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Origin of the large interfacial perpendicular magnetic anisotropy in MgO/Co\textsubscript{2}FeAl

Sicong Jiang,\textsuperscript{1,2} Safdar Nazir,\textsuperscript{1} and Kesong Yang\textsuperscript{1,2,3,*}

\textsuperscript{1}Department of NanoEngineering and Program of Chemical Engineering, University of California San Diego, La Jolla, California 92093-0448, USA
\textsuperscript{2}Program of Materials Science and Engineering, University of California San Diego, La Jolla, California 92093-0418, USA
\textsuperscript{3}Center for Memory and Recording Research, University of California San Diego, La Jolla, California 92093-0401, USA

Interfacial perpendicular magnetic anisotropy in the MgO/Co\textsubscript{2}FeAl heterostructure is desired for technological applications, while its origin of the large interfacial anisotropy constant ($K_i$) remains controversial. Here we show that, by modeling four types of interface models for MgO/Co\textsubscript{2}FeAl system using first-principles calculations, the MgO/Co\textsubscript{2} interface is energetically more favorable than MgO/FeAl interface, and the interfacial Co atoms at the former interface produce out-of-plane $K_i$ while the interfacial Fe atoms at the later interface produce in-plane $K_i$. The origin of this different behavior can be explained from the atomic-resolved and orbital-resolved $K_i$ along with the perturbation theory energy analysis. In addition, we also studied the influence of 26 capping layers on the interfacial magnetic anisotropy of MgO/Co\textsubscript{2}FeAl and found that Fe- and W-capping can significantly enhance the $K_i$ in the MgO/Co\textsubscript{2}FeAl with a particularly large $K_i$ of 4.90 mJ/m\textsuperscript{2} in the W-capped model. This work clarifies the atomistic origin of the interfacial perpendicular magnetic anisotropy and provides guidance to further enhance interfacial $K_i$ by adding capping layers in the MgO/Co\textsubscript{2}FeAl.

I. INTRODUCTION

Magnetic tunnel junctions (MTJs) consisting of two ferromagnetic (FM) layers separated by a thin insulating barrier are core components in spin-transfer-torque magnetic random-access memory (STT-MRAM).\textsuperscript{1,2} In particular, the perpendicular MTJs (p-MTJs) that possessed perpendicular magnetic anisotropy (PMA) have attracted great attention in recent years because of their promising applications in the next-generation spintronic devices towards using faster and smaller magnetic bits.\textsuperscript{3–6} In p-MTJs, PMA occurs at the interface between ferromagnetic thin film and insulating barrier and its strength is characterized by the magnetic anisotropy constant ($K_i$), which is defined as the anisotropy energy per unit area.\textsuperscript{7} To achieve a high thermal stability of the relative magnetization orientation of the two ferromagnetic electrodes, a large $K_i$ is desired. As p-MTJs shrink to the nanometer scale, a larger $K_i$ is necessary to sustain a sufficient thermal stability. A recent theoretical calculation indicated that a $K_i$ of 4.7 mJ/m\textsuperscript{2} is needed for a data retention time of ten years when the memory devices scale down to 10 nm.\textsuperscript{8}

PMA has been traditionally achieved at interfaces between ferromagnetic and nonmagnetic heavy metals such as Co/Pt, however, their $K_i$ is small (less than 1 mJ/m\textsuperscript{2}).\textsuperscript{9} In 2010, a large $K_i$ of 1.3 mJ/m\textsuperscript{2} was reported at MgO/CoFeB interface, and the MTJ based on this material interface exhibits a high tunnel magnetoresistance ratio of 120\% and a low switching current of about 49 $\mu$A.\textsuperscript{5} Since then, great research efforts have been made to tune $K_i$ at MgO/Fe interface\textsuperscript{7} or to explore the possibility of producing large $K_i$ at novel MgO-based interfaces.\textsuperscript{10,11} Co\textsubscript{2}FeAl, one prototype compound of full Heusler family, has received increasing interests as one possible alternative to Fe and CoFeB in the MgO-based p-MTJs in recent years because of its excellent properties including high spin polarization,\textsuperscript{12} low magnetic damping constant (about 0.001),\textsuperscript{13} and small lattice mismatch\textsuperscript{14} between Co\textsubscript{2}FeAl film and MgO substrate (~4 \%). The magnetic anisotropy at MgO/Co\textsubscript{2}FeAl interface was first reported in 2011 and was found very sensitive to the annealing.\textsuperscript{10,11,15} Jiang’s team\textsuperscript{15} and Inomata’s team\textsuperscript{10} both reported a PMA at MgO/Co\textsubscript{2}FeAl interface, independently, and found a magnetic anisotropy transition from in-plane to out-of-plane after annealing.\textsuperscript{10} In contrast, in-plane magnetic anisotropy was also found at MgO/Co\textsubscript{2}FeAl interface and showed different behavior with the annealing temperature.\textsuperscript{11,16} A very recent experimental study also reported an evolution of the PMA at the interface between MgO and Co\textsubscript{2}FeAl, i.e., a $K_i$ of zero for as-deposited samples and a $K_i$ of 1.14 (2.01) mJ/m\textsuperscript{2} for samples annealed at 320 (450)°C, which is attributed to the modification of the interface during the thermal treatment.\textsuperscript{17}

PMA is mainly determined by the magnetic ions of a few monolayers near the interfacial region and there exist two types of interfaces in the MgO/Co\textsubscript{2}FeAl heterostructure, i.e., MgO/Co\textsubscript{2} and MgO/FeAl. Accordingly, one may speculate that the different magnetic anisotropy is caused by the different interfacial terminations between MgO substrate and Co\textsubscript{2}FeAl film. Inomata’s team investigated the PMA at the MgO/Co\textsubscript{2}FeAl interface using angular-dependent x-ray magnetic circular dichroism (XMCD), and attributed the PMA mostly to the interfacial Fe atoms at the MgO/FeAl interface.\textsuperscript{18} Later, the same team also argued that the PMA at the Co\textsubscript{2}FeAl heterostructure is mainly contributed by the large perpendicular orbital magnetic moments of interfacial Fe ions from XMCD measurement.\textsuperscript{19} A prior theoretical study indicated that oxygen-top FeAl termination has the highest thermal stability on the basis of density functional theory calculations,\textsuperscript{20} which seems to support the above arguments. However, a recent
computational study indicated that FeAl-termination at MgO/Co$_2$FeAl interface lead to an in-plane instead of out-of-plane magnetic anisotropy, while Co-termination showed the PMA with $K_i$ up to 1.31 mJ/m$^2$.
21 Therefore, to clarify the atomic origin of the magnetic anisotropy at the MgO/Co$_2$FeAl interface, a comprehensive study of the interfacial magnetic properties and evaluation of the relative thermodynamic stability of the two types of materials interfaces are very necessary.

Additionally, a series of recent experimental and computational studies both indicated that metal-based capping layers have a significant influence on the $K_i$ of MgO/Co$_2$FeAl heterostructure,22,23 in which capping layers are often used to protect the ferromagnetic layers. For instance, Cr-capped MgO/Co$_2$FeAl showed an in-plane magnetic anisotropy with a $K_i$ of -0.46 mJ/m$^2$ while Ta-capped film exhibited a PMA with a $K_i$ of 0.74 mJ/m$^2$.22 Gabor et al also reported a similar $K_i$ of 0.67 mJ/m$^2$ in the Ta/Co$_2$FeAl/MgO multilayers even in the as-deposited state.23 As a result, adding one capping layer on MgO/Co$_2$FeAl heterostructure not only protects the ferromagnetic layer but also plays an important role in tuning the $K_i$. Consequently, a systematic evaluation of the influence of all the possible metal-based capping layers on the $K_i$ of MgO/Co$_2$FeAl heterostructure is of great importance, and so far, there has been no such a report.

In this research article, we reported a comprehensive study of the interfacial magnetic and energetic properties for the MgO/Co$_2$FeAl interface without and with capping layers, consisting of two sections. In the first section, we considered four types of MgO/Co$_2$FeAl models without capping layers, including MgO/Co$_2$FeAl, MgO/Co$_2$Co$_2$, MgO/Co$_2$Co$_2$, and MgO/FeAl...FeAl, and investigated their layer-resolved and atomic orbital-resolved $K_i$ and interfacial cleavage energy. In the second section, we systematically investigated the influence of 26 capping layers on the interfacial $K_i$ of the MgO/Co$_2$FeAl and MgO/Co$_2$Co$_2$ systems. Our calculations indicate that adding Fe- and W-capping layers can significantly increase the $K_i$ of the system, and particularly, W capping leads to a giant $K_i$ of 4.90 mJ/m$^2$ in MgO/Co$_2$FeAl/W model. This work clarified the atomic origin of the interfacial perpendicular magnetic anisotropy at MgO/Co$_2$FeAl, providing some guidance to develop novel p-MTJs with high thermal stability and large $K_i$.

II. COMPUTATIONAL DETAILS

DFT calculations with spin-orbit coupling (SOC) were carried out using Vienna  Ab-initio Simulation Package (VASP).24,25 The projector augmented wave (PAW) pseudopotentials were employed for treating electron-ion interactions,26 and the generalized gradient approximation (GGA) parameterized by Perdew-Burke-Ernzerhof (PBE) was used for exchange-correction functional.27

The cut-off kinetic energy for plane waves was set as 450 eV. Γ-centered k-point grids were set as 6 × 6 × 1 and 21 × 21 × 1 for ionic relaxation and static calculations, respectively, which were determined by a careful convergence test for the perpendicular magnetic anisotropy constant ($K_i$), total energy, and cleavage energy of the heterostructure models, see Fig. S1 in the Supporting Information.28 The convergence threshold for electronic self-consistency loop was set to 10$^{-6}$ eV. All the atomic positions and lattice structures were fully relaxed until the residual forces were smaller than 0.02 eV/Å in the structural relaxation. The density of states (DOS) was calculated using the tetrahedron method with Blöchl corrections.29 The in-plane lattice constant of the MgO/Co$_2$FeAl heterostructure model was fixed to the lattice constant of MgO (4.215 Å).

The $K_i$ was calculated by $(E_{[100]} - E_{[001]})/A$, where $E_{[100]}$ and $E_{[001]}$ represent total energy with magnetization along [100] and [001] direction in a fully self-consistent-field manner, respectively, and $A$ is the in-plane area. It is realized that another approach, i.e., a so-called “force theorem”, can also be used to calculate $K_i$, in which a fully self-consistent collinear calculation is required as the first step. After that, non-collinear calculations with magnetization along [100] and [001] direction are carried out using the frozen charge density produced from the collinear calculation, and then the $K_i$ can be calculated based on the energy differences.30 These two methods generally give consistent results for non-heavy metal systems, such as Fe/MgO and Fe/MgAl$_2$O$_4$.31 However, according to a recent theoretical report, the results might be different for systems with heavy metals, such as Pt and Ir.32 In this work, to avoid the failure of
perturbation theory, the first approach, that is, the fully self-consistent non-collinear SOC calculations were used for \( K_i \).

III. RESULTS AND DISCUSSION

A. Uncapped MgO/Co\(_2\)FeAl

We began our study by investigating the interfacial magnetic anisotropy (\( K_i \)) and energetic properties of un-capped MgO/Co\(_2\)FeAl. Co\(_2\)FeAl has a cubic crystal structure (L2\(_1\)) with a space group No.225 Fm\( \overline{3}\)m.\(^{11,33}\)

The calculated lattice constants of bulk Co\(_2\)FeAl and MgO are 5.697 and 4.215 Å, respectively, close to their experimental values 5.730 and 4.211 Å.\(^{43,34}\) To match the lattice constant of MgO substrate, a 45° rotation along [001] direction was made on the conventional lattice structure of Co\(_2\)FeAl, which yields a lattice mismatch of \(-4.4\%\). The negative sign here indicates that the Co\(_2\)FeAl film undergoes a tensile strain from the MgO substrate. In principle, there are four types of MgO/Co\(_2\)FeAl slab-based heterostructure models, with all the possible combinations between the two types of MgO/Co\(_2\)FeAl interfaces (MgO/Co\(_2\) and MgO/FeAl interfaces) and two types of Co\(_2\)FeAl surfaces (with Co\(_2\) and FeAl terminations), as shown in Fig. 1. The layers in the Co\(_2\)FeAl film from the MgO/Co\(_2\)FeAl interface to the Co\(_2\)FeAl surface are labeled as FL-I to FL-VIII, respectively. For convenience, the heterostructure model consisting of MgO/Co\(_2\) interface and FeAl-terminated surface is referred to as MgO/Co\(_2\)...FeAl, along with the other three models, MgO/Co\(_2\)...Co\(_2\), MgO/FeAl...Co\(_2\), and MgO/FeAl...FeAl.

In each model, Co\(_2\)FeAl film was built on the MgO substrate with a thickness of five monolayers along [001] direction, and a thickness of more than 15 Å vacuum was added on the film to avoid the interaction between images in the periodic lattice. Our test calculations show that increasing the thickness of MgO monolayers more than five has no effects on the magnetic anisotropy, which is consistent with the prior computational study,\(^{21}\) see Fig. S2 in the Supporting Information.\(^{28}\) It is realized that, however, when the MgO was grown on the ferromagnetic Co\(_2\)FeAl as over-layers, its thickness could be a crucial factor that influence the magnetic anisotropy of MgO/Co\(_2\)FeAl system according to a recent experimental study.\(^{35}\)

The \( K_i \) as a function of the thickness of Co\(_2\)FeAl film (number of layers) was studied for the four types of heterostructure models, MgO/Co\(_2\)...FeAl, MgO/Co\(_2\)...Co\(_2\), MgO/FeAl...Co\(_2\), and MgO/FeAl...FeAl. Our calculations show that the calculated \( K_i \) generally tends to be saturated when the number of Co\(_2\)FeAl layers is larger than five for all the types of heterostructure models, as shown in the Fig. S3 of Supporting Information.\(^{28}\)

This implies there exists a range of the film thickness to produce the desired perpendicular magnetic anisotropy. In fact, it was experimentally reported that the critical thickness for Co\(_2\)FeAl film to maintain out-of-plane \( K_i \) was around 1.1 nm after annealing at 300°C.\(^{10,36}\) Therefore, in this work, we choose seven layers (the thickness of Co\(_2\)FeAl film is about 0.8 nm) for MgO/Co\(_2\)...FeAl and MgO/FeAl...Co\(_2\) system, and eight layers (about 1 nm) for MgO/FeAl...Co\(_2\) and MgO/FeAl...FeAl system to build up the uncapped MgO/Co\(_2\)FeAl models. Additionally, it is worth noting that the MgO/FeAl...FeAl model has a positive \( K_i \) (with an easy magnetization axis along out-of-plane direction) when the Co\(_2\)FeAl film is ultra thin (one layer), and the \( K_i \) becomes negative (with an easy magnetization axis along in-plane direction) for multilayers of Co\(_2\)FeAl film. The calculated \( K_i \) of MgO/Co\(_2\)FeAl model with the designated film thickness are 0.60 mJ/m\(^2\) for MgO/Co\(_2\)...FeAl, 1.28 mJ/m\(^2\) for MgO/Co\(_2\)...Co\(_2\), 0.12 mJ/m\(^2\) for MgO/FeAl...Co\(_2\), and -1.13 mJ/m\(^2\) for MgO/FeAl...FeAl, as listed in Table I. Our calculated \( K_i \) of 1.28 mJ/m\(^2\) for MgO/Co\(_2\)...Co\(_2\) structure is in good agreement with experimental values of 1.04 mJ/m\(^2\) and 1.14 mJ/m\(^2\), and is also well consistent with a recent DFT calculation of 1.31 mJ/m\(^2\).\(^{21}\)

The effective anisotropy for the MgO/Co\(_2\)...Co\(_2\) model was estimated using the equation:\(^{37,38}\)

\[
K_{\text{eff}} = K_i - \frac{1}{2} \mu_0 M_s^2 t_{\text{eff}}
\]

where \( K_{\text{eff}} \) is the effective anisotropy per unit volume, \( t_{\text{eff}} \) is the thickness of the ferromagnetic layer, \( \mu_0 \) is the magnetic constant, and \( M_s \) is the saturation magnetization per unit volume. The term \( \frac{1}{2} \mu_0 M_s^2 \) represents demagnetizing energy per unit volume. In our calculations, the total magnetization for MgO/Co\(_2\)...Co\(_2\) is 17.15 \( \mu_B \), and the effective thickness is 7.944 Å. Accordingly, the saturation magnetization \( M_s \) can be estimated to be 1127 emu/cm\(^3\), which is close to the experimental value of 1140 emu/cm\(^3\).\(^{17}\) The term \( \frac{1}{2} \mu_0 M_s^2 t_{\text{eff}} \) can be estimated to be around 0.63 mJ/m\(^2\), which is much less than the \( K_i \) considered in this study. Therefore, it is reasonable to conclude that the effective anisotropy still favors the PMA in the MgO/Co\(_2\)...Co\(_2\) model.

To understand the origin of the \( K_i \), we calculated layer-resolved \( K_i \) for the four types of models, which clearly shows the atomic contributions to the \( K_i \), see Fig. 2. The layer-resolved \( K_i \) was calculated based on the energy difference in non-collinear calculations projected for the atom in each layer. As one can see, Al atom barely
FIG. 2. Calculated layer-resolved $K_i$ values of different atoms for (a) MgO/Co$_2$...FeAl, (b) MgO/Co$_2$...Co$_2$, (c) MgO/FeAl...Co$_2$, and (d) MgO/FeAl...FeAl structures. Label FL-I to FL-VIII corresponds with the layers from MgO/Co$_2$FeAl interface to Co$_2$FeAl surface. The purple and green bars represent two different Co atoms in the same layer, while the green and blue bars indicate Fe and Al atom, respectively in the same layer.

FIG. 3. Calculated atomic-resolved $K_i$ contributions from different orbital hybridizations. (a) and (b) are $d$-orbital hybridization of interfacial Co atoms in MgO/Co$_2$...FeAl and MgO/Co$_2$...Co$_2$ structure, respectively. (c) and (d) are $d$-orbital hybridization of interfacial Fe atom and $p$-orbital hybridization of interfacial Al atom in MgO/FeAl...Co$_2$ and MgO/FeAl...FeAl structure, respectively.

contributes to $K_i$, however, Co and Fe atoms play an important role in producing the $K_i$. For the models MgO/Co$_2$...FeAl and MgO/Co$_2$...Co$_2$, the two interfacial Co atoms in the FL-I layer contribute most of the out-of-plane $K_i$, resulting in a positive total $K_i$ of 0.60 mJ/m$^2$ and 1.28 mJ/m$^2$, respectively, see Fig. 2a and 2b. On the contrary, for the models MgO/FeAl...Co$_2$ and MgO/FeAl...FeAl, the interfacial Fe atoms (FL-I) and Co atoms (IF-II) cause negative $K_i$, which explains the relatively low $K_i$ (0.12 mJ/m$^2$) in MgO/FeAl...Co$_2$ and even negative $K_i$ (-1.13 mJ/m$^2$) in MgO/FeAl...FeAl. In the model MgO/FeAl...Co$_2$, the surface Co atoms in the layer FL-VIII cause a large out-of-plane $K_i$, cancels out the in-plane $K_i$, and leads to a total positive but low $K_i$, see Fig. 2c. In the model MgO/FeAl...FeAl, almost all the layers contribute in-plane $K_i$, leading to a to-
tual negative $K_i$, see Fig. 2d. Interestingly, although the models MgO/FeAl...Co$_2$ and MgO/FeAl...FeAl share the same interface, i.e., MgO/FeAl, their layer-resolved $K_i$ are significantly different, which may be attributed to the structure symmetry of the Co$_2$FeAl layer. That is, one additional Co$_2$ layer in the MgO/FeAl...Co$_2$ model can significantly change the layer-resolved $K_i$ compared to the model MgO/FeAl...FeAl in which the ferromagnetic Co$_2$FeAl layer is symmetrical. In short, our calculations reveal that the MgO/Co$_2$ interface produces the out-of-plane $K_i$ while the MgO/FeAl interface produces in-plane $K_i$.

To further understand the microscopic origin of $K_i$, we calculated orbital-resolved $K_i$ for the interfacial atoms, i.e., Co 3d orbitals at the MgO/Co$_2$ interface and Fe 3d and Al 3p orbitals at MgO/FeAl interface, as shown in Fig. 3. For the models MgO/Co$_2$...FeAl and MgO/Co$_2$...Co$_2$, the out-of-plane $K_i$ mainly comes from hybridization between $d_{xz}$ and $d_{yz}$ orbitals of the interfacial Co atoms at the MgO/Co$_2$ interface, around 0.25 mJ/m$^2$ and 0.20 mJ/m$^2$, respectively, as seen in Fig. 3a and 3b. The hybridization between $d_{xz}$ and $d_{yz}$ also contributes to the out-of-plane $K_i$ in both structures, however, the magnitude is much smaller. For the models MgO/FeAl...FeAl and MgO/FeAl...Co$_2$, $d_{xz}$ and $d_{y^2}$ orbital hybridization of Fe atoms at MgO/FeAl interface also yields out-of-plane $K_i$, about 0.37 mJ/m$^2$ and 0.08 mJ/m$^2$, respectively, as shown in Fig. 3c and 3d. However, the orbital hybridization between $d_{x^2-y^2}$ and $d_{xy}$, and $d_{x^2-y^2}$ and $d_{yz}$, leads to an in-plane (negative) $K_i$ and the resulting relatively low out-of-plane total $K_i$ for the model MgO/FeAl...Co$_2$ and even negative $K_i$ for MgO/FeAl...FeAl model.

The SOC effects on the magnetic anisotropy energy (MAE) can be derived from the second perturbation theory:

\[
MAE \approx (\xi)^2 \sum_{\sigma_i \sigma_i} \left| (\sigma_i | L_z | \sigma_i) \right|^2 - \left| (\sigma_i | L_z | \sigma_i) \right|^2
\]

where $\xi$ is the SOC constant; $\sigma_i^\uparrow$ and $\sigma_i^\downarrow$ denote the occupied (unoccupied) spin-up and spin-down eigenstates, respectively; $\epsilon_{\sigma_i^\uparrow}$ and $\epsilon_{\sigma_i^\downarrow}$ represent eigenvalues of occupied (unoccupied) spin-up and spin-down states, respectively; the $L_z$ ($L_z$) are the angular momentum operators. This theory has been used to successfully explain the $K_i$ distribution of interfacial Fe over Brilloiun zone in Fe/MgO, Fe/CuInSe$_2$, and Fe/MgAl$_2$O$_4$. For a system with a large spin polarization like MgO/Co$_2$FeAl, the coupling effects from the opposite spin channel can be neglected, and thus the MAE is mainly determined by the coupling between the occupied and unoccupied spin-down states near the Fermi level. In this case, the orbital coupling between occupied and unoccupied states yields a positive $K_i$ if these states share the same quantum number $|m|$, and the coupling yields a negative $K_i$ if the quantum numbers of these states differ by one. To be specific, the orbital coupling between occupied and unoccupied spin-down states, i.e., $d_{xy}$ and $d_{x^2-y^2}$ (with $|m| = 2$), and between $d_{xz}$ and $d_{yz}$ (with $|m| = 1$) will contribute to a positive $K_i$.

To qualitatively understand how the orbital hybridization determines magnetic anisotropy, we calculated projected density of states (PDOS) of $d$ orbitals for the interfacial Co atom in MgO/Co$_2$...Co$_2$ model and for the interfacial Fe atom in MgO/FeAl...FeAl model, as shown in Fig. 4a and 4b, respectively. For the MgO/Co$_2$...Co$_2$ model, spin-down $d_{yz}$ and $d_{xz}$ orbitals contribute both occupied and unoccupied states in the very vicinity (±0.1 eV) of the Fermi level, and hence their orbital coupling between occupied and unoccupied states leads to an out-of-plane $K_i$. This is also consistent with the orbital-resolved $K_i$ in Fig. 3b. For the MgO/FeAl...FeAl model, the orbital coupling between occupied $d_{xz}$ and unoccupied $d_{yz}$ states leads to positive $K_i$, as shown in the orbital-resolved $K_i$ in Fig. 3d, similar to the case of MgO/Co$_2$...Co$_2$ model. However, as discussed below from the $k$-space-resolved MAE, the orbital coupling between $d_{yz}$ ($d_{xz}$) and $d_{x^2-y^2}$ states leads to negative $K_i$, thus resulting in a negative $K_i$ in total.
"force theorem" approach\textsuperscript{44}, see Fig. 5a and 6a. The 
d-orbital projected band structures for the two models, 
MgO/Co\textsubscript{2}...Co\textsubscript{2} and MgO/FeAl...FeAl, are also 
shown in Fig. 5b and 6b, respectively. For the MgO/Co\textsubscript{2}...Co\textsubscript{2} 
model, as shown in Fig. 5a and 5b, its positive MAE at \( k \)-
points 1 and 2 arises from the coupling between occupied 
and unoccupied spin-down states \( d_{xz} \) and \( d_{yz} \) along \( \Gamma-M \) 
and \( \Gamma-X \), respectively. This conclusion is also in good 
agreement with our orbital-resolved \( K_1 \) values for inter-
facial Co atoms in Fig. 3b. For MgO/FeAl...FeAl model,
as shown in Fig. 6a and 6b, its positive MAE at k-point 1 arises from the coupling between occupied and unoccupied spin-down states $d_{xz}$ and $d_{yz}$ along Γ-X; while the negative MAE at k-points 2 and 3 comes from the coupling between occupied and unoccupied spin-down $d_{yz}$ and $d_{x^2-y^2}$ orbitals along Γ-X and between $d_{xz}$ and $d_{x^2-y^2}$ orbitals along Γ-M, respectively.

To evaluate relative interfacial thermal stability, we calculated cleavage energy of MgO/Co$_2$ and MgO/FeAl interfaces using the bulk heterostructure model of MgO/Co$_2$FeAl (without vacuum) based on the below equation:

$$E_{\text{cleav.}} = \left( E_{\text{Co}_2\text{FeAl}} + E_{\text{MgO}} - E_{\text{HS}}^{\text{MgO}/\text{Co}_2\text{FeAl}} \right)/2A \tag{3}$$

where $E_{\text{Co}_2\text{FeAl}}$, $E_{\text{MgO}}$, and $E_{\text{HS}}^{\text{MgO}/\text{Co}_2\text{FeAl}}$ are the total energy of Co$_2$FeAl slab, MgO slab, and MgO/Co$_2$FeAl heterostructure, respectively. $A$ is the in-plane interfacial area, and factor 2 in the denominator represents two symmetrical interfaces in the heterostructure model. The calculated cleavage energy was 117 meV/Å$^2$ for MgO/Co$_2$ interface and 82 meV/Å$^2$ for MgO/FeAl interface, indicating that the MgO/Co$_2$ interface is energetically more favorable than the MgO/FeAl interface. Accordingly, we can conclude that the MgO/Co$_2$ interface is more likely to be formed than the MgO/FeAl interface in the experiments. Considering the positive $K_i$ at MgO/Co$_2$ interface and the negative (or close to zero) $K_i$ at MgO/FeAl interface, this conclusion is also well consistent with the experimentally observed perpendicular magnetic anisotropy at the interface of MgO/Co$_2$FeAl.$^{10,17}$

The relative thermal stability of the two interface models can be understood from the interfacial bond length and the resulting bond strength. The local geometrical structures of the two interface models are shown in Fig. 7. The two Co-O bonds at MgO/Co$_2$ interface are equivalent, with a bond length of 2.05 Å, while at MgO/FeAl interface, the relaxed Fe-O and Al-O bonds are different mainly because of the different atomic radii for Fe and Al, with a bond length of 2.21 Å and 2.02 Å, respectively. Accordingly, the relatively low cleavage energy at MgO/FeAl interface can be attributed to the unmatched Fe-O and Al-O bond length and the resulting relatively weak bond strength, while the highly uniform interfacial structure (equivalent Co-O bonds) at the MgO/Co$_2$ interface leads to relatively high cleavage energy. Note that the unmatched bond strength between Fe-O and Al-O bonds can also be proven from the Bader charge analysis for the interfacial O atoms.$^{15}$

### B. Capped MgO/Co$_2$FeAl

In this section, we studied the influence of adding capping layers on the interfacial magnetic anisotropy of MgO/Co$_2$FeAl. A total number of 26 metal elements including 3$d$ (Ti, V, Cr, Mn, Fe, Ni, and Cu), 4$d$ (Zr, Nb, Mo, Tc, Ru, Rh, Pd, and Ag), 5$d$ (Hf, Ta, W, Re, Os, Ir, Pt, and Au) TMs, and 6$p$ (Pt, Pb, and Bi) metals were considered as capping layers. This is based on the consideration that these elements have a relatively large spin-orbit coupling (SOC) interaction that is likely to be capable of tuning the interfacial magnetic anisotropy.$^{7}$ The Co element is not included due to the large lattice mismatch between FCC-Co and MgO substrate ($\sim$16%). Since our calculations show that the MgO/Co$_2$ interface is energetically more favorable than the MgO/FeAl interface, here we only considered MgO/Co$_2$...FeAl and MgO/Co$_2$...Co$_2$ models. We built the capped-MgO/Co$_2$FeAl by adding MgO/Co$_2$ interface can be attributed to the unmatched Fe-O and Al-O bond length and the resulting relatively weak bond strength, while the highly uniform interfacial structure (equivalent Co-O bonds) at the MgO/Co$_2$ interface leads to relatively high cleavage energy. Note that the unmatched bond strength between Fe-O and Al-O bonds can also be proven from the Bader charge analysis for the interfacial O atoms.$^{15}$

**TABLE II.** Summary of total $K_i$ values of selected capping elements with lattice mismatch ($f$) smaller than 7%. The lattice mismatch is defined as $f = (a_f - a_s)/a_s$, where $a_s$ and $a_f$ are the lattice constant of substrate and film, respectively.

<table>
<thead>
<tr>
<th>$X$</th>
<th>$f$ (%)</th>
<th>MgO/Co$_2$...FeAl/X</th>
<th>MgO/Co$_2$...Co$_2$/X</th>
<th>$K_i$ (mJ/m$^2$)</th>
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the FCC-type or BCC-type structures of these metal elements on top of the Co$_2$FeAl film while maintaining the thickness of vacuum around 15 Å, see Fig. 8. It is noted that, for the MgO/Co$_2$...Co$_2$ model, there are two types of interfacial structures between Co$_2$FeAl film and BCC-type capping layer (including Tl, Pb, and Bi), and one type of interfacial structure between the Co$_2$FeAl film and FCC-type capping layer, as shown in the schematic crystal structures in Fig. 8. The layers of capping elemental compound are labeled as CL-I, CL-II, CL-III, CL-IV, and CL-V, respectively. In the case of V-, Cr-, Mn-, Fe-, Ni-, Cu-, and W-capped structures, to produce the best lattice match, a 45° rotation along [001] direction was made on the conventional bulk structure of BCC-type V, Cr, Mn, Fe, Ni, Cu, and W, leading to only one type of interfacial structure. By taking W-capped MgO/Co$_2$FeAl as one example, we also studied the total $K_i$ as a function of the number of capping layers, as shown in the Fig. S2 of Supporting Information. It shows that Fe-, Mo-, Pd-, Hf-, W-, and Au-capped MgO/Co$_2$...FeAl structures show a larger $K_i$ of 2.59, 1.37, 1.86, 1.67, 4.90, and 1.82 mJ/m$^2$ than the uncapped structure. The Tl-, Pb-, and Bi-capped MgO/Co$_2$FeAl structures with a type II structure also exhibit a large $K_i$ of 2.14, 2.29, and 2.08 mJ/m$^2$. It is especially worth mentioning that W capping leads to a giant $K_i$ value of 4.90 mJ/m$^2$ in MgO/Co$_2$...FeAl/W structure and a $K_i$ of 2.46 mJ/m$^2$ in the MgO/Co$_2$...Co$_2$/W structure. Interestingly, prior experimental and computational studies indicated that W can also improve $K_i$ in the Fe/W/MgO$^{23}$ and MgO/CoFeB/W/CoFeB/MgO$^{24}$ systems in which a thin W interface layer was inserted as doping. Additionally, our calculation for MgO/Co$_2$/Ta yield a $K_i$ value of 0.63 mJ/m$^2$, which is in good agreement with the experimental value of 0.67 mJ/m$^2$. To elucidate the origin of the giant $K_i$ in MgO/Co$_2$...FeAl/W structure, we calculated its layer-resolved $K_i$ and atomic orbital-resolved $K_i$ in Fig. 9. It clearly shows that the large $K_i$ of MgO/Co$_2$...FeAl/W is mainly contributed by the interfacial W atoms at the CL-I (3.22 mJ/m$^2$) and CL-II (0.88 mJ/m$^2$) layers. The $K_i$ from the interfacial Co atoms of Co$_2$FeAl is almost the same with that in the uncapped MgO/Co$_2$FeAl model, suggesting that the W capping layers has no significant influence on the magnetic anisotropy of the Co$_2$FeAl film but does enhance the total $K_i$ of the MgO/Co$_2$...FeAl/W system. The orbital-
resolved $K_i$ of the two interfacial W atoms at CL-I layer were plotted in Fig. 9c and 9d. It shows that the out-of-plane $K_i$ largely comes from the $d$ orbital hybridization between $d_{x^2-y^2}$ and $d_{xy}$ (around 0.50 mJ/m$^2$), and between $d_{xz}$ and $d_{yz}$ (0.24 mJ/m$^2$) in both W atoms.

IV. CONCLUSION

In conclusion, we have systematically investigated the interfacial magnetic and energetic properties in the MgO/Co$_2$FeAl heterostructure by modeling four types of interfacial models using first-principles calculations. Our results show that MgO/Co$_2$ interface can produce out-of-plane $K_i$ while MgO/FeAl interface can produce in-plane $K_i$, and the former interface is energetically more favorable than the latter one and thus is likely to be formed practically. The calculated $K_i$ of 1.28 mJ/m$^2$ in the MgO/Co$_2$...Co$_2$ structure is well consistent with the experimental value. In addition, the influence of 26 capping layers on the interfacial magnetic anisotropy was explored. It is found that Fe- and W-capping can significantly enhance the interfacial $K_i$ in the MgO/Co$_2$FeAl, and particularly, a giant $K_i$ of 4.90 mJ/m$^2$ can be achieved in the W-capped model. This work reveals the atomistic origin of the large perpendicular magnetic anisotropy at MgO/Co$_2$FeAl interface and offers insights to tune interfacial $K_i$ via adding capping layers in the MgO/Co$_2$FeAl.

V. ACKNOWLEDGMENT

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* kesong@ucsd.edu
28 See Supplemental Material at [URL will be inserted by publisher] for the convergence test results for $K_i$ and cleavage energy and the calculated $K_i$ for all the 26 capped MgO/Co$_2$FeAl models.

See Supplemental Material at [URL will be inserted by publisher] for the convergence test results for $K_i$ and cleavage energy and the calculated $K_i$ for all the 26 capped MgO/Co$_2$FeAl models.