

# First-Principles Study of Electric Field Effects on Magnetic Anisotropy in MgO/TM/Au (TM=Fe, Co) Systems

Shugo SUZUKI, Sho YASUDA, Kazuki EDAKAWA, and Saori SEKI

*Division of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan*

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We study the electric field (EF) effects on the magnetic anisotropy in the MgO/TM/Au (TM=Fe, Co) systems with (001) and (111) orientations using relativistic first-principles calculations based on the density functional theory. We find that the perpendicular magnetic anisotropy of the MgO/TM/Au(001) system is enhanced by the EF that decreases the number of electrons in the system. The magnetic anisotropy energy (MAE) and its EF dependence of the MgO/Fe/Au(001) system is found to be in a semi-quantitative agreement with the experimental results with successful reproduction of the sign of the measured EF dependence. Furthermore, the EF dependence of the MAE of the MgO/Co/Au(001) system is found to be very large due to the structural relaxation of the Co-O interatomic distance and the decrease in the number of electrons in the Co atom caused by the EF. This result is attributed to the general trend that the perpendicular magnetic anisotropy of the Co layer is affected significantly when in contact with an inert layer at an interlayer distance of about 2 Å. On the contrary, we find that the MgO/TM/Au(111) system shows almost no EF dependence of the MAE. This result is attributed to the existence of a strong TM-O covalent bond associated with the oxidation of the TM atom by the O atom.

KEYWORDS: electric field effects, magnetic anisotropy, MgO/Fe/Au, MgO/Co/Au, relativistic first-principles calculations, density functional theory

## 1. Introduction

In the last two decades, ultrathin ferromagnetic films have attracted much attention not only because of scientific interest but also because of its potential applications.<sup>1)</sup> Of great importance is the enhancement of the magnetic anisotropy energy (MAE) of a film due to the reduced symmetry at the surface or interface in comparison to that of the bulk. In recent years, preceded by work on ferromagnetic semiconductors,<sup>2-4)</sup> the

experimental studies of the electric field (EF) control of magnetic properties of ultrathin ferromagnetic films have been done extensively motivated by requirements to achieve ultra-low power consumption of magnetic memory storage devices.<sup>5-19)</sup> The mechanism of the EF effects on the MAE in ultrathin ferromagnetic films has also been studied theoretically.<sup>20-31)</sup>

More than 70 years ago, the origin of the MAE was proposed to be the spin-orbit coupling.<sup>32-34)</sup> A phenomenological description of the MAE at the surface or interface of a film was introduced by Néel;<sup>35)</sup> it was pointed out that the MAE can be enhanced at the surface or interface due to the reduced symmetry in comparison to the bulk. This prediction was confirmed by early experimental studies of ultrathin transition metal (TM) films;<sup>36-40)</sup> it was shown that the NiFe/Cu(111) system is ferromagnetic with the easy axis perpendicular to the plane of the film.

Extensive studies of the MAE of ultrathin ferromagnetic films began in the late 1980s based on the success of molecular beam epitaxy in ultrahigh vacuum as well as the success of highly accurate first-principles calculations with powerful supercomputers. The first-principles study by Gay and Richter showed that the easy axis of the freestanding Fe monolayer system is perpendicular to the plane.<sup>41-43)</sup> This explains why spin splitting but no spin polarization is observed in photoemission experiments on the ultrathin Fe film on the Ag(001) substrate.<sup>44)</sup> The perpendicular easy axis of this system was confirmed subsequently by the ferromagnetic resonance study.<sup>45)</sup>

Since then, a number of theoretical studies have been done on the MAE of ultrathin ferromagnetic films.<sup>46-73)</sup> Wang et al. succeeded in calculating the MAE in a highly stable way using the state-tracking method developed through the detailed analysis of the results obtained by the full-potential linearized augmented plane-wave method.<sup>48-51)</sup> Almost all of early first-principles studies were restricted to rather unrealistic freestanding TM monolayer systems although the theoretical studies on these systems are of fundamental importance. Aided by the increasing power of computers, recent first-principles studies take account of substrates or insulating layers or both.<sup>52-73)</sup> The first-principles calculations have become an indispensable tool for studying the MAE of ultrathin ferromagnetic films as well as that of multilayer systems.<sup>74-91)</sup>

The experimental studies of the EF effects on the magnetic properties in ultrathin ferromagnetic films have been done extensively in the last several years.<sup>5-19)</sup> Maruyama et al. found a large voltage-induced magnetic anisotropy change in the MgO/Fe/Au(001) system.<sup>6)</sup> They showed that a relatively small EF can cause a large change in the MAE,

$8.4 \mu\text{Jm}^{-2}$ , when the applied voltage is changed from 200 V to  $-200$  V. Subsequently, Shiota et al. evaluated the change in the MAE of the MgO/Fe<sub>80</sub>Co<sub>20</sub>/Au(001) system quantitatively;<sup>8,15)</sup> the MAE depends linearly on the EF with a slope of about  $30 \text{ fJm}^{-1}$ , i.e.,  $0.015 \text{ meV/TM per V/nm}$ . It is important to note that the sign of the EF dependence of the MAE found by Maruyama et al. and Shiota et al. is such that the perpendicular magnetic anisotropy is enhanced by the EF that decreases the number of electrons in the system.

Another experimental study of the EF effects on the magnetic properties in ultrathin ferromagnetic films was carried out by Chiba et al.<sup>12)</sup> They showed that the Curie temperature of the MgO/Co/Pt system is increased by the EF that increases the number of electrons in the system. Furthermore, using the ionic liquid film, they succeeded to achieve the change in the Curie temperature of about 100 K in the same system with the gate voltage change of  $\pm 2$  V.<sup>18)</sup> It is interesting to note that the sign of the EF dependence of the Curie temperature of the MgO/Co/Pt system is opposite to the sign of the EF dependence of the MAE of the MgO/Fe/Au(001) and MgO/Fe<sub>80</sub>Co<sub>20</sub>/Au(001) systems although it is not clear what relationship exists between the Curie temperature and the MAE in these systems.

The theoretical studies of the EF effects on the MAE in related systems were carried out using the first-principles calculations based on the density functional theory.<sup>20–31)</sup> Duan et al. demonstrated that there exist the EF effects on the MAE in the TM ferromagnetic films.<sup>20)</sup> Nakamura et al. showed that the MAE of the Fe(001) film can be controlled by the EF and that the interfacial FeO layer in the MgO/Fe/Au(001) system may play a key role in the MAE switching.<sup>21,25)</sup> Tsujikawa et al. found a large EF effect on the MAE in the Pt/Fe/Pt(001) and MgO/Fe/Pt(001) systems.<sup>23,28)</sup> These first-principles studies have successfully shed light on the EF control of the magnetic properties of ultrathin ferromagnetic films from the theoretical point of view.

Nevertheless, there exist some discrepancies between the experimental and theoretical results. In their study of the MgO/Fe/Au(001) system with and without an interfacial FeO layer between the MgO and Fe layers,<sup>25)</sup> Nakamura et al. found that the sign of the EF dependence of the MAE of the system without the interfacial FeO layer is opposite to the sign observed experimentally while they found that the sign of the EF dependence of the MAE of the system with the interfacial FeO layer is in agreement with the sign observed experimentally. Tsujikawa et al. also studied the MgO/Fe/Au(001) system but did not find a clear EF dependence of the MAE of this

system as opposed to the experimental observation.<sup>28)</sup> Further theoretical studies are thus necessary to resolve the discrepancies between the experimental and theoretical results and to understand the EF effects on the MAE in more detail.

The purpose of this work is to study the EF effects on the MAE in the MgO/TM/Au (TM=Fe, Co) systems with (001) and (111) orientations using relativistic first-principles calculations based on the density functional theory. For comparison, we also study the EF effects on the MAE in the freestanding TM monolayer systems, the hypothetical bilayer systems where each system consists of a fictitious-O monolayer and a TM monolayer, and the TM/Au systems. We describe the method of calculations in §2. The results and discussion are given in §3. Finally, we give the conclusions of this work in §4.

## 2. Method of Calculations

For all the systems studied in this work, we consider a single TM monolayer as the ferromagnetic layer in a system. We first study the freestanding TM monolayer systems with several values of the lattice constant taken to match not only the Au substrates but also other substrates to examine the effects of strain on the MAE and its EF dependence. We next study the hypothetical bilayer systems to examine the effects of oxidation of the TM atom by the O atom on the MAE and its EF dependence; each bilayer system consists of a fictitious-O monolayer and a TM monolayer. Finally, we study the MAE and its EF dependence of the TM/Au and MgO/TM/Au systems, where the substrates consist of two Au monolayers and the insulating layers consist of two Mg and two O monolayers. The schematic diagram is shown in Figs. 1(a) and (b) for the MgO/TM/Au(001) and MgO/TM/Au(111) systems, respectively.

We performed all-electron calculations using the scalar relativistic full-potential linear-combination-of-atomic-orbitals (SFLCAO) method and the fully relativistic full-potential linear-combination-of-atomic-orbitals (FFLCAO) method, both based on the density functional theory.<sup>92-94)</sup> We adopted the local spin density approximation using the Perdew-Wang parameterization of the Ceperley-Alder results as the exchange-correlation energy functional.<sup>95,96)</sup> Also, to calculate the electrostatic potential, we used the two-dimensional Ewald method.<sup>97,98)</sup> We first optimized the structure of a system using the SFLCAO method in the absence of or under the EF; in the SFLCAO method, both core and valence states are calculated using an appropriate averaging procedure of the spin-orbit coupling.<sup>94)</sup> We next calculated the MAE of the system with the op-

timized structure using the FFLCAO method in the absence of or under the EF; in the FFLCAO method, we solve the Kohn-Sham equations of the Dirac type not only for core states but also for valence states, thereby taking account of all the relativistic effects including the spin-orbit coupling.<sup>93)</sup>

The advantages of the SFLCAO/FFLCAO methods in studying the EF effects on the magnetic anisotropy in two-dimensional systems are as follows. Firstly, the present methods are well suited for studying two-dimensional systems because atomic orbitals can describe the existence of the periodicity along the in-plane directions and the lack of the periodicity along the perpendicular direction by forming the Bloch sums only in the in-plane directions. Secondly, the two-dimensional Ewald method implemented in the present methods not only eliminates a spurious electrostatic contribution but also enables us to calculate charged two-dimensional systems; the latter feature is indispensable to the study of the EF effects in two-dimensional systems when the system itself is an electrode. Thirdly, the use of the SFLCAO method for optimizing structures is important because the SFLCAO method is much faster than the FFLCAO method while the use of the FFLCAO method for calculating the MAE is important because the FFLCAO method calculates the MAE accurately by taking account of the spin-orbit coupling in a fully relativistic manner.

The EF was applied as follows. We consider a counter electrode placed far above the system and charged oppositely to the charge state of the system. That is, we introduce the following external potential originated in the counter electrode:

$$V_{\text{CE}}(z) = -\frac{2\pi e^2 \Delta N}{A_{\text{cell}}} z . \quad (1)$$

Here  $A_{\text{cell}}$  is the area of the unit cell:  $A_{\text{cell}} = a^2$  for the square lattice of the (001) systems and  $A_{\text{cell}} = \sqrt{3}a^2/2$  for the triangular lattice of the (111) systems with  $a$  representing the in-plane lattice constants of the systems. Also  $\Delta N$  represents the change in the number of electrons in the unit cell of the system; we consider  $\Delta N = -0.1, 0.0,$  and  $0.1$  in this work. Note that one half of the EF is originated in the counter electrode while the other half is originated in the system itself. We define the direction of the EF in such a way that a positive (negative) EF decreases (increases) the number of electrons in the system; in other words, a positive (negative) EF corresponds to a negative (positive) voltage applied to the counter electrode with respect to the system. The EF is  $-1.81 \Delta N/a^2 \times 10^3$  V/nm for the (001) systems and  $-2.09 \Delta N/a^2 \times 10^3$  V/nm for the (111) systems when  $a$  is given in units of Å. We calculated the MAE as well as the spin magnetic

moment,  $M_{\text{spin}}$ , in the absence of or under the EF, using the FFLCAO method. The MAE is the difference between the total energy for the in-plane magnetization and that for the perpendicular magnetization. We adopt the definition that the positive (negative) MAE corresponds to the perpendicular (in-plane) magnetic anisotropy. We do not include the contribution of the shape magnetic anisotropy originated in the magnetic dipole-dipole interaction to the MAE. The details of the structures of the systems, the atomic orbitals, and the Brillouin-zone integration are given in Appendix.

To understand the role of the MgO insulating layer, especially the effects of the oxidation of the TM atom by the O atom on the MAE and its EF dependence, we also study the hypothetical bilayer systems as follows. Suppose a bilayer system consisting of a fictitious-O monolayer and a TM monolayer at an interlayer distance  $d$ . We refer to the fictitious O atom as the O\* atom hereafter. The lattice constant is taken to match the Au substrate,  $a=2.88 \text{ \AA}$ . The atomic orbitals for the O\* atom are the same as those for the usual O atom given in Appendix while the nuclear charge and the initial electronic charge of the O\* atom are  $10e$  and  $-(10-\delta)e$ , respectively. Here we introduce an excess nuclear charge of  $2e$  and a parameter  $\delta$  that represents a deficiency in the number of electrons when compared to those in the closed shell configuration of the  $\text{O}^{2-}$  atom. The excess nuclear charge of  $2e$  and the electron deficiency  $\delta$  induce a transfer of electrons from the TM atom to the O\* atom, thereby controlling the oxidation number of the TM atom. That is,  $\delta$  represents the oxidation number of the TM atom,  $\text{TM}^{\delta+}$ , when the self-consistent procedure is converged and the excess nuclear charge of  $2e$  ensures that the O\* atom is in the closed-shell structure,  $\text{O}^{*2-}$ , at the convergence. We may consider that the excess nuclear charge of  $2e$  simulates the Madelung potential at the O-atom site due to the  $\text{Mg}^{2+}$  atoms in the MgO/TM/Au systems. The MAE and its EF dependence of the hypothetical bilayer systems were calculated changing  $\delta$  from 0.0 to 0.2 with  $d$  fixed at  $2.0 \text{ \AA}$  and also calculated changing  $d$  from  $1.8 \text{ \AA}$  to  $2.8 \text{ \AA}$  with  $\delta$  fixed at 0.0. Although the present approach with the hypothetical bilayer systems is rather uncommon, we believe that this approach may give us insight into the mechanism of the EF effects on the MAE of the MgO/TM/Au systems.

### 3. Results and Discussion

#### 3.1 Freestanding TM monolayer systems

We first study the freestanding TM monolayer systems. In Tables I and II, we show the MAE as well as  $M_{\text{spin}}$  for the TM(001) and TM(111) monolayer systems, respec-

tively. We also show the results reported by other theoretical studies when available. To examine the effects of strain on the MAE and its EF dependence, as originally studied by Wang et al. in the absence of the EF,<sup>49)</sup> we performed calculations with several values of the lattice constant taken to match not only the Au substrates,  $a=2.88 \text{ \AA}$ , but also other substrates shown in the parentheses in the tables.

Let us focus on the results obtained for the systems with  $a=2.88 \text{ \AA}$  (Au) in the absence of the EF, i.e.,  $\Delta N = 0.0$ . It may be useful to discuss here with the results obtained for the systems with  $a=2.89 \text{ \AA}$  (Ag) together because the two lattice constants are very close to each other and also because many of other theoretical studies of freestanding TM monolayer systems assumed the lattice constant of the Ag substrate. Note that the results obtained for  $a=2.88$  and  $2.89 \text{ \AA}$  are almost the same. The MAE of the Fe(001) and Fe(111) monolayer systems are 0.36 and 0.24 meV/cell with  $M_{\text{spin}}$  of 3.31 and 3.17  $\mu_B$ , respectively, showing a moderate perpendicular magnetic anisotropy. On the contrary, the MAE of the Co(001) and Co(111) monolayer systems are  $-3.16$  and  $-2.18$  meV/cell with  $M_{\text{spin}}$  of 2.18 and 2.10  $\mu_B$ , respectively, showing a strong in-plane magnetic anisotropy. The magnitude of the MAE of the Co monolayer systems is one order larger than that of the Fe monolayer systems. The MAE of the Fe(001) monolayer system calculated by Gay and Richter is 0.38 meV/cell.<sup>41)</sup> Also the MAE of the same system calculated by Wang et al. is 0.37 meV/cell.<sup>49)</sup> These results are in good agreement with our result, 0.36 meV/cell. On the other hand, our calculated MAE is slightly larger than that calculated by Nakamura et al., about 0.2 meV/cell, although the origin of the discrepancy is not clear. It is interesting to note that the MAE of a 15 monolayer thick Fe(001) film with a lattice constant of  $2.87 \text{ \AA}$  calculated by Duan et al., 0.38 meV per surface Fe atom, is close to our result.<sup>20)</sup>

When the positive (negative) EF is applied, i.e.,  $\Delta N=-0.1$  (0.1), the MAE of the Fe(001) monolayer system is increased (decreased) by 0.22 (0.34) meV/cell with a slope of about 0.01 meV/cell per V/nm. The EF dependence of the MAE of the Fe(001) film was calculated by Duan et al.;<sup>20)</sup> they obtained a slope of about 0.01 meV per surface Fe atom per V/nm for the 15 monolayer thick Fe(001) film in good agreement with our result including the sign of the EF dependence despite that the system is not exactly the same. The MAE of the Fe(111) monolayer system is increased (decreased) by 0.15 (0.07) meV/cell with a slope of about 0.005 meV/cell per V/nm. That is, for both Fe(001) and Fe(111) monolayer systems, the MAE is increased (decreased) when the number of electrons in the system is decreased (increased) by the EF. However, this behavior

is not a general trend; for example, although the Co(111) monolayer system shows a similar behavior that the MAE is increased (decreased) for the positive (negative) EF by 0.16 (0.38) meV/cell, the MAE of the Co(001) monolayer system is decreased by 0.09 and 0.45 meV/cell for the positive and negative EF, respectively, irrespective of the direction of the EF. Unfortunately, no general trend is found in the EF dependence of the MAE of the TM monolayer systems. On the contrary, the EF dependence of  $M_{\text{spin}}$  is very simple, always showing a monotonic behavior; when the positive (negative) EF is applied,  $M_{\text{spin}}$  is increased (decreased) by about  $0.1 \mu_{\text{B}}$  for all the TM monolayer systems. This is reasonable because the positive (negative) EF decreases (increases) the number of the 3d electrons in the TM atom by about 0.1.

We now examine the effects of strain on the MAE and its EF dependence. We find a trend that the MAE is increased with decreasing the lattice constant in agreement with the trend found by Wang et al. for the Fe(001) monolayer system in the absence of the EF.<sup>49)</sup> In particular, this trend is very clear for the Co monolayer systems. Furthermore, we find a trend that the EF dependence of the MAE is reduced with decreasing the lattice constant. For example, in the Fe(001) monolayer system with the lattice constant of  $3.16 \text{ \AA}$  (W), the difference between the MAE for  $\Delta N = \pm 0.1$  is about 1.24 meV/cell while the difference is reduced to 0.11 meV/cell for the same system but with the lattice constant of  $2.56 \text{ \AA}$  (Cu).

### 3.2 Hypothetical O\*/TM bilayer systems

We next study the hypothetical bilayer systems where each system consists of an O\* monolayer and a TM monolayer with the in-plane lattice constant taken to match the Au substrates,  $a = 2.88 \text{ \AA}$ , and with the interlayer distance  $d$ . We show the MAE as a function of the oxidation number  $\delta$  in Figs. 2 and 3 with  $d$  fixed at  $2.0 \text{ \AA}$ ; Figs. 2(a) and (b) are for the O\*/Fe(001) and O\*/Co(001) bilayer systems, respectively, and Figs. 3(a) and (b) are for the O\*/Fe(111) and O\*/Co(111) bilayer systems, respectively. In the figures, the triangles, the circles, and the squares represent the results for  $\Delta N = -0.1, 0.0,$  and  $0.1$ , respectively. The EF is given by  $-0.218 \Delta N \times 10^3 \text{ V/nm}$  and  $-0.252 \Delta N \times 10^3 \text{ V/nm}$  for the O\*/TM(001) and O\*/TM(111) bilayer systems, respectively.

A most remarkable point is that the EF dependence of the MAE of the O\*/Co bilayer systems is very large in the vicinity of  $\delta = 0.0$  although it is reduced considerably with increasing  $\delta$ ; the MAE of the O\*/Co(001) bilayer system with  $\delta = 0.0$  for  $\Delta N = -0.1, 0.0,$  and  $0.1$ , are 0.39,  $-0.19$ , and  $-1.47$  meV/cell, respectively, and thus the difference



between the MAE for  $\Delta N = \pm 0.1$  is almost 2 meV/cell; this change corresponds to a slope of about 0.04 meV/cell per V/nm. That is, the MAE of the O\*/Co bilayer systems is increased (decreased) with decreasing (increasing) the number of electrons in the Co atom at a fixed interlayer distance  $d = 2.0 \text{ \AA}$ . The behavior of the O\*/Co bilayer systems is in strong contrast to that of the O\*/Fe bilayer systems; the EF dependence of the MAE of the O\*/Fe bilayer systems is not very large and does not strongly depend on  $\delta$ .

In Figs. 4 and 5, we show the MAE as a function of the interlayer distance  $d$  with  $\delta$  fixed at 0.0; Figs. 4(a) and (b) are for the O\*/Fe(001) and O\*/Co(001) bilayer systems, respectively, and Figs. 5(a) and (b) are for the O\*/Fe(111) and O\*/Co(111) bilayer systems, respectively. Note that the O\* layer with  $\delta = 0.0$  acts as an inert layer because it is a layer of the Ne-like atoms whose atomic orbitals are those for the usual O atom. It is found that the MAE of the O\*/Co bilayer system depends strongly on  $d$  in the vicinity of  $2.0 \text{ \AA}$  while that of the O\*/Fe bilayer system does not. It should be noted that the EF dependence of the MAE of the O\*/Co bilayer systems is reduced when the Co-O\* interlayer distance moves away from  $2.0 \text{ \AA}$ . We also find that, with increasing  $d$ , the MAE of the O\*/TM bilayer systems approaches to the corresponding values of the TM monolayer systems with the lattice constant taken to match the Au substrate shown in Tables I and II. Also we again find that the MAE of the O\*/Co bilayer systems is increased (decreased) with decreasing (increasing) the number of electrons in the Co atom at a fixed interlayer distance  $d$  when it is in the vicinity of  $2 \text{ \AA}$ .

We emphasize that the MAE of the O\*/Co bilayer system with  $\delta = 0.0$  is increased (decreased) significantly with decreasing (increasing) the Co-O\* interlayer distance and also with decreasing (increasing) the number of electrons in the Co atom at a fixed interlayer distance  $d$  when it is in the vicinity of  $2 \text{ \AA}$ . This behavior is most likely a realization of a general trend of the Co layer; the perpendicular magnetic anisotropy of the Co layer is affected significantly when in contact with an inert layer at an interlayer distance of about  $2 \text{ \AA}$ . It is essential for such a large effect that the Co atom is not oxidized. We shall see later that the MAE of the Co/Au and MgO/Co/Au systems is increased in comparison to that of the corresponding Co monolayer systems due to the existence of the MgO and/or Au layers as an inert layer.

### 3.3 TM/Au and MgO/TM/Au systems

#### 3.3.1 optimized structures

In Tables III and IV, we show the  $x$ ,  $y$ , and  $z$  coordinates of the atoms in the TM/Au and MgO/TM/Au systems used in the calculations of the MAE; Tables III and IV are for the (001) and (111) systems, respectively. As seen in the tables, the structure of the TM/Au system is almost unchanged by the EF, irrespective of its direction. On the other hand, the structure of the MgO/TM/Au system, especially that of the MgO/TM/Au(001) system, is affected by the EF as mentioned below.

In the absence of the EF, the Fe-O interlayer distance in the MgO/Fe/Au(001) system and that in the MgO/Fe/Au(111) system are 2.09 and 1.81 Å, respectively. Also the Co-O interlayer distance in the MgO/Co/Au(001) system and that in the MgO/Co/Au(111) system are 2.06 and 1.79 Å, respectively. Note that the TM-O interlayer distance is identical to the TM-O interatomic distance because the O atom is placed on top of the TM atom in all the MgO/TM/Au systems studied in this work. It is important to note that the TM-O interatomic distances in the (111) systems are considerably smaller than those in the (001) systems; the difference is almost 0.3 Å. This indicates that there exists a strong covalent bond between the TM atom and the adjacent O atom in the MgO/TM/Au(111) systems while there is no such a strong TM-O covalent bond in the MgO/TM/Au(001) systems. In other words, the TM atoms are highly oxidized in the MgO/TM/Au(111) systems while not oxidized in the MgO/TM/Au(001) systems.

When the positive (negative) EF is applied, the TM-O interatomic distance in the MgO/TM/Au(001) system is decreased (increased) by about 0.05 Å. This is reasonable because the O atom is negatively charged so that it is pulled down (up) towards the negative (positive)  $z$  axis direction when the positive (negative) EF is applied. On the contrary, the TM-O interatomic distance in the MgO/TM/Au(111) system is almost unaffected by the EF; this is most likely due to the existence of the strong covalent bond between the TM atom and the adjacent O atom. It is also worth noting that the TM-Au interlayer distance as well as the Au-Au interlayer distance are almost unaffected by the EF for all the MgO/TM/Au systems; this indicates that the EF effects on the Au layers are relatively small due to the screening effect of the TM layer.

### 3.3.2 MAE in (001) systems of TM=Fe in absence of EF

We now study the MAE and  $M_{\text{spin}}$  in the TM/Au and MgO/TM/Au systems. In Table V, we show the calculated MAE and  $M_{\text{spin}}$  of the TM/Au and MgO/TM/Au systems. For comparison, we again show the MAE and  $M_{\text{spin}}$  of the TM monolayer systems with the lattice constant taken to match the Au substrate. Furthermore, for the MgO/TM/Au systems with  $\Delta N = \pm 0.1$ , we show the MAE and  $M_{\text{spin}}$  calculated with the structure obtained in the absence of the EF, i.e.,  $\Delta N = 0.0$ , to examine the effects of the structural relaxation caused by the EF on the MAE and  $M_{\text{spin}}$ .

We begin with the (001) systems of TM=Fe. In the absence of the EF, the MAE of the Fe/Au(001) system, 0.31 meV/cell, is close to that of the Fe monolayer system, 0.36 meV/cell, both showing a perpendicular magnetic anisotropy. Li et al. and Szunyogh et al. studied the Fe/Au(001) system and also found a perpendicular magnetic anisotropy;<sup>47,53)</sup> our result is in a qualitative agreement with their results although the calculated MAE by Li et al. and Szunyogh et al., 0.57 and 0.61 meV/cell, respectively, are about twice as large as the one obtained in this work. The quantitative difference may be due to the difference in the method of calculations for the MAE although the origin of the discrepancy is not clear. It is worth noting that our calculated  $M_{\text{spin}}$  of the Fe/Au(001) system, 3.07  $\mu_{\text{B}}$ , is considerably larger than that of the bulk Fe, 2.2  $\mu_{\text{B}}$ , although it is reduced to some extent in comparison to that of the Fe(001) monolayer system, 3.31  $\mu_{\text{B}}$ ; the reduction of  $M_{\text{spin}}$  is due to the interaction between the 3d orbitals of Fe and the 6s orbitals of Au in the Fe/Au(001) systems. The interaction between TM layers and noble metal substrates was studied theoretically by Fu et al. and the behavior of  $M_{\text{spin}}$  of the TM atom in ultrathin ferromagnetic films on noble metal substrates was thoroughly elucidated.<sup>99)</sup>

The MAE of the MgO/Fe/Au(001) system in the absence of the EF calculated in this work is 0.60 meV/cell, which is about twice as large as those of the Fe(001) monolayer and Fe/Au(001) systems, showing an enhanced perpendicular magnetic anisotropy. Our calculated MAE is in good agreement with that calculated by Tsujikawa et al., 0.50 meV/cell.<sup>28)</sup> Also our result is in a qualitative agreement with the results of calculations by Nakamura et al.; they found that the MAE of the Fe/MgO(001) system is larger by about 1.0 meV/cell than that of the freestanding Fe(001) monolayer system.<sup>25)</sup> That is, the MgO insulating layer enhances the perpendicular magnetic anisotropy. This is in agreement with the experimental observation by Maruyama et al.; they found that

the MgO/Fe interface has a positive contribution to the MAE of the MgO/Fe/Au(001) system.<sup>6)</sup> However, our calculated MAE of the MgO/Fe/Au(001) system is about twice as large as that measured by Maruyama et al.,  $580 \mu\text{J}/\text{m}^2$ , i.e.,  $0.30 \text{ meV}/\text{cell}$ . One possible origin of the discrepancy is that the number of Fe monolayers in the sample used in the experiment is in the range from two to four monolayers while that assumed in this work is only one monolayer. Another possible origin is the surface segregation of Au atoms, which is not considered in this work. The effects of the number of Fe monolayers and/or the surface segregation of Au atoms on the MAE may be important and should be examined in more detail.<sup>30)</sup> It is worth noting that  $M_{\text{spin}}$  of the MgO/Fe/Au(001) system decreases by  $0.2 \mu_{\text{B}}$  in comparison to that of the Fe/Au(001) system. This may again suggest that the Fe atom is not oxidized by the O atom because the oxidation should result in the increase in  $M_{\text{spin}}$  of the Fe atom.

### 3.3.3 MAE in (001) systems of TM=Fe under EF

For the positive (negative) EF, i.e.,  $\Delta N = -0.1$  ( $0.1$ ), all the (001) systems of TM=Fe show an increase (decrease) in the MAE. In particular, the EF dependence of the MAE is considerably large for the Fe/Au(001) system, about  $0.03 \text{ meV}/\text{cell}$  per V/nm. This is more than twice as large as that of the Fe(001) monolayer system,  $0.01 \text{ meV}/\text{cell}$  per V/nm. That is, the Au(001) substrate enhances the EF dependence of the MAE considerably. On the other hand, the EF dependence of the MAE of the MgO/Fe/Au(001) system, about  $0.006 \text{ meV}/\text{cell}$  per V/nm, is much smaller than that found for the Fe/Au(001) system. That is, the MgO insulating layer suppresses the EF dependence of the MAE of the MgO/Fe/Au(001) system in comparison to that of the Fe/Au(001) system. However, the trend that the positive (negative) EF increases (decreases) the MAE is the same as that found for the Fe/Au(001) system. The MAE calculated with the structure obtained in the absence of the EF, i.e.,  $\Delta N = 0.0$ , shows a similar behavior in comparison to those calculated with the structures optimized under the EF.

The trend found for the MgO/Fe/Au(001) system in this work is in agreement with the experimental observation by Maruyama et al.<sup>6)</sup> Also our result is in a semi-quantitative agreement with the experimental result obtained by Shiota et al.;<sup>15)</sup> they found the EF dependence of the MAE of the MgO/Fe<sub>80</sub>Co<sub>20</sub>/Au(001) system to be  $30 \text{ fJ}\text{V}^{-1}\text{m}^{-1}$ , i.e.,  $0.015 \text{ meV}/\text{TM}$  per V/nm. This is in a reasonable agreement with our result,  $0.006 \text{ meV}/\text{cell}$  per V/nm. The sign and the order of magnitude of the EF dependence of the MAE of the MgO/Fe/Au(001) system are reproduced successfully.

### 3.3.4 MAE in (001) systems of TM=Co in absence of EF

We next examine the results obtained for the (001) systems of TM=Co. In the absence of the EF, the MAE of the Co monolayer system shows a strong in-plane magnetic anisotropy of  $-3.16$  meV/cell. The Au substrate increases the MAE to  $-1.65$  meV/cell in the Co/Au(001) system and the MgO insulating layer further increases the MAE to  $-0.42$  meV/cell in the MgO/Co/Au(001) system although both systems still show an in-plane magnetic anisotropy. We may understand the effect of the MgO insulating layer on the MAE by considering the results shown in Fig. 4(b), where the MAE of the O\*/Co(001) bilayer system is increased with decreasing the Co-O\* interlayer distance. This may be originated in the general trend that the perpendicular magnetic anisotropy of the Co layer is affected significantly when in contact with an inert layer, i.e., the O\* layer with  $\delta=0.0$  in that case, at an interlayer distance of about  $2 \text{ \AA}$ . The increase in the MAE of the Co/Au(001) system in comparison to that of the Co(001) monolayer system is also most likely a realization of the general trend of the Co layer; the Au layer acts as an inert layer in the Co/Au(001) system.

### 3.3.5 MAE in (001) systems of TM=Co under EF

The MAE of the Co(001) monolayer system is almost unchanged for the positive EF, i.e.,  $\Delta N=-0.1$ , while it is moderately decreased for the negative EF, i.e.,  $\Delta N=0.1$ . On the other hand, the MAE of the Co/Au(001) system shows a moderate increase, irrespective of the direction of the EF. For both systems, however, the change in the MAE by the EF is not very large in comparison to the magnitude of the MAE itself. On the contrary, the MAE of the MgO/Co/Au(001) system is increased (decreased) substantially when the positive (negative) EF is applied; in particular, the EF dependence of the MAE for the positive EF is very large, i.e., about  $0.09$  meV/cell per V/nm. We find that the MAE of the MgO/Co/Au(001) system is positive and significantly large for  $\Delta N=-0.1$ , i.e.,  $1.46$  meV/cell, showing a large perpendicular magnetic anisotropy. If we assume the contribution of the shape magnetic anisotropy to the MAE to be  $0.1$  meV/cell, the easy axis is perpendicular to the plane for  $\Delta N < -0.05$ , i.e., the EF larger than  $+11$  V/nm; although this EF is very large, the ionic liquid film may enable us to apply such a large EF. Since the EF dependence of the MAE of the MgO/Co/Au(001) system is very large, this system is a promising candidate for the EF control of the MAE switching. Although there are no experimental results available for comparing the EF dependence of the MAE of the MgO/Co/Au(001) system, it is

considerably larger than the EF dependence of the MAE estimated by Shiota et al. for the MgO/Fe<sub>80</sub>Co<sub>20</sub>/Au(001) system, 0.015 meV/TM per V/nm.<sup>15)</sup> It is worth noting that  $M_{\text{spin}}$  of the MgO/Co/Au(001) system is decreased by 0.1  $\mu_{\text{B}}$  in comparison to that of the Co/Au(001) system. This may again suggest that the Co atom is not oxidized by the O atom as already found in the above for the Fe atom in the MgO/Fe/Au(001) system.

It should be noted that the EF dependence of the MAE of the MgO/Co/Au(001) system calculated with the structure obtained in the absence of the EF behaves differently for the negative EF; the MAE shows an increase for the negative EF in contrast to the decrease obtained with the optimized structure. This is similar to the EF dependence of the MAE obtained for the Co/Au(001) system. The decrease in the MAE of the MgO/Co/Au(001) system found when calculated with the structure optimized for the negative EF is clearly due to the effect of the structural relaxation caused by the EF. This can be understood as follows. When the negative EF is applied, the Co-O interatomic distance is increased by about 0.05 Å as shown in Table III. As a result, the MAE of the system is decreased according to the general trend of the Co layer; the MgO insulating layer acts as an inert layer in this case. Also a moderate increase in the MAE for the positive EF calculated with the optimized structure is found when compared with that calculated with the unoptimized structure. We can understand this as follows. When the positive EF is applied, the Co-O interatomic distance is decreased by about 0.05 Å as shown in Table III. As a result, the MAE of the system is increased according to the general trend of the Co layer. Note that the effect of the change in the Co-O\* interatomic distance on the MAE is considerable when the distance is in the vicinity of 2 Å as shown in Fig. 4(b). This coincides with the Co-O interatomic distance in the MgO/Co/Au(001) system, which is also about 2 Å. Therefore, one important origin of the large EF dependence of the MAE of the MgO/Co/Au(001) system is the structural relaxation caused by the EF, i.e., the change in the Co-O interatomic distance.

### 3.3.6 MAE in (111) systems in absence of EF

Finally, we study the TM/Au(111) and MgO/TM/Au(111) systems. In the absence of the EF, the MAE of the Fe/Au(111) system, 0.02 meV/cell, is smaller than that of the Fe(111) monolayer system, 0.24 meV/cell, and that of the Fe/Au(001) system, 0.31 meV/cell. On the contrary, the MAE of the Co/Au(111) system, 0.16 meV/cell, is considerably larger than that of the Co(111) monolayer system, -2.18 meV/cell, and

that of the Co/Au(001) system,  $-1.65$  meV. It is interesting to note that the MAE of the Co/Au(111) system is even positive, showing a perpendicular magnetic anisotropy; this is in a strong contrast to the in-plane magnetic anisotropy found for the Co monolayer and Co/Au(001) systems. The remarkable increase in the MAE in the Co/Au(111) system is also likely due to the general trend of the Co layer; the Au layer acts as an adjacent inert layer in this case. It is worth noting that the effect of the Au substrate on the MAE is larger in the Co/Au(111) system than in the Co/Au(001) system because the atomic density in the Au(111) surface is larger than that in the Au(001) surface. A similar trend was found previously in related systems; the theoretical study of the Co and Au (111) multilayer system by Kyuno et al. showed that the system exhibits a perpendicular magnetic anisotropy with an MAE of  $1.11$  meV/cell and the theoretical study of the Au/Co/Au(111) systems by Újfalussy et al. also showed that the system exhibits a perpendicular magnetic anisotropy with an MAE of about  $1$  meV/cell.<sup>55,78)</sup> In both systems, the Co layer is sandwiched by the Au layers; this may be the reason why the MAE calculated by Kyuno et al. and Újfalussy et al., both of which are about  $1$  meV/cell, is considerably larger than our calculated MAE of the Co/Au(111) system,  $0.16$  meV/cell. It is interesting to note that even the sign of the MAE as well as its magnitude depends on the surface orientation of the substrate not to mention the substrate material. Such a dependence of the MAE on the surface orientation was shown theoretically on the MAE of the Fe monolayer on the Pt substrate; the MAE of the Fe/Pt(001) system is positive while that of the Fe/Pt(111) system is negative.<sup>66,71-73)</sup> Even an inert substrate such as Ag and Au affects the MAE so that its behavior is considerably different from those of the freestanding TM monolayer systems as noted previously.<sup>42)</sup>

The MAE of the MgO/TM/Au(111) systems is considerably increased by introducing the MgO insulating layer in comparison to that of the TM/Au(111) systems; the MAE is  $1.16$  meV/cell for TM=Fe and  $1.43$  meV/cell for TM=Co, both showing a strong perpendicular magnetic anisotropy. The increase in the MAE may be related to the effect of the oxidation of the TM atom by the O atom. The noticeable oxidation of the TM atom is indicated by the increase in  $M_{\text{spin}}$  as well as the small TM-O interatomic distance already mentioned above.  $M_{\text{spin}}$  of the MgO/TM/Au(111) systems is increased by about  $0.2 \mu_B$  for TM=Fe and  $0.4 \mu_B$  for TM=Co in comparison to those of the TM/Au(111) system; this may be due to the decrease in the number of the 3d electrons in the TM atom. That is, the increase in  $M_{\text{spin}}$  indicates the oxidation of the

TM atom by the O atom in the MgO/TM/Au(111) systems. This is in a strong contrast to the result that the TM atom in the MgO/TM/Au(001) system is not oxidized by the O atom. We can understand this as follows. The O atom on top of the TM atom in the (111) systems is surrounded by four metal atoms while that in the (001) systems is surrounded by six metal atoms. This difference in the coordination number of the O atom results in the more significant oxidation of the TM atom by the O atom in the (111) systems than in the (001) systems.

### 3.3.7 MAE in (111) systems under EF

For the positive EF, the MAE of all the TM/Au(111) and MgO/TM/Au(111) systems is almost unchanged. For the negative EF, the MAE of all the TM/Au(111) and MgO/TM/Au(111) systems is also almost unchanged except for a moderate change in the MAE of the MgO/Fe/Au(111) system. Thus the EF dependence of the MAE of the (111) systems is not large. The MAE of the systems under the EF calculated with the unoptimized structures is almost the same as those calculated with the optimized structures. This is because the TM-O interatomic distance in the MgO/TM/Au(111) systems is almost unaffected by the EF; the change in the TM-O interatomic distance in the MgO/TM/Au(111) system is about  $\pm 0.005$  Å, which is one order of magnitude smaller than those found for the MgO/TM/Au(001) systems, about  $\pm 0.05$  Å.

## 4. Conclusions

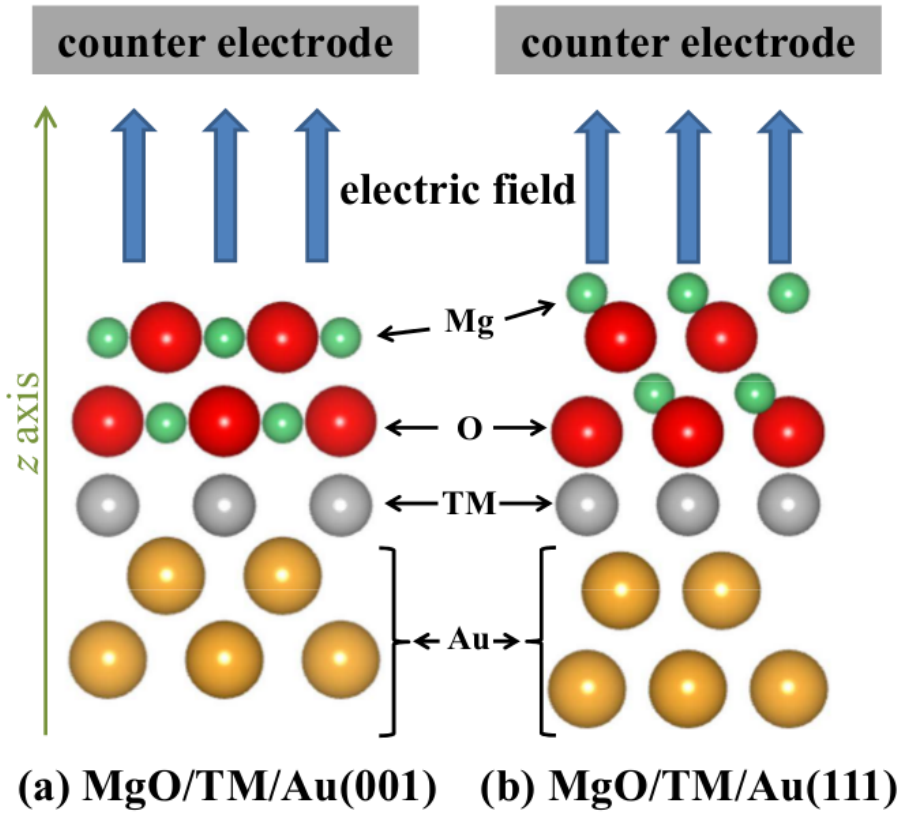
We have studied the EF effects on the MAE in the MgO/TM/Au (TM=Fe, Co) systems with (001) and (111) orientations using relativistic first-principles calculations based on the density functional theory within the local spin density approximation. For comparison, we also studied the EF effects on the MAE in the freestanding TM monolayer systems, the hypothetical bilayer systems where each system consists of an O\* monolayer and a TM monolayer, and the TM/Au systems. In the absence of or under the EF, we first optimized the structures of the systems using the SFLCAO method and then calculated the MAE of the systems with the optimized structures using the FFLCAO method. We found that the perpendicular magnetic anisotropy of the MgO/TM/Au(001) system is enhanced by the EF that decreases the number of electrons in the system. The calculated MAE and its EF dependence of the MgO/Fe/Au(001) system was found to be in a semi-quantitative agreement with the experimental results with successful reproduction of the sign of the measured EF dependence. Also the EF



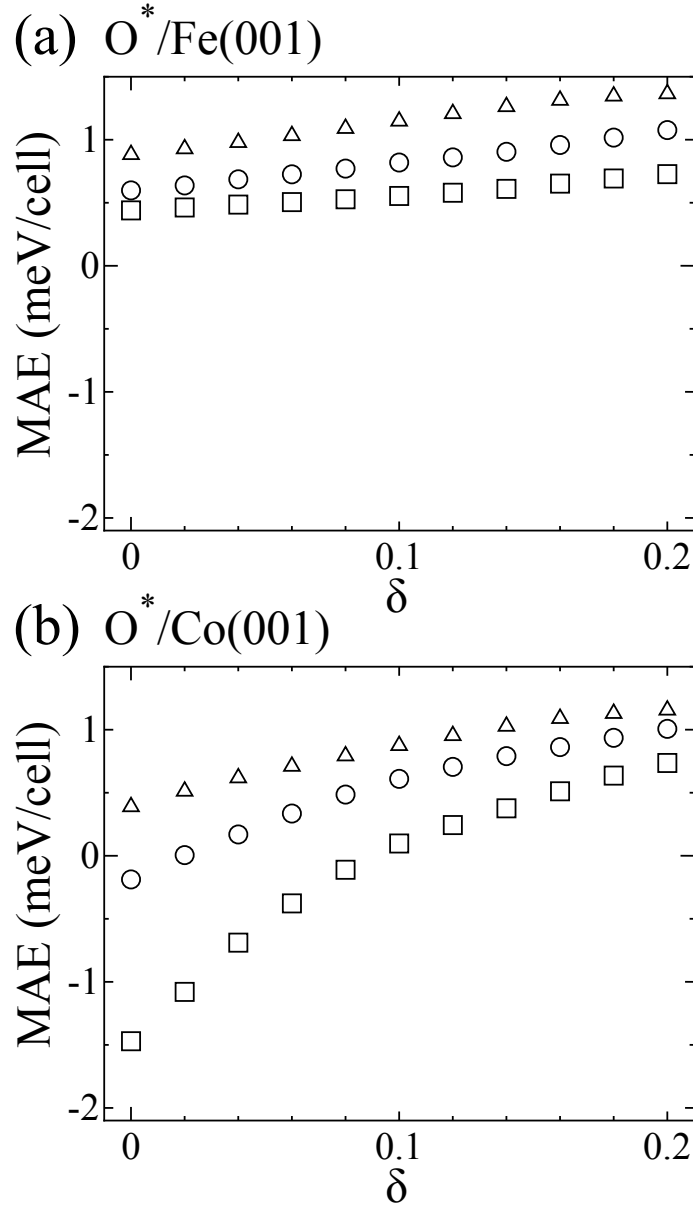
dependence of the MAE of the MgO/Co/Au(001) system was found to be very large due to the structural relaxation of the Co-O interatomic distance and the decrease in the number of electrons in the Co atom caused by the EF. We attributed this result to the general trend that the perpendicular magnetic anisotropy of the Co layer is affected significantly when in contact with an inert layer at an interlayer distance of about 2 Å. On the contrary, we found that the MgO/TM/Au(111) system shows almost no EF dependence of the MAE. We attributed this result to the existence of the strong TM-O covalent bond associated with the oxidation of the TM atom by the O atom.

### **Acknowledgment**

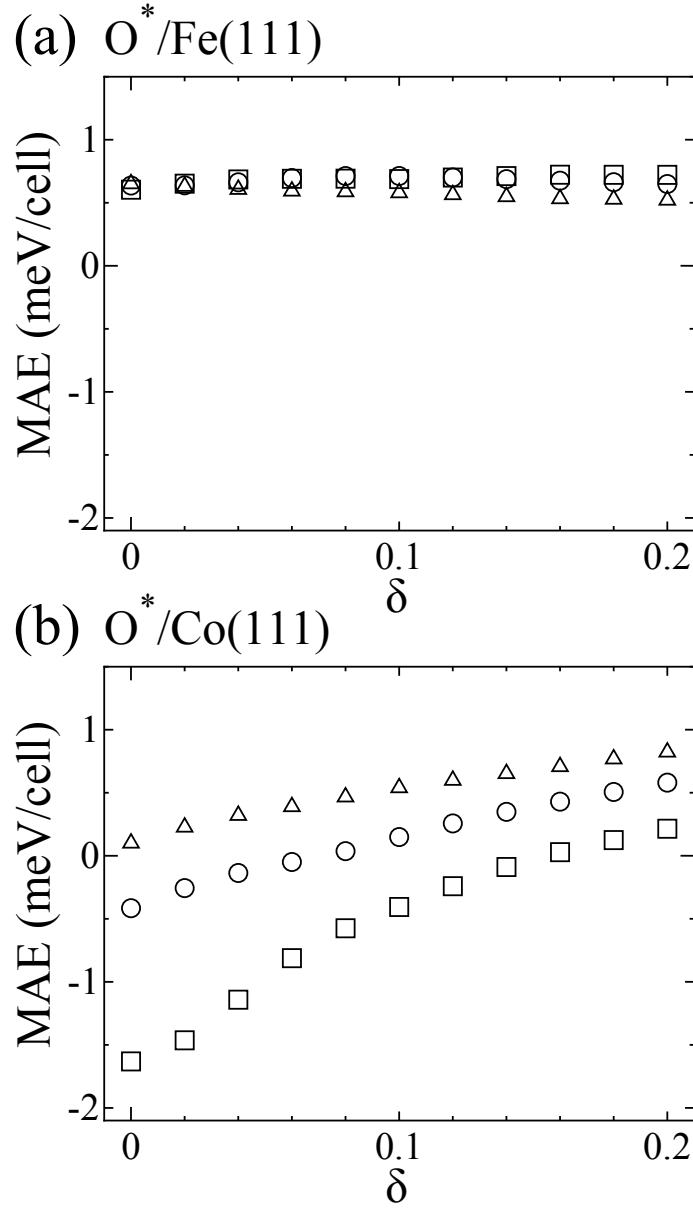
We would like to thank Y. Suzuki for helpful discussions and comments. We would also like to thank T. Oikawa for introducing us to the subject and supporting us through the investigations.



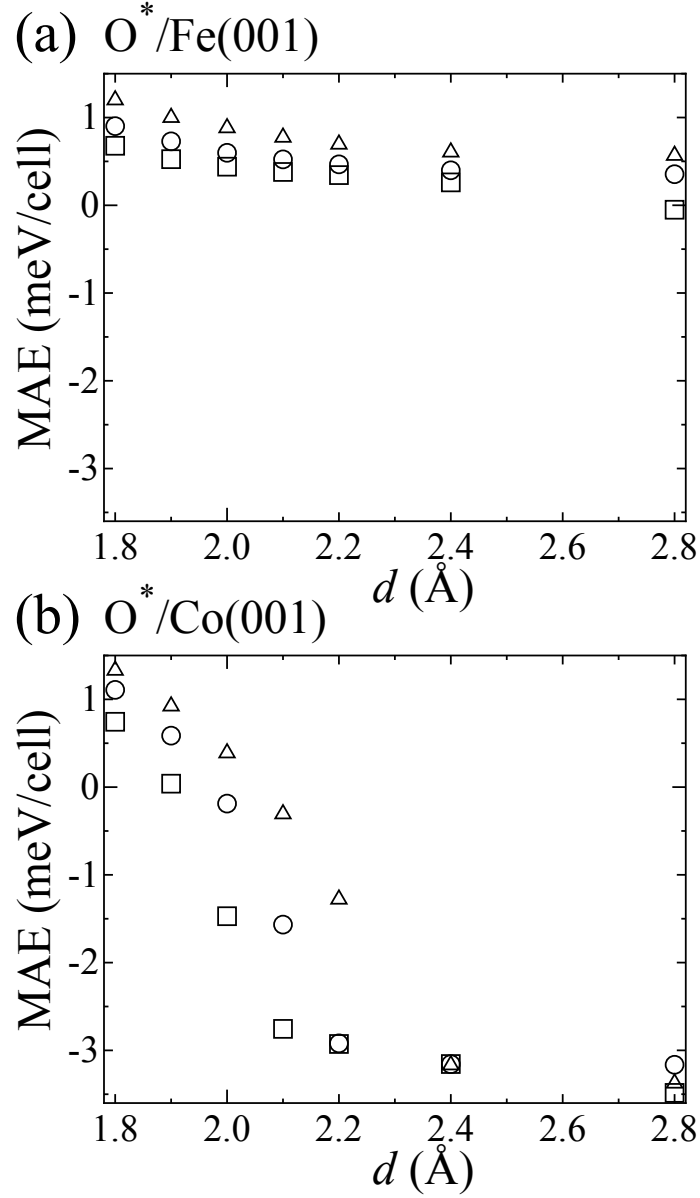
**Fig. 1.** (Color online) Schematic diagram of (a) MgO/TM/Au(001) and (b) MgO/TM/Au(111) systems where TM=Fe, Co. The system consists of the MgO insulating layer, the TM monolayer, and the Au substrate. The electric field is applied by introducing the counter electrode far above the system. The direction of the electric field is defined in such a way that a positive (negative) electric field decreases (increases) the number of electrons in the system, pointing upward (downward) along the positive (negative)  $z$  axis direction.



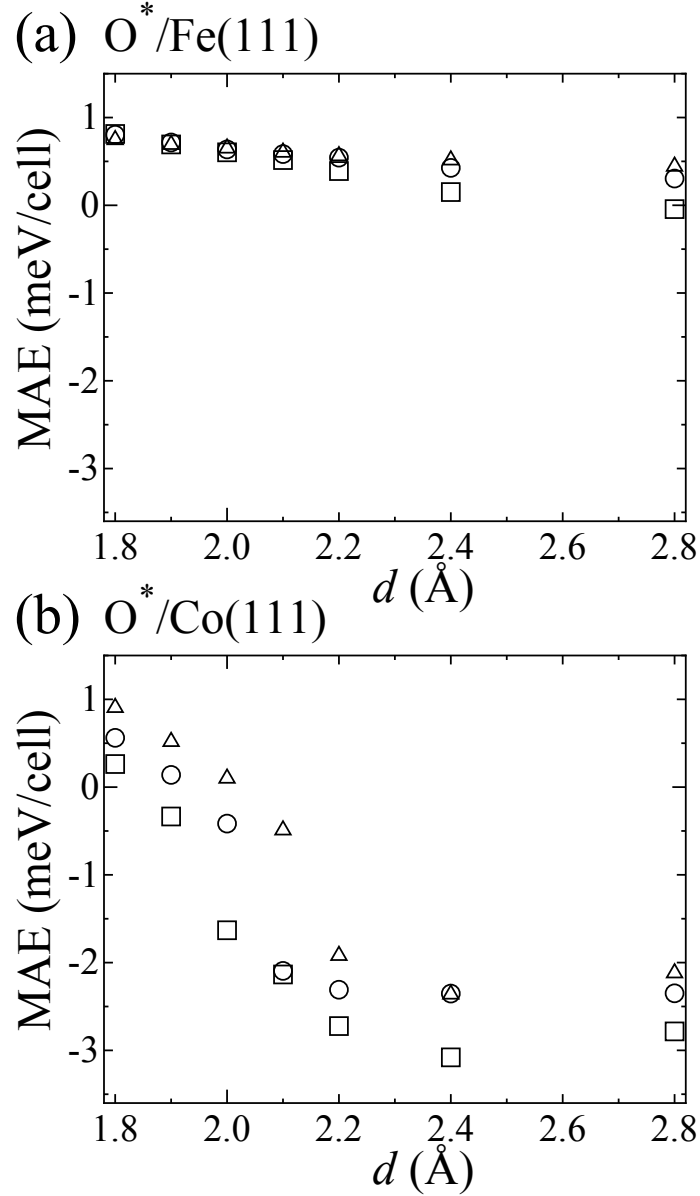
**Fig. 2.** Magnetic anisotropy energy, MAE, as a function of the oxidation number  $\delta$  of the TM atom (TM=Fe, Co) in (a)  $O^*/Fe(001)$  and (b)  $O^*/Co(001)$  bilayer systems with the lattice constant taken to match the Au(001) substrate,  $a=2.88 \text{ \AA}$ , and the interlayer distance fixed at  $d=2.0 \text{ \AA}$ . The triangles, the circles, and the squares represent the results for  $\Delta N=-0.1, 0.0,$  and  $0.1,$  respectively. The electric field is given by  $-0.218 \Delta N \times 10^3 \text{ V/nm}$  with the definition that a positive (negative) electric field decreases (increases) the number of electrons in a system.



**Fig. 3.** Magnetic anisotropy energy, MAE, as a function of the oxidation number  $\delta$  of the TM atom (TM=Fe, Co) in (a) O\*/Fe(111) and (b) O\*/Co(111) bilayer systems with the lattice constant taken to match the Au(111) substrate,  $a=2.88 \text{ \AA}$ , and the interlayer distance fixed at  $d=2.0 \text{ \AA}$ . The triangles, the circles, and the squares represent the results for  $\Delta N=-0.1$ ,  $0.0$ , and  $0.1$ , respectively. The electric field is given by  $-0.252 \Delta N \times 10^3 \text{ V/nm}$  with the definition that a positive (negative) electric field decreases (increases) the number of electrons in a system.



**Fig. 4.** Magnetic anisotropy energy, MAE, as a function of the distance  $d$  between the O\* and TM (TM=Fe, Co) layers in (a) O\*/Fe(001) and (b) O\*/Co(001) bilayer systems with the lattice constant taken to match the Au(001) substrate,  $a=2.88$  Å, and the oxidation number of the TM atom fixed at  $\delta=0.0$ . The triangles, the circles, and the squares represent the results for  $\Delta N=-0.1$ , 0.0, and 0.1, respectively. The electric field is given by  $-0.218 \Delta N \times 10^3$  V/nm with the definition that a positive (negative) electric field decreases (increases) the number of electrons in a system.



**Fig. 5.** Magnetic anisotropy energy, MAE, as a function of the distance  $d$  between the O\* and TM (TM=Fe, Co) layers in (a) O\*/Fe(111) and (b) O\*/Co(111) bilayer systems with the lattice constant taken to match the Au(111) substrate,  $a=2.88$  Å, and the oxidation number of the TM atom fixed at  $\delta=0.0$ . The triangles, the circles, and the squares represent the results for  $\Delta N=-0.1$ , 0.0, and 0.1, respectively. The electric field is given by  $-0.252 \Delta N \times 10^3$  V/nm with the definition that a positive (negative) electric field decreases (increases) the number of electrons in a system.

**Table I.** Magnetic anisotropy energy, MAE (in meV/cell), and spin magnetic moment,  $M_{\text{spin}}$  (in  $\mu_{\text{B}}$ /cell), for the freestanding Fe(001) and Co(001) monolayer systems for the change in electron number  $\Delta N = -0.1, 0.0,$  and  $0.1$  and the lattice constant,  $a$  (in  $\text{\AA}$ ), taken to match the substrates shown in parentheses. The electric field is given by  $-1.81 \Delta N/a^2 \times 10^3$  V/nm with the definition that a positive (negative) electric field decreases (increases) the number of electrons in a system.

System	$a$	$\Delta N = -0.1$		$\Delta N = 0.0$					$\Delta N = 0.1$		
		MAE	$M_{\text{spin}}$	MAE		$M_{\text{spin}}$			MAE	$M_{\text{spin}}$	
Fe(001)	3.16 (W)	0.65	3.50	0.37	0.27 <sup>a)</sup>		3.43	3.43 <sup>a)</sup>		-0.59	3.39
	3.03 (V)	0.62	3.43	0.30	0.41 <sup>a)</sup>		3.38	3.36 <sup>a)</sup>		-0.39	3.30
	2.89 (Ag)	0.59	3.39	0.36	0.37 <sup>a)</sup>	0.38 <sup>b)</sup>	3.32	3.22 <sup>a)</sup>	3.20 <sup>b)</sup>	0.02	3.23
				0.19 <sup>c)</sup>	0.22 <sup>d)</sup>	3.16 <sup>c)</sup>	3.16 <sup>d)</sup>				
	2.88 (Au)	0.58	3.39	0.36			3.31			0.02	3.23
	2.75 (Pd)	0.62	3.31	0.43	0.34 <sup>a)</sup>		3.24	3.20 <sup>a)</sup>		0.42	3.16
	2.56 (Cu)	0.74	3.21	0.54	0.42 <sup>a)</sup>		3.13	3.04 <sup>a)</sup>		0.63	3.04
0.61 <sup>e)</sup>				0.63 <sup>f)</sup>	2.97 <sup>f)</sup>						
Co(001)	3.16 (W)	-5.59	2.33	-6.44			2.28			-6.75	2.21
	3.03 (V)	-4.58	2.28	-4.49			2.23			-5.03	2.18
	2.89 (Ag)	-3.31	2.25	-3.20	-3.60 <sup>g)</sup>	-2.59 <sup>h)</sup>	2.18	2.20 <sup>g)</sup>	2.17 <sup>h)</sup>	-3.66	2.13
	2.88 (Au)	-3.25	2.25	-3.16			2.18			-3.61	2.13
	2.75 (Pd)	-2.27	2.23	-2.23			2.15			-2.49	2.08
	2.56 (Cu)	-1.27	2.19	-1.31	-1.35 <sup>h)</sup>	-1.49 <sup>h)</sup>	2.11	2.06 <sup>h)</sup>	2.03 <sup>h)</sup>	-1.37	2.03
				-1.25 <sup>i)</sup>	-1.37 <sup>c)</sup>	2.06 <sup>i)</sup>	2.09 <sup>c)</sup>				
			-1.37 <sup>d)</sup>	-1.26 <sup>f)</sup>		2.08 <sup>d)</sup>	2.07 <sup>f)</sup>				

a) Reference 49; perturbative calculations based on the force theorem.

b) Reference 41; perturbative calculations based on the force theorem.

c) Reference 21; perturbative calculations based on the force theorem.

d) Reference 21; self-consistent calculations.

e) Reference 43; perturbative calculations based on the force theorem.

f) Reference 69; self-consistent calculations.

g) Reference 42; perturbative calculations based on the force theorem.

h) Reference 54; perturbative calculations based on the force theorem.

i) Reference 56; perturbative calculations based on the force theorem.

**Table II.** Magnetic anisotropy energy, MAE (in meV/cell), and spin magnetic moment,  $M_{\text{spin}}$  (in  $\mu_{\text{B}}$ /cell), for the freestanding Fe(111) and Co(111) monolayer systems for the change in electron number  $\Delta N = -0.1, 0.0,$  and  $0.1$  and the lattice constant,  $a$  (in  $\text{\AA}$ ), taken to match the substrates shown in parentheses. The electric field is given by  $-2.09 \Delta N/a^2 \times 10^3$  V/nm with the definition that a positive (negative) electric field decreases (increases) the number of electrons in a system.

System	$a$	$\Delta N = -0.1$		$\Delta N = 0.0$				$\Delta N = 0.1$		
		MAE	$M_{\text{spin}}$	MAE		$M_{\text{spin}}$		MAE	$M_{\text{spin}}$	
Fe(111)	3.20 (Hf)	0.12	3.42	-0.16		3.36		-0.73	3.28	
	2.95 (Ti)	0.34	3.30	0.15		3.22		-0.01	3.13	
	2.89 (Ag)	0.40	3.26	0.23		3.18		0.15	3.09	
	2.88 (Au)	0.39	3.26	0.24		3.17		0.17	3.08	
	2.77 (Pt)	0.36	3.18	0.21	0.58 <sup>a)</sup>	0.60 <sup>b)</sup>	3.10	3.06 <sup>b)</sup>	0.32	3.01
	2.75 (Pd)	0.39	3.16	0.19		3.08		0.29	2.99	
	2.56 (Cu)	0.48	2.99	0.27		2.90		0.35	2.82	
Co(111)	3.20 (Hf)	-5.87	2.26	-4.62		2.20		-3.77	2.13	
	2.95 (Ti)	-2.64	2.20	-2.79		2.12		-2.96	2.05	
	2.89 (Ag)	-2.07	2.18	-2.23		2.10		-2.58	2.03	
	2.88 (Au)	-2.02	2.18	-2.18		2.10		-2.56	2.02	
	2.77 (Pt)	-1.24	2.14	-1.43	-1.56 <sup>a)</sup>	-1.65 <sup>b)</sup>	2.06	2.08 <sup>b)</sup>	-1.92	1.97
	2.75 (Pd)	-1.11	2.14	-1.28		-4.03 <sup>c)</sup>		2.05	-1.80	1.96
	2.56 (Cu)	-0.39	2.05	-0.55		-0.85 <sup>d)</sup>		1.96	1.83 <sup>d)</sup>	-0.92

a) Reference 73; perturbative calculations based on the force theorem.

b) Reference 73; self-consistent calculations.

c) Reference 84; perturbative calculations based on the force theorem.

d) Reference 56; perturbative calculations based on the force theorem.



**Table III.** Structures of the TM/Au(001) and MgO/TM/Au(001) (TM=Fe, Co) systems for the change in electron number  $\Delta N = -0.1, 0.0,$  and  $0.1$ . The  $x$  and  $y$  coordinates (in Å) are chosen according to the lattice constant of Au(001) substrate with the in-plane primitive vectors  $\mathbf{a}_1 = (a/\sqrt{2}, a/\sqrt{2}, 0)$  and  $\mathbf{a}_2 = (-a/\sqrt{2}, a/\sqrt{2}, 0)$  where  $a=2.88$  Å. The  $z$  coordinates (in Å) are optimized under the electric field of  $-0.218 \Delta N \times 10^3$  V/nm with the definition that a positive (negative) electric field decreases (increases) the number of electrons in a system.

System	Atom	$x$	$y$	$z$		
				$\Delta N = -0.1$	$\Delta N = 0.0$	$\Delta N = 0.1$
Fe/Au(001)	Fe	0.00	0.00	0.00	0.00	0.00
	Au	0.00	2.04	-1.70	-1.67	-1.69
	Au	0.00	0.00	-3.76	-3.73	-3.76
MgO/Fe/Au(001)	Mg	0.00	0.00	4.21	4.16	4.21
	O	0.00	2.04	4.13	4.17	4.26
	Mg	0.00	2.04	2.08	2.05	2.06
	O	0.00	2.04	2.04	2.09	2.14
	Fe	0.00	0.00	0.00	0.00	0.00
	Au	0.00	2.04	-1.75	-1.75	-1.75
	Au	0.00	0.00	-3.82	-3.82	-3.83
Co/Au(001)	Co	0.00	0.00	0.00	0.00	0.00
	Au	0.00	2.04	-1.62	-1.60	-1.61
	Au	0.00	0.00	-3.68	-3.66	-3.67
MgO/Co/Au(001)	Mg	0.00	0.00	4.19	4.13	4.17
	O	0.00	2.04	4.10	4.14	4.23
	Mg	0.00	2.04	2.05	2.00	2.00
	O	0.00	2.04	2.02	2.06	2.10
	Co	0.00	0.00	0.00	0.00	0.00
	Au	0.00	2.04	-1.68	-1.68	-1.69
	Au	0.00	0.00	-3.76	-3.76	-3.78

**Table IV.** Structures of the TM/Au(111) and MgO/TM/Au(111) (TM=Fe, Co) systems for the change in electron number  $\Delta N = -0.1, 0.0,$  and  $0.1$ . The  $x$  and  $y$  coordinates (in Å) are chosen according to the lattice constant of Au(111) substrate with the in-plane primitive vectors  $\mathbf{a}_1 = (a, 0, 0)$  and  $\mathbf{a}_2 = (-a/2, \sqrt{3}a/2, 0)$  where  $a=2.88$  Å. The  $z$  coordinates (in Å) are optimized under the electric field of  $-0.252 \Delta N \times 10^3$  V/nm with the definition that a positive (negative) electric field decreases (increases) the number of electrons in a system.

System	Atom	$x$	$y$	$z$		
				$\Delta N = -0.1$	$\Delta N = 0.0$	$\Delta N = 0.1$
Fe/Au(111)	Fe	0.00	0.00	0.00	0.00	0.00
	Au	1.44	0.83	-2.09	-2.08	-2.09
	Au	0.00	0.00	-4.50	-4.48	-4.51
MgO/Fe/Au(111)	Mg	0.00	0.00	5.29	5.25	5.27
	O	1.44	0.83	4.15	4.16	4.16
	Mg	0.00	1.67	2.79	2.76	2.77
	O	0.00	0.00	1.80	1.81	1.81
	Fe	0.00	0.00	0.00	0.00	0.00
	Au	1.44	0.83	-2.14	-2.13	-2.14
	Au	0.00	0.00	-4.57	-4.56	-4.57
Co/Au(111)	Co	0.00	0.00	0.00	0.00	0.00
	Au	1.44	0.83	-2.04	-2.03	-2.05
	Au	0.00	0.00	-4.43	-4.42	-4.47
MgO/Co/Au(111)	Mg	0.00	0.00	5.27	5.24	5.25
	O	1.44	0.83	4.15	4.15	4.17
	Mg	0.00	1.67	2.77	2.75	2.75
	O	0.00	0.00	1.79	1.79	1.80
	Co	0.00	0.00	0.00	0.00	0.00
	Au	1.44	0.83	-2.08	-2.07	-2.08
	Au	0.00	0.00	-4.50	-4.49	-4.50

**Table V.** Magnetic anisotropy energy, MAE (in meV/cell), and spin magnetic moment,  $M_{\text{spin}}$  (in  $\mu_{\text{B}}$ ), for the TM monolayer, TM/Au, and MgO/TM/Au (TM=Fe, Co) systems with (001) and (111) orientations for the change in electron number  $\Delta N = -0.1, 0.0,$  and  $0.1$ . The electric field is given by  $-0.218 \Delta N \times 10^3$  V/nm and  $-0.252 \Delta N \times 10^3$  V/nm for the (001) and (111) systems, respectively, with the definition that a positive (negative) electric field decreases (increases) the number of electrons in a system.

System	$\Delta N = -0.1$		$\Delta N = 0.0$		$\Delta N = 0.1$	
	MAE	$M_{\text{spin}}$	MAE	$M_{\text{spin}}$	MAE	$M_{\text{spin}}$
Fe(001)	0.58	3.39	0.36	3.31	0.02	3.23
Fe/Au(001)	1.11	3.13	0.31	3.07	-0.32	3.04
MgO/Fe/Au(001)	0.73 0.61 <sup>a)</sup>	2.90 2.91 <sup>a)</sup>	0.60	2.84	0.47 0.46 <sup>a)</sup>	2.85 2.85 <sup>a)</sup>
Co(001)	-3.25	2.25	-3.16	2.18	-3.61	2.13
Co/Au(001)	-1.32	2.07	-1.65	2.02	-1.31	1.97
MgO/Co/Au(001)	1.46 1.25 <sup>a)</sup>	1.96 1.97 <sup>a)</sup>	-0.42	1.90	-1.01 -0.06 <sup>a)</sup>	1.90 1.91 <sup>a)</sup>
Fe(111)	0.39	3.26	0.24	3.17	0.17	3.08
Fe/Au(111)	0.18	3.12	0.02	3.07	-0.08	3.02
MgO/Fe/Au(111)	1.25 1.22 <sup>a)</sup>	3.31 3.30 <sup>a)</sup>	1.16	3.29	1.51 1.27 <sup>a)</sup>	3.31 3.30 <sup>a)</sup>
Co(111)	-2.02	2.18	-2.18	2.10	-2.56	2.02
Co/Au(111)	0.01	1.98	0.16	1.94	0.12	1.90
MgO/Co/Au(111)	1.35 1.44 <sup>a)</sup>	2.34 2.33 <sup>a)</sup>	1.43	2.33	1.43 1.43 <sup>a)</sup>	2.33 2.33 <sup>a)</sup>

a) Calculated with the same structure as that for  $\Delta N = 0.0$ .

## Appendix

We determined the structures of the systems as follows. The  $x$  and  $y$  coordinates of the atoms in a system were chosen according to the in-plane lattice constant of the system,  $a$ . The in-plane primitive vectors are  $\mathbf{a}_1 = (a/\sqrt{2}, a/\sqrt{2}, 0)$  and  $\mathbf{a}_2 = (-a/\sqrt{2}, a/\sqrt{2}, 0)$  for the square lattice of the (001) systems and  $\mathbf{a}_1 = (a, 0, 0)$  and  $\mathbf{a}_2 = (-a/2, \sqrt{3}a/2, 0)$  for the triangular lattice of the (111) systems. In this work, we do not consider the surface reconstruction of the Au substrates and assume that the TM atom is at the hcp hollow site of the Au(111) substrate for the TM/Au(111) and MgO/TM/Au(111) systems. Also, for the MgO/TM/Au systems, we consider the geometry where the O atom is on top of the TM atom rather than at the hollow site surrounded by TM atoms. Li and Freeman confirmed that the former geometry is energetically more favorable for (001) orientation.<sup>100)</sup> We confirmed that this is also the case for (111) orientation. The  $z$  coordinates of the atoms in the TM/Au and MgO/TM/Au systems were optimized using the SFLCAO method. We fixed the center of mass of the system during the optimization and used the force criterion for stopping the structure optimization of 0.01 eV/Å.

The atomic orbitals used as the basis functions are as follows: the 1s, 2s, 2p, and 3s orbitals of the neutral Mg atom, the 3s, 3p, and 3d orbitals of the Mg<sup>2+</sup> atom, the 1s, 2s, and 2p orbitals of the neutral O atom, the 2s and 2p orbitals of the O<sup>2+</sup> atom, the 3d orbitals of the O<sup>6+</sup> atom, the 1s, 2s, 2p, 3s, 3p, 3d, and 4s orbitals of the neutral TM atom, the 3d, 4s, and 4p orbitals of the TM<sup>2+</sup> atom, the 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d, and 6s orbitals of the neutral Au atom, and the 5d, 6s, and 6p orbitals of the Au<sup>2+</sup> atom. It is worth noting that the use of the atomic orbitals of positively charged atoms as well as those of neutral atoms is crucial to the description of the contraction of atomic orbitals associated with cohesion. The Brillouin-zone integration was carried out using the good-lattice-point method;<sup>101)</sup> we used 34  $\mathbf{k}$  points for the structure optimization and 610  $\mathbf{k}$  points for the calculations of the MAE. To speed up the convergence, we used a Fermi distribution smearing of eigenstates with a width of 30 meV.

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