

Strain-induced magnetic anisotropy in spinel ferrites

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Magnetic anisotropy is one of the more important properties of magnetic materials. Since the magnetic anisotropy arises from spin-orbit interaction accompanying local/global symmetry reduction, both the anisotropy energy and sign can be controlled by a relatively slight perturbation such as lattice strain. Because of their large spin-orbit interaction, most magnetic materials exhibiting large magnetic anisotropy energy contain heavy metals or rare earth elements such as palladium, platinum, bismuth, neodymium samarium and so on.

Among some 3d-transition metal oxides with degeneracy arising from their peculiar electron configuration in the t_{2g} states, orbital momentum of $\sim 1 \mu_B$ is seen on the 3d ions. If the relatively large orbital momentum couples with the spin momentum, a large magnetic anisotropy can emerge even in the absence of rare metals. In fact, some spinel ferrites containing Co^{2+} ions have been known to show large anisotropy as well as high coercivity¹. The crystal field for Co^{2+} ions in a bulk cobalt ferrite is primarily cubic because of the Co^{2+} ions being located at the octahedral sites (B-sites). Moreover, since the B-site cations of the second nearest neighbor form a trigonal crystal field, the t_{2g} electron configuration of the Co^{2+} ions is split into a single lowest level and two degenerate levels. Since the single electron occupying the doubly degenerate states has $\sim 1 \mu_B$, it therefore exhibits a large cubic magnetic anisotropy K_1 as well as magnetization enhancement^{2,3}.

When cobalt ferrite is grown as epitaxially strained thin films, the films undergo compressive/tensile stress depending on the lattice misfit between the cobalt ferrite and the substrate. The induced uniaxial magnetic anisotropy K_u from the uniaxial strain (or tetragonal distortion) can be understood by a phenomenological treatment within the framework of the magnetoelastic effect. The induced K_u is also interpreted by an electronic model as equivalent to K_1 of the bulk cobalt ferrite⁴. Since the tetragonal distortion also splits the t_{2g} electron configuration of Co^{2+} into a single lowest level and double degenerate levels like in the bulk case, a significantly large K_u is induced. The epitaxial films of cobalt ferrite grown on a square lattice such as the surface of $\text{MgO}(001)$ (tensile stress) and $\text{MgAl}_2\text{O}_4(001)$ (compressive stress) are tetragonally distorted and consequently show K_u . If the induced K_u is greater than the demagnetization energy of $2\pi M_s^2 \sim 1.0 \text{ Merg/cm}^3$, the film exhibits perpendicular magnetization. Practically, we have demonstrated that a high-quality epitaxial film of $\text{Co}_{0.75}\text{Fe}_{2.25}\text{O}_4(001)/\text{MgO}(001)$ exhibits K_u as large as 10.0 Merg/cm^3 .⁵

Thus, in order to develop new candidate materials for permanent magnets, it seems to be a promising strategy to intentionally induce a lattice strain in spinel ferrites containing Co^{2+} ions. According to the phenomenological model, a larger distortion produces a higher magnetic anisotropy in a linear relationship. However, this picture is valid only for a small distortion. To evaluate the potential of cobalt ferrite as a large magnetic anisotropy material, it is worth investigating how we can apply epitaxial strain and induce a large K_u . Moreover, by introducing a large lattice distortion into the bulk or particles of cobalt-based spinel ferrite, this magnetic compound may become a new candidate material of the rare-earth free magnet. In this presentation, we will show our attempts to enhance the magnetic anisotropy of cobalt ferrite in both film- and particle-forms.

Epitaxial films of $\text{Co}_{0.75}\text{Fe}_{2.25}\text{O}_4(001)$ were grown by reactive magnetron sputtering with an alloy target. In order to induce a large lattice distortion into the films, we investigated many different oxide substrates and buffer layers. We found that the inverse spinel of $\text{Mg}_2\text{SnO}_4(001)$ is appropriate as a buffer layer with a large lattice misfit and that a 10-nm-thick $\text{Co}_{0.75}\text{Fe}_{2.25}\text{O}_4(001)$ film grown on $\text{Mg}_2\text{SnO}_4(001)$ exhibits K_u larger than 25.0 Merg/cm^3 . To our knowledge, this is the largest K_u ever reported in a spinel ferrite thin film. Although the lattice misfit is as large as $\sim 3.1\%$, the induced K_u can be quantitatively explained by the magnetoelastic theory.

Since lattice strain of several percent effectively induces large K_u in cobalt ferrite, we attempted to spontaneously distort the spinel ferrite particles via the Jahn-Teller effect. Jahn-Teller ions such as Cu^{2+} were chosen on a trial basis though expected saturation magnetization for this compound is small. $(\text{Cu}, \text{Co})\text{Fe}_2\text{O}_4$ particles were prepared by coprecipitation method followed by flux treatment of KBr. After the flux treatment, $(\text{Cu}, \text{Co})\text{Fe}_2\text{O}_4$ with a cubic spinel was obtained. Post annealing process in the atmosphere facilitated the crystal structure transformation from cubic to tetragonal. Although the magnetization curve of $\text{Co}_{0.1}\text{Cu}_{0.9}\text{Fe}_2\text{O}_4$ particles grown before the post annealing process shows coercivity as small as

300 Oe, after annealing 2200 Oe of coercivity was observed, reflecting the induced tetragonal distortion. All the experimental results indicate that Jahn-Teller ions definitely induce local/global distortion into the spinel structure and the distortion increases the magnetic anisotropy through the locally distorted crystal field of the Co^{2+} ions.

References

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