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Atomic-layer Alignment Tuning for Giant Perpendicular Magnetocrystalline Anisotropy of 3d Transition-metal Thin Films

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Abstract

The magnetocrystalline anisotropy (MA) of Fe-based transition-metal thin films, consisting of only magnetic 3d elements, was systematically investigated from first-principles FLAPW calculations. The results predict that giant MA with a perpendicular magnetic easy axis (PMA) can be achieved by tuning the atomic-layer alignments in an Fe-Ni thin film. This giant PMA arises from the spin-orbit coupling interaction between occupied and unoccupied Ni \(d_{x^2-y^2,xy}\) bands crossing the Fermi level. A promising 3d transition-metal thin film for the MgO-based magnetic tunnel junctions with the giant PMA was thus demonstrated.

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Much interest in magnetic tunnel junctions (MTJs) with a perpendicular magnetic easy axis [perpendicular magnetocrystalline anisotropy (PMA)], consisting of ferromagnetic transition-metal thin films with a MgO barrier, has rapidly increased in ultrahigh density and nonvolatile spin-electronics.[1, 2] Currently, experimental efforts have successfully synthesized artificial transition-metal thin films including rare-earth and noble (Pt, Pd) elements,[3–9] which exhibit large PMA that promisingly overcomes the shape in-plane magnetic anisotropy and thermal fluctuations on a device level.

In parallel, efforts for searching promising PMA materials with no requirement of such additional rare-earth/noble elements have remained a great challenge.[10–14] A key feature dealing with large PMA systems of the 3d transition-metals is in understanding and controlling the spin-orbit coupling interaction (SOC), \( H_{soc} = \xi(r)\sigma \cdot \ell \), in ferromagnetic thin films and at surfaces and interfaces.[15] For the 3d transition-metals, since the SOC strength, \( \xi(r) \), is weak due to the weak Coulomb potential near the 3d atom’s nucleus, the magnetocrystalline anisotropy (MA) energy generally reduces to \( 10^{-3} \) meV in cubic bulk systems, i.e., much smaller than that in rare-earth/noble materials. However, at surfaces and interfaces, the MA energy reaches as much as \( 10^{-1} \) meV, induced by symmetry lowering and orbital localization at surfaces/interfaces. Remarkably, recent findings of the PMA in Fe/MgO(001)[16, 17] and CoFeB/MgO(001)[2, 18, 19] interfaces, where a weak Fe \( d_{z^2} \)–O \( p_z \) hybridization at the interface enhances the PMA, have let to an important avenue toward the successful MTJ devices with the PMA.

In our search for PMA materials, the MA of Fe-based transition-metal thin films, consisting of only magnetic 3d elements of Mn, Fe, Co, and Ni, was systematically investigated by means of first principles full-potential linearized augmented plane-wave (FLAPW) method.[20, 21] As a major achievement, here, we find that apart from the interfacial PMA [2, 16–18], a giant PMA can be achieved by tuning the atomic-layer alignments in an Fe-Ni film, arising from the SOC between occupied and unoccupied Ni \( d_{x^2-y^2,xy} \) bands crossing the Fermi level (\( E_F \)). Thus, a tailored 3d transition-metal thin film for the MTJs with giant PMA, without the rare-earth/noble elements, was demonstrated.

Calculations were performed based on generalized gradient approximation (GGA)[22] by using the FLAPW method with a single slab geometry, in which the core states are treated fully relativistically and the valence states are treated semi-relativistically (SRA), i.e., without SOC. The LAPW functions with a cutoff of \( |\mathbf{k} + \mathbf{G}| \leq 3.9 \) a.u. and muffin-tin
(MT) sphere radii of 2.2 a.u. for Mn, Fe, Co, and Ni atoms are used, where the angular-momentum expansion inside the MT spheres is truncated at $\ell=8$ for the wave functions, charge and spin densities, and potential.

To determine the MA, the second variational method[23] for treating the SOC was performed by using the calculated eigenvectors in the SRA, and the MA energy, $E_{MA}$, is determined by the force theorem,[24, 25] which is defined as the energy eigenvalue difference for the magnetization oriented along the in-plane and the perpendicular directions to the film plane. The use of 7056 special k-points in the two-dimensional Brillouin zone (BZ) was sufficient to suppress numerical fluctuations less than 0.01 meV in the $E_{MA}$.

As models of the thin films, as shown in Fig. 1, we employed five and seven-layer slabs with a bcc-like-layer stacking, where both sides of the films are terminated by Fe layers for taking an advantage to include the Fe/MgO interfaces. Possible atomic-layer alignments with the Fe and the other 3$d$ elements (Mn, Co, and Ni), type I, II, and III structures for the five-layer film and type I-VI structures for the seven-layer film, are considered. For simplicity, symmetric alignments along the $z$-axis were imposed. For the magnetic structure, a ferromagnetic state with the lowest energy state, except an anti-parallel Mn moment at the center-layer in the type III Fe-Mn structure, is considered. The in-plane lattice constant is assumed to match the calculated value of bulk MgO, $a=3.01\,\text{Å}$, and all atomic positions are fully optimized by atomic force calculations.

The calculated $E_{MA}$ are summarized in Fig. 1, where the $E_{MA}$ of the pure Fe film is also given by the dashed horizontal lines. The pure Fe films have a positive $E_{MA}$, 0.86 and 0.80 meV/$a^2$ for both five and seven-layer films, which indicates that the magnetization energetically favors pointing in the perpendicular (PMA) direction. In the five-layer film for all Fe-Mn, Fe-Co, and Fe-Ni films, the $E_{MA}$ tends to decreases or be negative values compared to that of the pure Fe film.

Interestingly, in the seven-layer film, we observed a large positive $E_{MA}$, 2.24 and 1.79 meV/$a^2$, for the type II and III Fe-Ni structures,[26] which are larger than that in the pure Fe film by a factor of more than two. This notes that the atomic-layer ordering of an alternating Fe and Ni layers in the type II structure enhances the PMA over that in the type III structure. The Fe double-layers on both sides of the film in the type II Fe-Ni structure is also found to need for the PMA. This was confirmed from the fact that the type V Fe-Ni structure, with the same Fe and Ni layer ordering but terminated by Fe monolayers,
has a negative value of the $E_{MA}$, -0.55 meV/$a^2$.

In addition, we carried out calculations for the type II Fe-Ni structure covered by double-layers of MgO, (MgO)$_2$/Fe$_2$/Ni/Fe/Ni/Fe$_2$//(MgO)$_2$, and found that the $E_{MA}$ results in 2.99 meV/$a^2$, i.e., increases by 0.75 meV/$a^2$ over that without the MgO, due to the interfacial PMA at the Fe/MgO interfaces. The $E_{MA}$ value, that corresponds to 5.42×10$^7$ erg/cm$^3$, exceeds enough over the shape MA energy, 1.5×10$^7$ erg/cm$^3$, of the film with magnetization of 1.54×10$^3$ emu/cm$^3$. Thus, a promising 3d transition-metal thin film for the MgO-based MTJs with the giant PMA was tailored.

Experimentally, the film with the bcc-like-layer stacking of the Ni layer on Fe(001), as seen in the type II Fe-Ni structure, may be fabricated. From the fact that the bcc-like B2 structure in bulk FeNi is only 0.15 eV/atom higher in energy than the fcc-like L1$_0$ structure, the bcc-like growth is expected in a film thin enough. Furthermore, a constraint of the in-plane lattice constant from the Fe (or MgO in the present case) substrate may avoid the fcc-like-layer stacking, since the lattice constants of the L1$_0$ structure (2.51 Å) is too small compared to that of the substrate. Indeed, bcc Ni overlayers, up to three monolayers, were epitaxially grown on a bcc Fe(001) in experiments. Defects in films to the PMA may be further inevitable in experiments. As in Fig. 1 (b), an atomic disorder (different layer-stacking) may give rise to a large variation in the $E_{MA}$. It however notes that when the films have terminated by more than Fe double-layers, the $E_{MA}$ always remains in positive values, as mentioned above; it may be valid even if the atomic disorder is introduced.

To verify the giant PMA in the type II Fe-Ni structure, we extended our calculations to thicker films with the alternate ordering of the Fe and Ni layers terminated by the Fe double-layers. Results are shown by solid circles in Fig. 2, where those of the pure Fe films are also presented. The pure Fe films always have positive $E_{MA}$ and almost no dependence on the film thickness, which indicates that the $E_{MA}$ comes from the surface contribution. For the present system, the $E_{MA}$ increases significantly, by 1.5 meV/$a^2$ in the seven-layer film over that in the five-layer film, but the $E_{MA}$ almost saturates when the film thickness increases further. With the thirteen-layer model where the Ni layer at the center is replaced by an Fe layer, i.e., Fe$_2$/Ni/Fe/Ni/Fe/Fe/Fe/Fe/Ni/Fe/Ni/Fe$_2$, the $E_{MA}$ is found to increase up to 3 meV/$a^2$, as shown by an open circle in Fig. 2. Thus, the bcc-like-layer stacking of Fe$_2$/Fe/Ni/Fe/Ni/Fe$_2$ gives rise to the PMA.

Figure 3 shows the partial density of states (DOS) in the Ni MT sphere of the type II
Fe-Ni structure, Fe\textsubscript{2}/Ni/Fe/Ni/Fe\textsubscript{2}, where the DOS around \( E_F \) arises from the minority-spin state while the majority spin state is almost fully occupied and is located from 0.5 to 4.0 eV below \( E_F \). As illustrated in the inset, the Ni atom locates at a \( C_{4v} \) symmetry site, surrounded by eight nearest-neighbor Fe atoms, four Ni atoms on the same plane and one Ni (Fe) atom above (below). The ligand field from the nearest-neighbor Fe atoms splits the \( d \) state into the cubic-like \( t_{2g} \) and \( e_g \) levels, and the tetragonal symmetry further splits the \( t_{2g} \) state into two irreducible representations, a singlet \( b_2 (d_{xy}) \) and a doublet \( e (d_{xz,yz}) \), and the \( e_g \) state into two irreducible representations, singlets \( a_1 (d_{z^2}) \) and \( b_1 (d_{x^2-y^2}) \).

In the minority-spin state in Fig. 3, three characteristic features are observed. First, the cubic-like \( t_{2g} \) state, i.e., the \( d_{xz,yz} \) and \( d_{xy} \) orbitals, hybridize with the nearest-neighbor Fe atoms, so these bands with a bonding character are pushed down in energy from 1.0 to 2.5 eV below \( E_F \). Since the antibonding state is mainly attributed in the counterpart Fe atoms, the DOS of the Ni \( d_{xz,yz} \) and \( d_{xy} \) orbitals around \( E_F \) is small. Secondly, for the cubic-like \( e_g \) state, the hybridization between neighboring Ni atoms with the \( d_{x^2-y^2} \) orbitals on the same plane pushes the antibonding state in energy close to \( E_F \). Finally, the DOS peaks of the antibonding \( d_{z^2} \) state shift above and below \( E_F \) so as to reduce the DOS at \( E_F \) due to the Ni and Fe atoms above and below along the \( z \)-axis.

The \( E_{MA} \) contribution on the \( k \)-space, \( E_{MA}(k) \), of the type II Fe-Ni structure is shown in Fig. 4 (a). Although there is the negative contribution to the \( E_{MA} \), most of the BZ shows the positive contribution that favors energetically the PMA. Particularly, a very large positive contribution appears close to around \( 5/12(\bar{X}+\bar{M}) \), as indicated by an arrow in the figure. With a correlation in the \( E_{MA}(k) \) and the minority-spin band structure from \( \Gamma \) to \( 1/2(\bar{X}+\bar{M}) \), as shown in Fig. 4 (b) and (c), the large positive peak in the \( E_{MA}(k) \) is identified from the SOC between the \( d_{x^2-y^2} \) and \( d_{xy} \) bands crossing \( E_F \).

According to perturbation theory,[30] the SOC between occupied and unoccupied states with the same (different) \( m \) magnetic quantum number through the \( \ell_z (\ell_x) \) operator gives a positive (negative) contribution to the \( E_{MA} \), as

\[
E_{MA} \approx \xi^2 \sum_{o,u} \left[ \frac{|< o | \ell_z | u >|^2 - |< o | \ell_x | u >|^2}{\epsilon_u - \epsilon_o} \right],
\]

where \( o \) (\( u \)) and \( \epsilon_o \) (\( \epsilon_u \)) represent eigenstates and eigenvalues, respectively, of occupied (unoccupied) minority-spin states. In the present system, around \( 5/12(\bar{X}+\bar{M}) \), the \( \ell_z \) matrix of the first term in Eq. 1 leads to a large positive value in the \( E_{MA} \), since the eigenstates
The $d_{x^2-y^2,xy}$ bands have the largest $|m|$ value (2) and a small energy splitting between the occupied and occupied states increases the $E_{\text{MA}}$ significantly through the denominator in Eq. 1. In contrast, the $\ell_x$ matrix of the second term in Eq. 1, i.e., $<0|\ell_x|\pm1>$ and $<\pm2|\ell_x|\pm1>$, has a small contribution to the $E_{\text{MA}}$, since less DOS of the $d_{m=\pm1}(d_{xz,yz})$ components appears around $E_F$, as pointed out in Fig. 3 (a). Thus, the SOC between the Ni $d_{x^2-y^2,xy}$ bands crossing $E_F$ leads to the giant PMA.

In summary, we systematically investigated the PMA of the Fe-based transition-metal thin films, consisting of only magnetic 3$d$ elements, by means of first-principles FLAPW calculations. As demonstrated by possible atomic-layer alignments with the Fe and the other 3$d$ elements (Mn, Co, and Ni) in the five and seven-layer films, we found that the large PMA can be archived by tuning the atomic-layer alignments in the Fe-Ni film, i.e., the bcc-like-layer stacking of Fe$_2$Ni/Fe/Ni/Fe$_2$ plays a key role. This was further confirmed from calculations for the thicker films, and the calculated $E_{\text{MA}}$ reaches as much as 3 meV/$a^2$. The calculated band structure shows that the giant PMA arises from the SOC between the occupied and unoccupied Ni $d_{x^2-y^2,xy}$ bands crossing $E_F$.

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[19] The PMA at the CoFeB/MgO interface in experiments (Ref. [2]) is expected to contribute mainly in the interfacial Fe-O hybridization, according to results in Ref. [18].
[26] The validity of the force theorem was confirmed by self-consistent total energy calculations
including the SOC, where the $E_{MA}$ in the self-consistent calculations is 2.40 meV/a$^2$ for the type II Fe-Ni structure.


[29] In films capped by double-layers of MgO, the $E_{MA}$ was confirmed to increase always over that without the MgO, e.g., by 0.10 and 0.31 meV/a$^2$ for the nine and eleven-layer films, and by 0.36 and 0.19 meV/a$^2$ for the type I and III structures in Fig. 1 (b), where the magnitude depends on the film thickness and the layer-stacking alignment.

Figures
FIG. 1: (Color online) Calculated $E_{MA}$ for (a) five and (b) seven-layer slabs of Fe-based transition-metal thin films with a bcc-like-layer stacking with Mn, Co, and Ni layers, where both sides of the films are terminated by Fe layers. Dashed horizontal lines represent results for pure Fe films. In insets, models employed are illustrated, type I, II, and III structures for the five-layer film and type I-VI structures for the seven-layer film, where open and solid circles represent Fe and the other 3$d$ elements (Mn, Co, and Ni), respectively.
FIG. 2: (Color online) Calculated $E_{MA}$ of Fe-Ni films (circles) as a function of the film thickness. Solid circles represent results for films with an alternate ordering of Fe and Ni layers terminated by Fe double-layers on both sides of the films, and an open circle for a film Fe$_2$/Ni/Fe/Ni/Fe/Ni/Fe/Fe/Ni/Fe/Fe/Ni/Fe/Ni/Fe$_2$. Notations illustrate atomic-layer orderings of the Fe and Ni layers in the films. Results of the pure Fe films are shown by solid diamonds.
FIG. 3: (Color online) Calculated orbital-decomposed DOS in the Ni MT sphere of type II Fe-Ni structure, Fe$_2$/Ni/Fe/Ni/Fe$_2$, where (a) and (b) show those of the cubic-like $t_{2g}$ and $e_g$ states; the former (latter) is composed of $d_{xz(yz)}$ and $d_{xy}$ ($d_{z^2}$ and $d_{x^2-y^2}$). As shown in an inset, the Ni atom locates a $C_{4v}$ symmetry site, surrounded by eight nearest-neighbor Fe atoms, four Ni atoms on the same plane, and one Ni (Fe) atom above (below).
FIG. 4: (Color online) (a) Calculated $E_{\text{MA}}$ contribution in $k$-space, $E_{\text{MA}}(k)$, of type II Fe-Ni structure, Fe$_2$/Ni/Fe/Ni/Fe$_2$. Solid lines (pink area) and dashed lines (light blue) represent positive and negative contributions to the $E_{\text{MA}}$, respectively. An arrow (white) points to a $k$-position that has a largest positive contribution. (b) Calculated $E_{\text{MA}}(k)$ and (c) minority-spin band structure along directions drawn by solid lines in (a). In (c), solid circles represent bands having components of $d_{x^2−y^2}$ (red) and $d_{xy}$ (blue) orbitals (possessing more than 5%) in the Ni MT sphere.