structure as Fe_3O_4 with half of the B-site Fe atoms replaced by Co

atoms (i.e., $\text{Fe}_A[\text{CoFe}]_B\text{O}_4$), resulting in a lattice constant of 8.39 \AA [4]. Mössbauer spectroscopy measurements show that the substitutions distribute randomly over the B-sites throughout the magnetite crystal [5,6]. In contrast to the negative fourth order anisotropy constant K_1 and the [1 1 1] easy axis of cubic Fe_3O_4 , the Co atoms in the cubic spinel structure of CoFe_2O_4 give rise to a relatively large but positive K_1 [7] with the [1 0 0] easy axis. The measured Curie temperature slightly decreases with the Co content [8], while impurity effects also decrease the Verwey temperature of doped magnetite [9].

The band structure of cubic Fe_3O_4 was calculated within the framework of the local-spin-density approximation (LSDA) by several investigators [10–13]. All these calculations gave a consistent half-metallic result with a magnetic moment of $4 \mu_{\text{B}}/\text{fu}$. The cubic CoFe_2O_4 was also demonstrated to be a half-metallic compound with a magnetic moment of $3 \mu_{\text{B}}/\text{fu}$ in band calculations [11]. On the other hand, no magnetocrystalline anisotropy energy (MAE) calculations have been reported perhaps because of the smallness of MAE and the large amount of computing time required. We have recently performed anisotropy energy calculations for cubic as well as strained magnetite [13]. The obtained results agree with the experimental data quite well. The purpose of this work is to investigate the anisotropy energies of the Co-substituted magnetite under uniaxial strains.

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For a cubic crystal bearing a uniaxial strain along $[001]$, the out-of-plane anisotropy constant is

$$K_{\text{out}} = E_{[100]} - E_{[001]}, \quad (1)$$

where $E_{[100]}$ and $E_{[001]}$ are the total energies for the magnetization along $[100]$ and $[001]$, respectively [13]. The computing method used in this work has been described in Ref. [13]. We first performed the self-consistent scalar-relativistic calculations for each considered strain by using the linear muffin-tin orbitals (LMTO) method. The randomly distributed B-site substitutions of Co atoms were treated by using the virtual crystal approximation. The number of k points over the irreducible wedge (IW) used in the self-consistent calculations was about 600 over 1/16 of the body-centered tetragonal Brillouin-zone (BZ). After the self-consistent calculation for each strain considered, we used the resultant potential to perform the fully relativistic band structure calculation once for each of the $[100]$ and $[001]$ magnetization orientations. The anisotropy energy was calculated as the difference in the eigenvalue sums between the two magnetization directions considered. For the anisotropy calculations, the number of k points over the IW used was approximately 1200 over 2/16 BZ. The calculated K_{out} is well converged (within 10^{-4} eV/fu) with respect to the number of k points used.

The self-consistent band structures (BS) and density of states (DOS) of the cubic CoFe_2O_4 are shown in Figs. 1 and 2, respectively. Due to the same spinel structure as well as the close atomic numbers, the half-metallic BS and DOS of CoFe_2O_4 are quite similar to those of Fe_3O_4 [13]. There is a gap of 0.57 eV at the Fermi level for the majority spin, while the conductivity results only from the partially filled minority-spin B-site 3d-band. The calculated spin moment in the Fe(A) atomic sphere of CoFe_2O_4 is $3.39 \mu_B$, being very close to $3.41 \mu_B$ of Fe(A) in Fe_3O_4 [13]. However, the average moment of $2.98 \mu_B$ for B-site of CoFe_2O_4 is about $0.5 \mu_B$ smaller than Fe(B) of Fe_3O_4 [13]. This is due to the fact that half of the B-site Fe atoms are randomly substituted by Co atoms of smaller spin moments. The moment of oxygen is $0.11 \mu_B$ which is the same as that in Fe_3O_4 [13]. The total moment of CoFe_2O_4 is thus $3 \mu_B/\text{fu}$. Since the spin-orbit coupling is small, the calculated orbital moments affect the spin moments only slightly.

We considered lateral strains in the (001) plane of CoFe_2O_4 with the cell volume unchanged. The most significant changes in BS and DOS under strains are in the majority-spin B-site 3d- e_g bands near the Fermi level. This band broadens, especially near the Γ point, with increasing magnitude of strains. Thus, at large strains, the top of the B-site 3d-band at the Γ point exceeds the Fermi level, and the half-metallic behavior turns into a normal metal state for high compressive ($\varepsilon \leq -1.3\%$) and high extensive ($\varepsilon \geq 2.1\%$) strains. In the

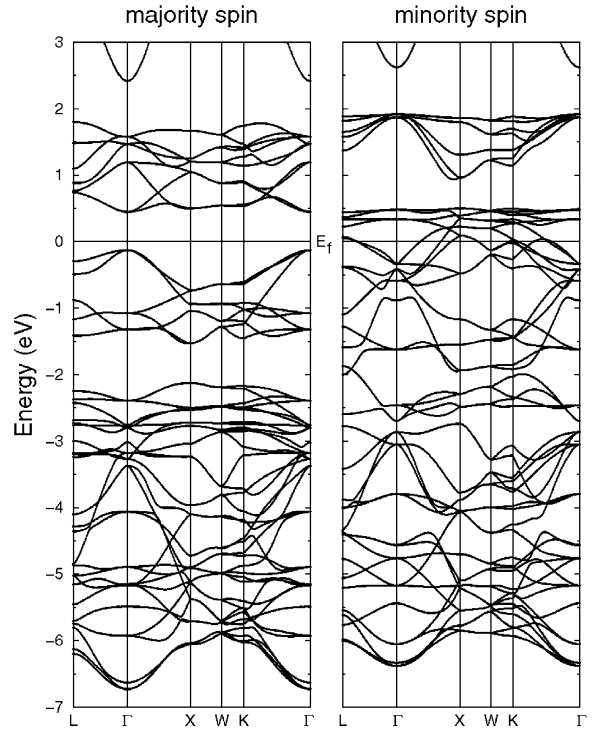


Fig. 1. Band structure of cubic CoFe_2O_4 .

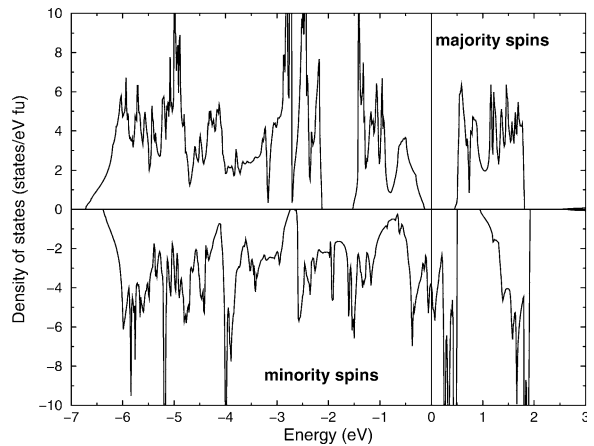


Fig. 2. Spin-decomposed densities of states for cubic CoFe_2O_4 .

meantime, the total magnetic moment is slightly suppressed during the insulator–metal transition in the majority spin.

The calculated out-of-plane anisotropy constant K_{out} (circle) of CoFe_2O_4 as a function of strain is shown in Fig. 3(a). The corresponding strains for CoFe_2O_4 on NiO, MgO, and CoO substrates as well as K_{out} (square) for Fe_3O_4 [13] are also shown in the figure. For both

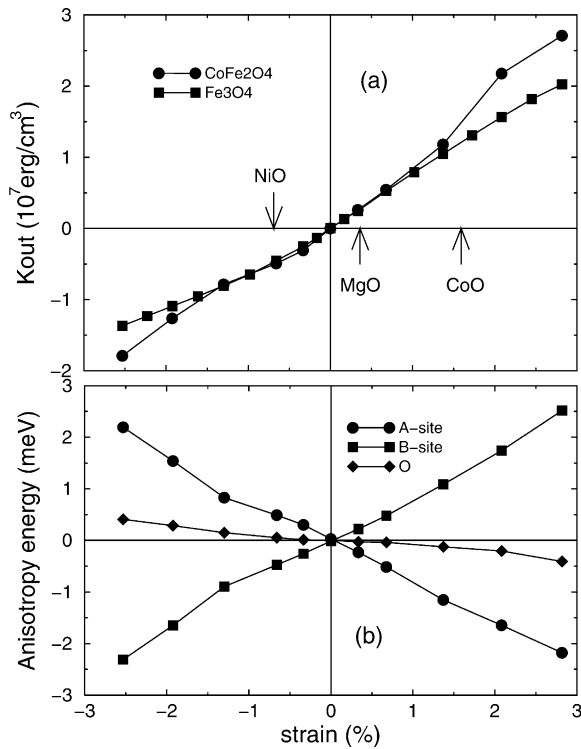


Fig. 3. (a) K_{out} of CoFe_2O_4 and Fe_3O_4 as a function of strain. (b) Site-decomposed anisotropy energies for CoFe_2O_4 as a function of strain.

CoFe_2O_4 and Fe_3O_4 , K_{out} show more or less linear dependences on the strain with slightly larger slopes in the positive strain region. For small strains ($-1.3\% \leq \varepsilon \leq 0.7\%$), K_{out} of CoFe_2O_4 is about the same as K_{out} of Fe_3O_4 . However, for high compressive and high extensive strains, the magnitude of K_{out} is enlarged by the Co substitutions in the B-site. The negative values of K_{out} for the negative strains indicate that a CoFe_2O_4 film on a substrate with a smaller lattice constant such as NiO would prefer an in-plane magnetization. On the other hand, for a CoFe_2O_4 film on a substrate of larger lattice constant such as MgO and CoO, the positive K_{out} implies the out-of-plane magnetization. There have been

several measurements on the K_{out} of the Fe_3O_4 film on MgO and CoO substrates and remarkably, they agree well with the calculated K_{out} of Fe_3O_4 under extensive strain [13–15]. However, we are not aware of any similar measurement for CoFe_2O_4 films.

In Fig. 3(b), we present the site-decomposed anisotropy energies of CoFe_2O_4 between [100] and [001] directions of magnetization as a function of strain. Despite the rather different electronic structures near the Fermi level for A- and B-sites (Figs. 1 and 2), the contributions from A- and B-sites are about the same amount, but in the opposite sign. The contribution from the oxygen atom is small. Since the number of B-sites is twice as many as that of A-sites, K_{out} is approximately equal to half of the sum of the anisotropy energies from B-sites.

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