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Magnetocrystalline anisotropy of ϵ -Fe₂O₃

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The epsilon Fe₂O₃ 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 -Fe₂O₃ and Co-doped ϵ -Fe₂O₃. The preferential magnetization direction in the nanoparticles of ϵ -Fe₂O₃ 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 -Fe₂O₃ 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). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.5007659>

I. INTRODUCTION

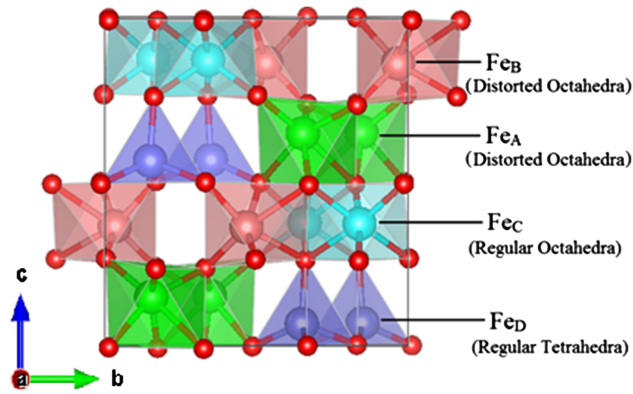
The metastable oxide ϵ -Fe₂O₃, a rare polymorph of Fe₂O₃, has recently attracted interest as a material for photoelectrochemistry and as the only magnetoelectric Fe₂O₃ phase.¹ The oxide was first identified by Forestier and Guiot-Guillain in 1934 but has actually been an ingredient of Tenmoku glaze on Chinese pottery for about a thousand years.² This rare phase of Fe₂O₃ is orthorhombic and has the space-group Pna2₁.¹ Figure 1 shows the bulk crystal structure of ϵ -Fe₂O₃. The unit cell contains 8 formula units of Fe₂O₃, 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 experiments⁵ indicate collinear ferrimagnetism.

Coercivities *H_c* as high as 20 kOe [2 T] have been reported for ϵ -Fe₂O₃ nanoparticles,⁴ but these high coercivities may reflect the small spontaneous magnetization *M_s* rather than a particularly high anisotropy constant *K₁*,⁶ since *H_c* ~ 2*K₁*/*M_s*. The coercivity of 20 kOe of nanoparticles of ϵ -Fe₂O₃ is reduced to an in-plane coercivity of 8 kOe⁷ in epitaxially stabilized (001) thin films on SrTiO₃ (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 -Fe₂O₃ nanomagnets by the substitution of rhodium. To understand the coercive behavior of ϵ -Fe₂O₃, 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 -Fe₂O₃. 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_2O_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_2O_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 Lebacqz. An energy cutoff of 530 eV was used for representing the electronic wave functions.

Aside from bulk ϵ - Fe_2O_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

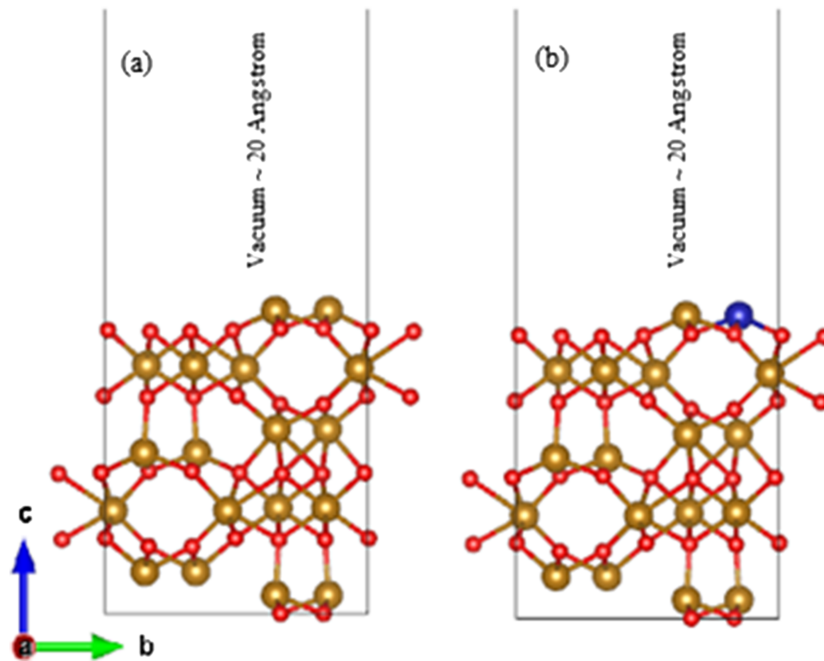


FIG. 2. Investigated thin-film structures: (a) ϵ - Fe_2O_3 thin film in the a - b plane (x - y plane), and (b) Co-substituted oxide. (Red, orange, and blue colors are used to indicate O, Fe, and Co, respectively.)

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 ($\beta, \alpha, \alpha, \beta$), ($\alpha, \beta, \alpha, \beta$), ($\alpha, \alpha, \beta, \beta$), and ($\alpha, \alpha, \alpha, \alpha$), the configuration ($\beta, \alpha, \alpha, \beta$) has the lowest calculated energy in both bulk ε -Fe₂O₃ and in the Co-free and Co-substituted thin films. For this reason, the following subsections deal with ($\beta, \alpha, \alpha, \beta$) 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 -Fe₂O₃), since no information is available for ε -Fe₂O₃. 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 -Fe₂O₃ 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 -Fe₂O₃ 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

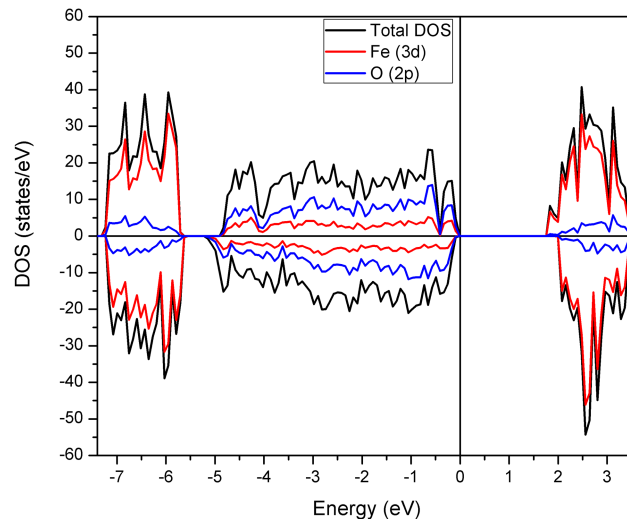
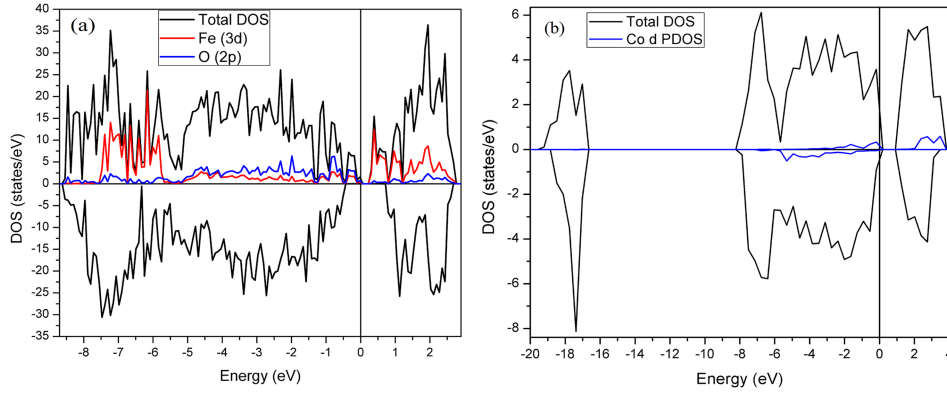


FIG. 3. The total density of states of bulk ε -Fe₂O₃ with partial density of states of Fe 3d and O 2p states.

FIG. 4. The total densities of states in (a) pristine and (b) Co-substituted thin films of ϵ -Fe₂O₃.TABLE I. The anisotropy constants K_1 and K_1' for bulk ϵ -Fe₂O₃, thin-film ϵ -Fe₂O₃, and Co-substituted thin-film ϵ -Fe₂O₃.

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}

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

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 -Fe₂O₃ 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/m³), 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 -Fe₂O₃ as well as cobalt-free and cobalt containing thin films of ϵ -Fe₂O₃. 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 -Fe₂O₃ 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.

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