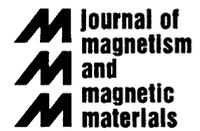




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# First-principles investigations of the magnetocrystalline anisotropy in strained Ni-substituted magnetite ( $\text{NiFe}_2\text{O}_4$ )

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## Abstract

The magnetocrystalline anisotropy energy of  $\text{NiFe}_2\text{O}_4$  under uniaxial strain along  $[001]$  direction has been studied by using the linear muffin-tin orbital method within the density functional theory. The calculated uniaxial anisotropy constant  $K_{\text{out}}$  is positive for extensive in-plane strains and is negative for compressive in-plane strains. The large value of positive  $K_{\text{out}}$  indicates that a  $\text{NiFe}_2\text{O}_4$  film under an extensive in-plane strain would strongly prefer the out-of-plane magnetization. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Magnetite; Ferrites; Anisotropy – magnetic; Electronic structure

Magnetite ( $\text{Fe}_3\text{O}_4$ ) is one of the most studied magnetic oxides because of the interesting electronic and magnetic properties as well as the potential industrial applications in magnetic multilayer devices. Above the Verwey transition temperature (120 K) [1], it crystallized in the inverse cubic spinel structure with one Fe atom on the tetrahedral A-site and two Fe atoms on the octahedral B-site per formula unit (fu). The high temperature phase of magnetite is a half-metallic ferrimagnet with magnetic moment on A-site antiparallel to the moment on B-site, resulting in a saturation moment of  $4\mu_{\text{B}}/\text{fu}$ . At the Verwey temperature, there is a sharp decrease in the conductivity by two orders of magnitude with a reduction in the magnetic moment to the low temperature phase [2]. Meanwhile, the metal–insulator transition is accompanied with a structure transition from cubic to monoclinic [3]. In spite of the long history of research on magnetite, the mechanism of the Verwey transition remains to be a challenging problem.

The Ni-substituted magnetite (nickel ferrite) has been studied experimentally by several authors recently for further investigation on the electronic, magnetic, and anisotropic properties of magnetite. Similar to the magnetite and the cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ), trevorite

( $\text{NiFe}_2\text{O}_4$ ) is also a half-metallic magnet with a smaller saturation magnetic moment of  $2.2\mu_{\text{B}}/\text{fu}$  [4].  $\text{NiFe}_2\text{O}_4$  forms in the same cubic spinel structure as  $\text{Fe}_3\text{O}_4$  with half of the B-site Fe atoms replaced by Ni atoms (i.e.,  $\text{Fe}_A[\text{NiFe}]_B\text{O}_4$ ), resulting in a lattice constant of  $8.35\text{ \AA}$  [5]. Mössbauer spectroscopy measurement showed that the Ni substitutions prefer the B-site sublattice of magnetite and distribute randomly over the crystal [6,7]. In an element-selective X-ray magnetic circular dichroism experiment [8], the orbital contribution to the magnetic moment for nickel atom in trevorite was found to be 12%. In contrast to the Co substitutions in cubic magnetite, which give rise to a relatively large but positive fourth order anisotropy constant  $K_1$  [4],  $\text{NiFe}_2\text{O}_4$  results in a smaller but negative  $K_1$ , being of the same sign as  $K_1$  of  $\text{Fe}_3\text{O}_4$ . Consequently,  $[111]$ ,  $[001]$ , and  $[1\bar{1}1]$  are the easy directions of magnetization for cubic  $\text{Fe}_3\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ , and  $\text{NiFe}_2\text{O}_4$ , respectively.

The local-spin-density approximation has been used to calculate the band structure of cubic  $\text{Fe}_3\text{O}_4$  by several authors [9–12]. They all give a consistent half-metallic electronic structure with a magnetic moment of  $4\mu_{\text{B}}/\text{fu}$ . Further, the half-metallic band structure has been obtained for cubic  $\text{CoFe}_2\text{O}_4$  with a magnetic moment of  $3\mu_{\text{B}}/\text{fu}$  in band calculations [11,13]. However, because of the smallness and the large amount of

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computing requirement for large spinel cell, no magnetocrystalline anisotropy energy calculations for magnetite and substituted magnetites have been reported. We have recently performed anisotropy energy calculations for cubic and strained magnetite ( $\text{Fe}_3\text{O}_4$ ) [12] as well as Co-substituted magnetite ( $\text{CoFe}_2\text{O}_4$ ) [13]. The obtained results for  $\text{Fe}_3\text{O}_4$  agree with experimental data quite well. The purpose of this work is to investigate the anisotropy energies of the Ni-substituted magnetite ( $\text{NiFe}_2\text{O}_4$ ) under uniaxial strains.

The out-of-plane anisotropy constant  $K_{\text{out}}$  for a cubic crystal under a uniaxial strain along  $[001]$  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 [12]. The computing method used in this work has been described in Ref. [12]. We first performed self-consistent scalar-relativistic calculations for each considered strain by using the linear muffin-tin orbitals method. The randomly distributed B-site substitutions of Ni atoms were treated by using the virtual crystal approximation. About 600  $k$  points over the irreducible wedge (IW) was used in the self-consistent calculations over 1/16 of the body-centered tetragonal Brillouin zone (BZ). After the self-consistent calculation for each strain considered, the resultant potential was used to perform the fully relativistic band structure calculation once for each of the  $[100]$  and  $[001]$  magnetization orientations. The anisotropy energy was then obtained 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  $K_{\text{out}}$  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  $\text{NiFe}_2\text{O}_4$  are shown in Figs. 1 and 2, respectively. Because of the same cubic spinel structure as well as the close atomic numbers, the half-metallic BS and DOS of  $\text{NiFe}_2\text{O}_4$  are quite similar to those of  $\text{Fe}_3\text{O}_4$  [12] and  $\text{CoFe}_2\text{O}_4$  [13]. For  $\text{NiFe}_2\text{O}_4$ , the gap of 0.37 eV in the majority spin at the Fermi level is smaller as compared with 0.54 eV for  $\text{Fe}_3\text{O}_4$  [12] and 0.57 eV for  $\text{CoFe}_2\text{O}_4$  [13]. Due to the Ni substitution, the upper edge of the B-site 3d- $e_g$  band is only 0.014 eV lower than the Fermi level. Whereas 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  $\text{NiFe}_2\text{O}_4$  is  $3.36 \mu_B$ , being close to  $3.39 \mu_B$  of  $\text{CoFe}_2\text{O}_4$  [13] and  $3.41 \mu_B$  of  $\text{Fe}_3\text{O}_4$  [12]. Because of the random substitutions in half B-sites by Ni atoms of smaller spin moments, the average moment for B-site of  $\text{NiFe}_2\text{O}_4$  is  $2.45 \mu_B$ , being about 1 and  $0.5 \mu_B$  smaller than B-site moment in  $\text{Fe}_3\text{O}_4$  [12] and in  $\text{CoFe}_2\text{O}_4$  [13], respectively. The moment of oxygen is

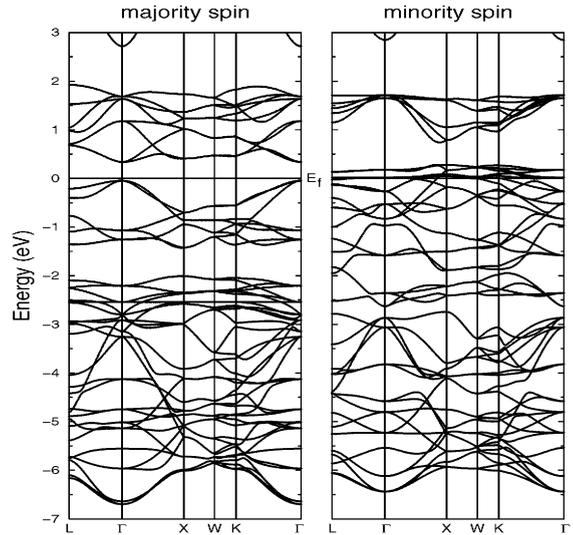


Fig. 1. Band structure of cubic  $\text{NiFe}_2\text{O}_4$ .

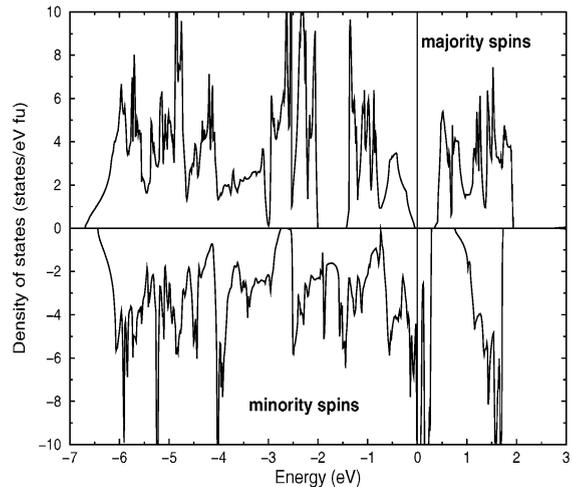


Fig. 2. Spin-decomposed densities of states for cubic  $\text{NiFe}_2\text{O}_4$ .

$0.11 \mu_B$  which is the same as obtained in  $\text{Fe}_3\text{O}_4$  [12] and in  $\text{CoFe}_2\text{O}_4$  [13]. The calculated total moment for  $\text{NiFe}_2\text{O}_4$  is  $2 \mu_B/\text{fu}$ . Although the spin-orbit coupling is small and slightly reduces the B-site spin moment to  $2.44 \mu_B$ , the calculated orbital moment for Ni atom in B-sites under  $[001]$  magnetization is  $0.32 \mu_B$ . Hence the orbital contribution to the magnetic moment would be 12%, being in good agreement with recent experiment measurement [8].

We considered lateral strains in the  $(001)$  plane of  $\text{NiFe}_2\text{O}_4$  with fixed cell volume. Similar to the visible changes in BS and DOS of  $\text{Fe}_3\text{O}_4$  [12] and of  $\text{CoFe}_2\text{O}_4$  [13] under strain, the majority-spin B-site 3d- $e_g$  band below the Fermi level broadens, especially near the  $\Gamma$  point. Since this band top of  $\text{NiFe}_2\text{O}_4$  is quite close to

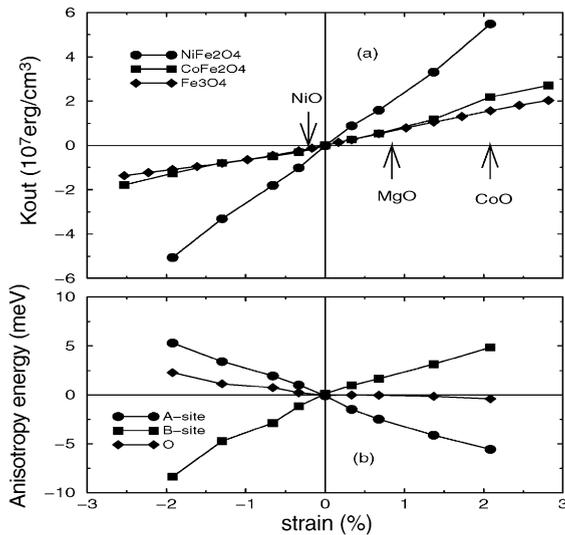


Fig. 3. (a)  $K_{out}$  of  $\text{NiFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  as a function of strain. (b) Site-decomposed anisotropy energies for  $\text{NiFe}_2\text{O}_4$  as a function of strain.

the Fermi level, the band broadening simply eliminates the majority-spin gap at the Fermi level under all the strains considered. Thus, the half-metallic behavior exists only for cubic  $\text{NiFe}_2\text{O}_4$  and would turn into normal metal state under both compressive and extensive strains. Note that the upper edge of this band in  $\text{Fe}_3\text{O}_4$  [12] and in  $\text{CoFe}_2\text{O}_4$  [13] are, respectively, 0.14 and 0.12 eV lower than the Fermi level. They remain to be half-metallic under strains within an interval from about  $-1.3\%$  to  $2.1\%$ . Besides the insulator-metal transition in the majority spin, the total magnetic moment of  $\text{NiFe}_2\text{O}_4$  is slightly suppressed by the applied strains.

The calculated anisotropy constant  $K_{out}$  (circle) of  $\text{NiFe}_2\text{O}_4$  as a function of strain is shown in Fig. 3(a). The corresponding strains for  $\text{NiFe}_2\text{O}_4$  on NiO, MgO, and CoO substrates as well as  $K_{out}$  for  $\text{Fe}_3\text{O}_4$  (diamond) [12] and  $\text{CoFe}_2\text{O}_4$  (square) [13] are also shown in the figure.  $K_{out}$  for the three compounds all show more or less linear dependences on the strain with slightly larger slopes in the positive strain region. For both  $\text{CoFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ ,  $K_{out}$  are quite similar to each other under small strains, while the magnitude of  $K_{out}$  for  $\text{CoFe}_2\text{O}_4$  is slightly larger under high strains [13]. However,  $K_{out}$  for  $\text{NiFe}_2\text{O}_4$  is 2–5 times larger than  $K_{out}$  for both  $\text{CoFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  as shown in the figure. The negative values of  $K_{out}$  for the negative strains indicate

that a  $\text{NiFe}_2\text{O}_4$  film on a substrate with a smaller lattice constant such as NiO would prefer an in-plane magnetization. On the other hand, for a  $\text{NiFe}_2\text{O}_4$  film on a substrate of larger lattice constant such as MgO and CoO, the positive  $K_{out}$  implies the perpendicular magnetization. The relatively large magnitude of positive  $K_{out}$  for  $\text{NiFe}_2\text{O}_4$  under extensive strain indicates that the  $\text{NiFe}_2\text{O}_4$  thin film is the best candidate among the three compounds studied for manipulating the out-of-plane magnetization. There have been several measurements on the  $K_{out}$  of  $\text{Fe}_3\text{O}_4$  film on MgO and CoO substrates and remarkably, they agree well with the calculated  $K_{out}$  of  $\text{Fe}_3\text{O}_4$  under extensive strain [12]. However, we are not aware of any similar measurement for  $\text{NiFe}_2\text{O}_4$  films.

The site-decomposed anisotropy energy of  $\text{NiFe}_2\text{O}_4$  between  $[100]$  and  $[001]$  directions of magnetization as a function of strain is shown in Fig. 3(b). Although the electronic structures near the Fermi level for A- and B-site (Figs. 1, 2) are rather different, the contributions from A- and B-site are about the same size but opposite in sign, while the contribution from an oxygen atom is small.  $K_{out}$  is approximately equal to half of the sum of the anisotropy energies from B-sites, since the number of B-sites is twice as many as that of A-sites.

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