12-28-2017

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Magnetocrystalline anisotropy of ε-Fe$_2$O$_3$

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The epsilon Fe$_2$O$_3$ phase of iron oxide has been studied to understand the spin structure and the magnetocrystalline anisotropy in the bulk and in thin films of ε-Fe$_2$O$_3$ and Co-doped ε-Fe$_2$O$_3$. The preferential magnetization direction in the nanoparticles of ε-Fe$_2$O$_3$ is along the *a*-axis [M. Gich *et al.*, Chem. Mater. **18**, 3889 (2006)]. Compared to the bulk band gap of 1.9 eV, the thin-film band gap is reduced to 1.3 eV in the Co-free films and to 0.7 eV in the film with partial Co substitution. The easy magnetization direction of the bulk and Co-free ε-Fe$_2$O$_3$ is along the *c*-axis, but it switches to the *a*-axis on Co substitution. All three systems exhibit in-plane anisotropies associated with the orthorhombic crystal structure of the oxide. *© 2017 Author(s).*
https://doi.org/10.1063/1.5007659

I. INTRODUCTION

The metastable oxide ε-Fe$_2$O$_3$, a rare polymorph of Fe$_2$O$_3$, has recently attracted interest as a material for photoelectrochemistry and as the only magnetoelectric Fe$_2$O$_3$ phase.[1] The oxide was first identified by Forestier and Guiot-Guillain in 1934 but has actually been an ingredient of Tenmoku glaze on Chinese pottery for about a thousand years.[2] This rare phase of Fe$_2$O$_3$ is orthorhombic and has the space-group Pna2$_1$.[1] Figure 1 shows the bulk crystal structure of ε-Fe$_2$O$_3$. The unit cell contains 8 formula units of Fe$_2$O$_3$, thus having a total of 40 atoms. The experimental lattice parameters are $a = 5.095$ Å, $b = 8.789$ Å and $c = 9.437$ Å.[3]

The interatomic exchange coupling is A-type antiferromagnetic, characterized by the spin directions (β, α, α, β) for the (Fe$_A$, Fe$_B$, Fe$_C$, Fe$_D$) atoms. Fe$_A$ and Fe$_B$ are coordinated by distorted octahedrals, Fe$_C$ exhibits a regular octahedral coordination, and Fe$_D$ is tetrahedrally coordinated. Since the four Fe atoms are nonequivalent, the spin structure is ferrimagnetic, with a magnetization of about 0.1 T and a Curie temperature of 510 K. However, it is only partially clear whether the spin structure is collinear or noncollinear.[1,3,4] Recent in-field Mössbauer experiments[5] indicate collinear ferrimagnetism.

Coercivities H_c as high as 20 kOe [2 T] have been reported for ε-Fe$_2$O$_3$ nanoparticles,[4] but these high coercivities may reflect the small spontaneous magnetization M_s rather than a particularly high anisotropy constant K_1,[6] since $H_c \sim 2K_1/M_s$. The coercivity of 20 kOe of nanoparticles of ε-Fe$_2$O$_3$ is reduced to an in-plane coercivity of 8 kOe[7] in epitaxially stabilized (001) thin films on SrTiO$_3$ (111). Tanskanen *et al.*[8] reported coercivity of 1.6 kOe for thin films grown by atomic layer deposition. Namai *et al.*[9] enhanced the coercivity of ε-Fe$_2$O$_3$ nanomagnets by the substitution of rhodium. To understand the coercive behavior of ε-Fe$_2$O$_3$, it is necessary to explain and describe the magnetocrystalline anisotropy of the oxide.

In this paper, we use *ab-initio* calculations to investigate the spin structure and magnetic anisotropy of bulk and thin-film ε-Fe$_2$O$_3$. Concerning the magnetic anisotropy, we reproduce the experimental findings and address the important point that orthorhombic crystals have two

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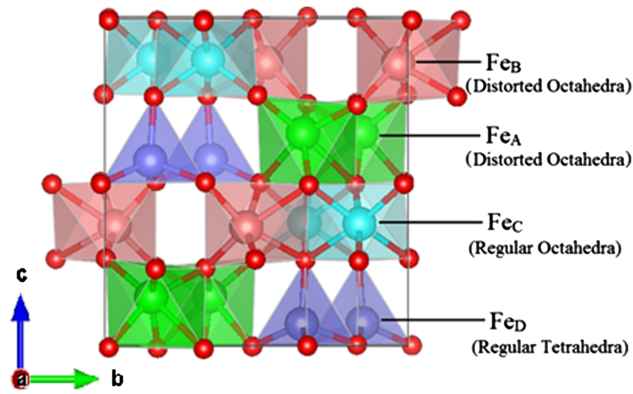
FIG. 1. Bulk crystal structure of ε-Fe$_2$O$_3$.

lowest-order anisotropy constants, namely K_1 and K_1'.[10] Finally, we outline the effects of Co substitution, which enhances the anisotropy by creating more than half-filled $3d$ shells, and of the surface contribution to the magnetic anisotropy of ε-Fe$_2$O$_3$.

II. METHOD

We have used the Vienna *ab-initio* simulation package (VASP),[11–13] employing the generalized gradient approximation (GGA),[14] a Hubbard U,[15] and a projector-augmented wave (PAW)[13] potential. The magnetocrystalline anisotropy (Sect. III. C) was determined by evaluating the total energies for magnetization directions parallel to the x-, y-, and z-directions, using spin-orbit coupling as implemented in VASP by Kresse and Lebacq. An energy cutoff of 530 eV was used for representing the electronic wave functions.

Aside from bulk ε-Fe$_2$O$_3$ (Fig. 1), we have investigated the thin-film structures shown in Fig. 2. The films of thickness 10.18 Å were constructed as supercells along the z-direction and a vacuum of
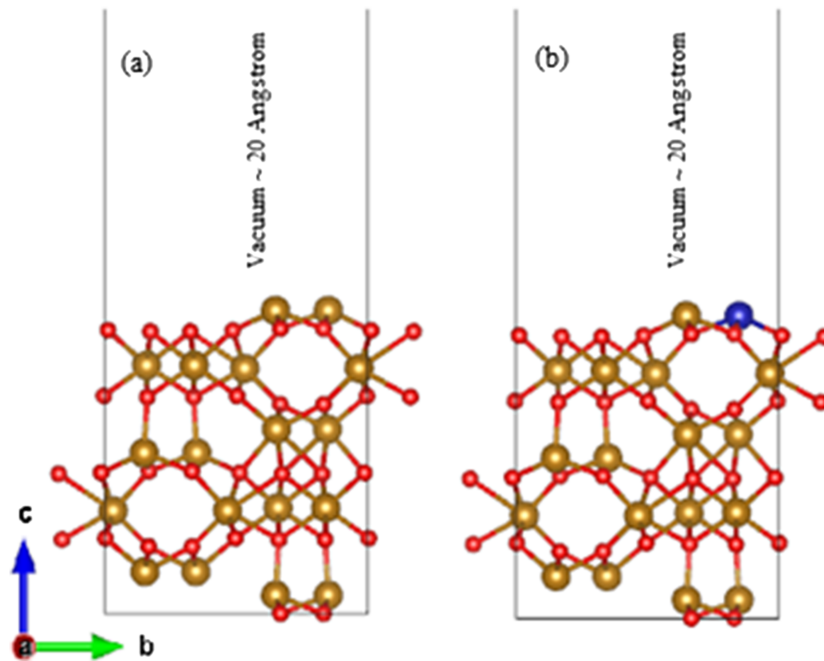

FIG. 2. Investigated thin-films structures: (a) ε-Fe$_2$O$_3$ thin film in the *a-b* plane (*x-y* plane), and (b) Co-substituted oxide. (Red, orange, and blue colors are used to indicate O, Fe, and Co, respectively.)

20 Å inserted between the periodic images of the film to avoid interaction effects. The Co-substituted thin film was obtained by just replacing one of the two Fe_D atoms by a Co atom in the top layer. The optimized lattice parameters for bulk are $a = 5.125$ Å, $b = 8.854$ Å and $c = 9.563$ Å.

III. RESULTS AND DISCUSSION

Among the possible spin structures (β, α, α, β), *(α, β, α, β)*, (α, α, β, β), and (α, α, α, α), the configuration (β, α, α, β) has the lowest calculated energy in both bulk ε-Fe_2O_3 and in the Co-free and Co-substituted thins films. For this reason, the following subsections deal with (β, α, α, β) spin structures exclusively.

A. Bulk calculations

Volume optimization and ionic relaxation were performed for the bulk structure, and the electronic structure was calculated using a *k*-point grid of $5 \times 3 \times 3$. The *U-J* parameter used in the calculations is 4 eV. This value corresponds to the *U* of hematite (α-Fe_2O_3), since no information is available for ε-Fe_2O_3. Figure 3 shows the density of states for the bulk structure. The predicted band gap is 1.9 eV, in agreement with the *ab-initio* studies of Yoshikiyo *et al.*[16] The magnetic moment of 0.143 μ_B per unit cell comes nearly exclusively from Fe atoms and indicates an A-type antiferromagnetic ordering resulting in a ferrimagnetic ground state.

B. Thin-film calculations

The electronic structure of the thin films was calculated after volume optimization and complete relaxation, using a *k*-point grid of $5 \times 3 \times 1$. The density of states of the thin film and Co-substituted thin film is shown in Fig. 4.

The ε-Fe_2O_3 thin film shows a band gap of 1.3 eV in the spin-down channel, whereas the spin-up channel near the Fermi level is occupied by Fe surface states. For the Co-substituted thin film, there are surface states due to the Co atoms, but the band gap of about 0.732 eV is same for both spin channels.

C. Magnetocrystalline anisotropy

The magnetocrystalline anisotropies of bulk and thin-film ε-Fe_2O_3 were calculated by including the spin-orbit coupling and evaluating the total magnetic energy as a function of the magnetization angle (Sect. II). The Brillouin-zone integration for the anisotropy calculations was performed
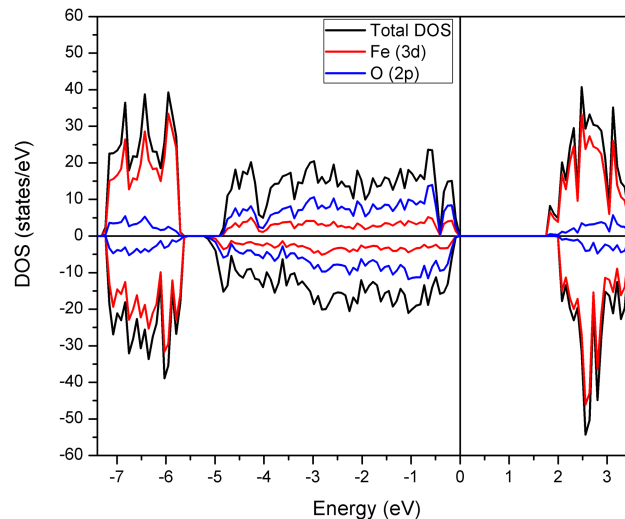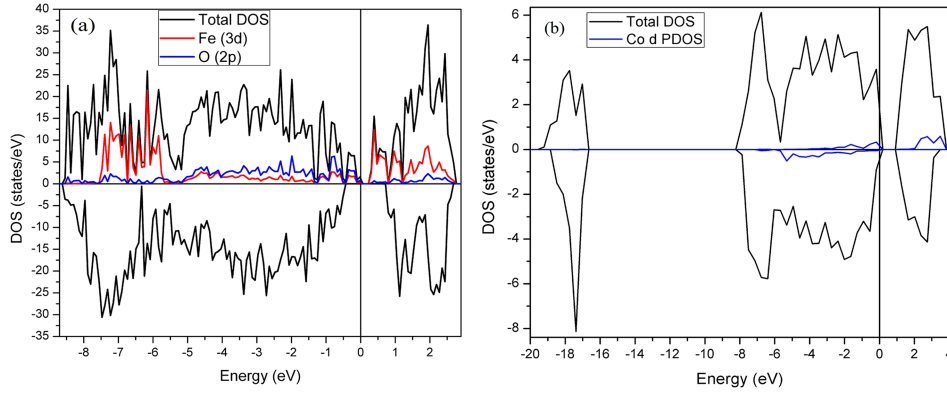

FIG. 3. The total density of states of bulk ε-Fe_2O_3 with partial density of states of Fe 3*d* and O 2*p* states.

FIG. 4. The total densities of states in (a) pristine and (b) Co-substituted thin films of ε-Fe$_2$O$_3$.

TABLE I. The anisotropy constants K_1 and K_1' for bulk ε-Fe$_2$O$_3$, thin-film ε-Fe$_2$O$_3$, and Co-substituted thin-film ε-Fe$_2$O$_3$.

System	E_x (eV)	E_y (eV)	E_z (eV)	K_1 (kJ/m^3)	K_1' (kJ/m^3)
Bulk ε-Fe$_2$O$_3$	−273.63460089	−273.63460877	−273.63461010	4.93	2.91
Co-free thin film	−293.26412576	−293.26415896	−293.26417920	2.36	3.88
Co-substituted thin film	−291.92083283	−291.92080945	−291.92080544	-0.47	-2.73

using Monkhorst-Pack k-point meshes of $11 \times 11 \times 11$ for the bulk and $11 \times 11 \times 1$ for the thin films.

Due to the orthorhombic crystal structure it is sufficient to evaluate the energy for the three principal directions $\mathbf{e}_x$, $\mathbf{e}_y$, and $\mathbf{e}_z$ along the a-, b-, and c-axes, respectively. The definition[10,17]

$$\frac{E}{V} = K_1 \sin^2\theta + K_1' \sin^2\theta \cos 2\phi \tag{1}$$

yields $K_1 = (E_y - E_z)/V$ and $K_1' = (E_x - E_y)/V$. In these equations, V is the volume of the unit-cell and E_x, E_y and E_z are the energies when the spins are aligned in the x-, y- and z-directions, respectively. The calculated bulk and thin-film energies are listed in Table I.

Bulk ε-Fe$_2$O$_3$ behaves like a uniaxial easy-axis magnet ($K_1 > 0$) with a preferred magnetization direction in the z-direction and in-plane anisotropy ($K_1' \neq 0$), except that the in-plane anisotropy is very high (of second order), as contrasted to fourth-order in-plane anisotropy in tetragonal structures and the sixth-order in-plane anisotropy in hexagonal and trigonal (rhombohedral) structures. The same situation is found for the Co-free thin films, except the respective magnitudes of K_1 is smaller and K_1' is larger than in the bulk. The Co addition yields a spin-reorientation transition, the easiest axis switching from the z- to the x-direction and relatively small 'in-plane' anisotropy in the y-z plane (b-c plane). The calculated anisotropies are all relatively small (several kJ/m^3), but the small magnetization and the orthorhombic crystal structure helps to create high coercivity, because K_1' imposes additional restrictions on magnetization rotations.

IV. CONCLUSIONS

In summary, we have used the first-principle calculations to study the electronic structure of the bulk ε-Fe$_2$O$_3$ as well as cobalt-free and cobalt containing thin films of ε-Fe$_2$O$_3$. Compared to the bulk band gap of 1.9 eV, the thin-film band gap is reduced to 1.3 eV in the Co-free films and to 0.7 eV in the film with partial Co substitution. The easy magnetization direction of the bulk and Co-free ε-Fe$_2$O$_3$ is along the c-axis, but it switches to the a-axis on Co substitution. All three systems exhibit substantial in-plane anisotropies associated with the orthorhombic crystal structure of the oxide.

ACKNOWLEDGMENTS

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