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Magnetic states of Mn and Co atoms at Co₂MnGe/MgO interfaces seen via soft x-ray magnetic circular dichroism

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The magnetic states of Mn and Co atoms in Co-rich Co₂MnGe Heusler alloy thin films facing an MgO barrier were studied by means of soft x-ray magnetic circular dichroism (XMCD). In particular, the Co₂MnGe film-thickness dependence of the Mn and Co magnetic moments was investigated. With a decrease in the Co₂MnGe film thickness to 1–2 monolayers (MLs), the spin magnetic moment of Mn decreased and the Mn L₂,₃-edge x-ray absorption spectra (XAS) showed a Mn²⁺-like multiplet structure in MnO, in contrast to samples thicker than 4 ML, indicating that the Mn atoms of the 1 and 2 ML samples were oxidized. The Co spin magnetic moment increased slightly with decreasing thickness. A Co²⁺-like multiplet structure in CoO was not observed in all the Co L₂,₃-edge XAS and XMCD, indicating that, even in the ultrathin samples, the Co atoms were not oxidized, and were more strongly spin polarized than those in the thicker samples. Co spin magnetic moments of 1.40–1.77 μ_B larger than the theoretical value for ideal stoichiometric Co₂MnGe (≈1 μ_B) and the Co-rich film composition imply the presence of Co antisites that would lower the spin polarization.

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I. INTRODUCTION

Magnetic tunnel junctions (MTJs) have recently been widely studied as magnetic storage devices and magnetic sensors. To improve their performance, it is very important to understand the nature of spin-dependent conduction and develop MTJs having a high tunnel magnetoresistance (TMR) ratio with highly spin-polarized ferromagnetic electrodes. In this context, a fully epitaxial MTJ made of an MgO tunnel barrier and half-metallic ferromagnetic electrodes is very promising because the single-crystalline MgO enables coherent tunneling through the Δ₁ band that is conserving the 1 band that is conserving the spin magnetic moments at the Fermi level . In this model, if Co-based full Heusler alloys are perfectly half metallic, i.e., if P₁ and P₂ are equal to 1, the TMR ratio given by Julliére’s formula 12 must be infinite. The TMR ratio of several hundred percent in real Heusler alloy/MgO MTJs implies that the half metallicity might have deteriorated for some reason.

A disorder-free XᵢYZ full Heusler alloy has the L₂₁ crystal structure having four fcc sublattices. When the elements Y and Z are randomly located, the crystal structure changes to B2. When Y, Z, and X are disordered, it changes to A2. The crystal structure change from L₂₁ to B2 or A2 is one of the possible reasons to reduce the spin polarizations at E_F. A numerical study 13 suggests that lattice distortions and the existence of impurities at the interfaces could also reduce the spin polarization. Hence, high-quality interfaces are the key for obtaining high TMR ratios. Thus, it is very important to characterize the interfacial magnetic and electronic states of Heusler alloy/MgO MTJs.

In this study, we investigated the magnetic and electronic structures of Mn and Co atoms in CMG facing an MgO barrier using soft x-ray magnetic circular dichroism (XMCD). XMCD is an element- and orbital-selective measurement, i.e., a technique that can distinguish the Mn 3d electronic states from the Co 3d ones. We studied the CMG-film-thickness dependence of XMCD and magnetic moments of seven CMG/MgO samples with various CMG thicknesses ranging from 1 to 172 monolayers (MLs). Since it is desir-
able for the electrodes in MTJs to be as thin as possible from the viewpoint of applications, it was important to investigate whether the thinner samples maintained the magnetic and electronic properties of the thicker ones. Since the XMCD probing depth was at most \( \approx 5 \) nm,\(^{14} \) the XMCD for the thinner samples predominantly reflected the interfacial magnetic and electronic states while that for thicker samples contained information about the interfacial and bulk states.

### II. EXPERIMENT

#### A. Sample preparation and structural characterization

We prepared two types of layer structures. Ultrathin CMG films with thicknesses (\( t_{\text{CMG}} \)) of 1.1 nm (4 ML), 0.57 nm (2 ML), and 0.29 nm (1 ML) were deposited on an Fe underlayer to stabilize the ferromagnetism of these ultrathin CMG films at RT and to prevent island growth of the thin films. Their sample-layer structures were as follows: (from the substrate side) MgO buffer layer (10 nm)/Fe underlayer (50 nm)/CMG thin film/MgO barrier (2 nm)/\( \text{AlO}_x \) (1 nm) capping layer, grown on a MgO(001) single-crystal substrate [type-1 layer structure, Fig. 1(a)]. Relatively thick CMG films with \( t_{\text{CMG}} = 50 \) nm (172 ML), 2.9 nm (10 ML), and 1.7 nm (6 ML) were deposited on an MgO buffer layer. Their sample layer structures were as follows: (from the substrate side) MgO buffer layer (10 nm)/CMG thin film/MgO barrier (2 nm)/\( \text{AlO}_x \) (1 nm) capping layer [type-2 layer structure, Fig. 1(b)]. As a reference, we prepared a 4-ML-thick CMG film on the MgO buffer layer with type-1 layer structure. An ML of \( \text{Co}_2\text{MnGe} \) contains a Co plane and a Mn-Ge plane. A unit cell of CMG, which has a lattice parameter of 0.5743 nm, corresponds to 2 ML. Each sample layer was successively deposited in an ultrahigh vacuum chamber with a base pressure: about 6 \( \times 10^{-8} \) Pa. The sputtering was performed by rotating the sample about the vertical axis but the angle between the sputter-deposited Al layer to an \( \text{O}_2 \) atmosphere (\( \sim 1 \times 10^{-5} \) Pa) for 2 h. We determined the XMCD film composition by an inductively coupled plasma analysis with an accuracy of 2–3% for each element. The CMG film composition was Co-rich (or both Mn- and Ge-deficient) \( \text{Co}_2\text{Mn}_{0.77}\text{Ge}_{0.23}.^{10,17} \)

We observed 111 diffraction spots for a 50-nm-thick, Mn- and Ge-deficient CMG film deposited on an MgO buffer at RT and subsequently annealed \( \text{in situ} \) 500 °C by electron diffraction, indicating the L2\(_1\) structure.\(^{17} \) A cross-sectional high-resolution transmission electron microscope lattice image (HRTEM) showed that the identically prepared, Mn- and Ge-deficient 50-nm-thick CMG layer and the 2-nm-thick MgO barrier were grown epitaxially and were single crystalline.\(^{17} \) The cross-sectional HRTEM image also confirmed that extremely smooth and abrupt interfaces were formed for the CMG/MgO barrier layer structure.\(^{17} \) The epitaxial growth of all the layers with the (001) basal plane was confirmed for each successive layer in the MgO buffer/Fe underlayer/CMG/MgO structure and in the MgO buffer/CMG/MgO structure by \( \text{in situ} \) RHEED observations.

#### B. XMCD measurements

XMCD measurements were made by using circularly polarized soft x-rays on polarization-variable undulator beamline BL-16A and off-plane circularly polarized soft x-rays on bending magnet beamline BL-11A of the Photon Factory. The degree of circular polarization (\( P_c \)) was evaluated to be \( P_c = \pm 95 \pm 4\% \) on BL-16A, and \( P_c = +87 \pm 4\% \) on BL-11A. The photon helicity (\( h \)) was fixed on BL-11A and reversed on BL-16A. The total-electron yield method was employed in the XAS and XMCD measurements. The angle between the incident x-rays and sample surface normal, \( \theta \), was changed by rotating the sample about the vertical axis but was usually set to 0°. XMCD measurements were also done at a “magic angle” of \( \theta = 54.7° \) (3 \( \cos^2 \theta - 1 = 0 \)), which allowed an accurate determination of the spin magnetic moment \( m_{\text{spin}} \).\(^{18,19} \) Using a superconducting-magnet XMCD apparatus, magnetic fields of \( B = \pm 3 \) T were applied to the sample parallel or antiparallel to \( h \) with \( \theta = 0° \) and 54.7°. All the measurements were made at RT.

### III. EXPERIMENTAL RESULTS

#### A. Mn \( L_{2,3}\)-edge XMCD

Figure 2(a) shows the photon-flux-normalized polarization-dependent XAS (\( \mu_p \) and \( \mu_s \)) at the Mn \( L_{2,3} \) \( (2p_{1/2,3/2} \rightarrow 3d \) absorption) edges. Figure 2(b) displays the Mn \( L_{2,3}\)-edge XMCD (\( \Delta \mu = \mu_p - \mu_s \)) spectra. Here, \( \mu_p \) and \( \mu_s \) stand for the absorption coefficients for the photon helicity (\( h \)) parallel and antiparallel to the Mn 3d majority spin

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**FIG. 1.** (Color online) Schematic of CMG/MgO layer structure for (a) thin samples: type-1 layer and (b) thick samples: type-2 layer.
direction. A linear background has been subtracted from each XAS spectrum. In the XAS spectra for the 172-, 10-, 6-, and 4-ML samples, a shoulder was observed in the higher energy region of the Mn L₃ peak, and the Mn L₂ peak was split into a doublet. These features are characteristic of bulk CMG and CMS.²⁶ Because the probing depth of XAS and XMCD for barrier structure in addition to the interfacial one of the CMG/MgO spectra of the 172-ML sample reflect the bulk electronic region of the Mn atom in CMG. The XAS spectrum. In the XAS spectra for the 172-ML sample, the XAS/XMCD spectra include signals from the lower side interface. However, signals from the lower side interface are reduced by exp(−θ) where θ is the probing depth of XAS and XMCD. Indeed, there was no detectable difference between the 172-ML sample and the other type-2 samples (4, 6, and 10 ML), indicating that contribution from the lower MgO/CMG interface was not significant even if it existed. The XMCD signal was reduced from the lower side interface. Thus, the lower side interface does not significantly affect the electronic structure for t_CMG > 4 ML.

Next, we determine m_{spin} and the orbital magnetic moment (m_{orb}) of the Mn atom by applying the sum rules²³,²⁴ to the obtained XAS and XMCD spectra. The contribution of the intraatomic magnetic dipole operator term T, in the spin sum rule is negligibly small for thicker crystalline samples because the Mn site in CMG has high symmetry. However, this assumption may not necessarily be valid for thinner samples because of their lowered symmetry. To accurately determine m_{spin}, we also measured Mn L₂,₃-edge XAS and XMCD for the 1- to 10-ML samples at the magic angle of θ=54.7°, where the contribution of T vanishes.²⁵ Since there are overlapping regions of L₁ and L₂ due to strong exchange interaction between the Mn 2p core hole and the Mn 3d electrons in MnO.²⁶ XAS and XMCD, we corrected the obtained m_{spin} by a factor 10/68, as given by Teramura et al.²⁵ We used the Mn 3d hole number of 4.5 (Ref. 26) which was taken from the band-structure calculations.²⁷ The results for θ=0° and 54.7° are shown in Fig. 3.

The spin magnetic moment for θ=0° deduced by neglecting the T term, m_{spin}^{0°}(Mn), was larger than 3 μ_B for t_CMG = 6, 10, and 172 ML. m_{spin}^{0°}(Mn) dramatically decreased with decreasing t_CMG for t_CMG < 4 ML, and m_{spin}^{0°}(Mn) for t_CMG = 1 ML was as small as 1.15 μ_B, while m_{spin}^{0°}(Mn) for the bulklike 172- and 10-ML samples was larger than the theoretical value of 3.04 μ_B.²⁷ The spin moment for the magic angle of θ=54.7° without any contribution from T, m_{spin}^{54.7°}(Mn), is also shown as a function of t_CMG in Fig. 3(a). The values for each thickness are summarized in Table I. The
difference between $m_{\text{spin}}^{0^\circ}(\text{Mn})$ and $m_{\text{spin}}^{54.7^\circ}(\text{Mn})$, i.e., the $T_z$ term, is small even for the thin samples. The considerably reduced $m_{\text{spin}}^{0^\circ}(\text{Mn})$ and $m_{\text{spin}}^{54.7^\circ}(\text{Mn})$ for the 1-ML sample indicate that the Mn atoms were oxidized. The orbital magnetic moment for $\theta=0^\circ$, $m_{\text{orb}}^{0^\circ}(\text{Mn})$, was found to be 0.05–0.10 $\mu_B$ for all the samples [Fig. 3(b) and Table I], that is, $m_{\text{orb}}^{0^\circ}(\text{Mn})$ did not show any clear film-thickness dependence. For all the samples, $m_{\text{orb}}(\text{Mn})$ and $m_{\text{orb}}(\text{Co})$ had the same sign, indicating that the Mn 3$d$ state was more than half filled, with an electron occupation number of $n_{3d}(\text{Mn}) > 5$, which was consistent with the theoretical Mn 3$d$ hole number of $n_{3d}(\text{Mn}) = 4.5$ (Ref. 26) used for the sum rules.

Saito et al.\textsuperscript{28} reported CMS-film-thickness-dependent XMCDD and theoretical studies on slightly Co-rich Co$_2$Mn$_{0.91}$Si$_{0.93}$/MgO also grown on an Fe underlayer. Their experimental $m_{\text{spin}}(\text{Mn})$ in CMS increased with decreasing CMS thickness, except for a 1-ML sample, and the theoretical $m_{\text{spin}}(\text{Mn})$ in the case of Mn-Si termination was consistent with their XMCDD results. The $m_{\text{spin}}(\text{Mn})$ of CMS was reduced only for the 1-ML sample but the XAS and XMCDD spectra for the 1-ML sample did not show any Mn$^{5+}$-like multiplet structure indicating the absence of oxidation.\textsuperscript{28} On the other hand, the present experimental results on the Co-rich CMG/MgO showed reduced $m_{\text{spin}}(\text{Mn})$ due to the oxidation of Mn atoms in the 1- and 2-ML samples. The quality of the crystal structure of the ultrathin Co-rich CMS samples should not be as good as that of the slightly Co-rich 1-ML CMS. The structural difference would be related to the different oxidation tendencies.

### B. Co L$_{2,3}$-edge XMCDD

Figure 4(a) shows the photon flux-normalized, polarization-dependent XAS at the Co L$_{2,3}$ edges. Figure 4(b) displays the Co L$_{2,3}$-edge XMCDD spectra. For all the samples, a shoulder, which is common to bulk samples,\textsuperscript{30} was observed in the higher energy region of the Co L$_2$-edge XAS. The XMCDD signals increased as the film thickness decreased, implying that the Co atoms in the ultrathin samples were strongly spin polarized. No CoO-like multiplet structure\textsuperscript{29} was found in any of the samples, indicating that the Co atoms were not oxidized even in the ultrathin samples. In addition, the differences in XAS and XMCDD between the 4-ML samples with and without Fe were not so large.

We determined the Co magnetic moments by using the sum rules\textsuperscript{23,24} similarly to the Mn L$_{2,3}$ edges. While the Co atoms in the thicker samples are in the highly symmetric $T_d$ crystal field, we measured Co L$_{2,3}$-edge XAS and XMCDD at the magic angle of $\theta=54.7^\circ$ in order to accurately determine the spin moment. We used a theoretical Co 3$d$ hole number of 2.2 (Ref. 26) in applying the sum rules. The results are shown in Fig. 5.

The Co spin moment for $\theta=0^\circ$, obtained by neglecting the $T_z$ term, $m_{\text{spin}}^{0^\circ}(\text{Co})$, was 1.40 $\mu_B$ for the 172-ML sample and was enhanced to 1.77 $\mu_B$ for the 1-ML sample while $m_{\text{spin}}^{0^\circ}(\text{Co})$ was around 1.40 $\mu_B$ for $t_{\text{CMG}} \approx 2$ ML. For all the samples, $m_{\text{spin}}^{0^\circ}(\text{Co})$ was larger than the theoretical value of 0.98 $\mu_B$.\textsuperscript{27} The spin moment for the magic angle of $\theta = 54.7^\circ$ without any contribution from $T_z$, $m_{\text{spin}}^{54.7^\circ}(\text{Co})$, is also shown as a function of $t_{\text{CMG}}$ in Fig. 5. The magnetic-moment values for each thickness are summarized in Table I. The difference between $m_{\text{spin}}^{0^\circ}(\text{Co})$ and $m_{\text{spin}}^{54.7^\circ}(\text{Co})$ was small, as expected.

![Co L$_{2,3}$-edge XMCDD](image)

**FIG. 4.** (Color online) Normal-incidence ($\theta=0^\circ$) Co L$_{2,3}$-edge XAS and XMCDD of Co-rich Co$_2$Mn$_{0.91}$Si$_{0.93}$/MgO samples with various CMS thicknesses. (a) XAS measured at 300 K and $B_z = \pm 3$ T. $\mu_\alpha$ and $\mu_\mu$ are the absorption coefficients for photon helicity parallel and antiparallel to the Co 3$d$ majority spin, respectively. (b) XMCDD spectra given by $\Delta \mu = \mu_+ - \mu_-$. (c) Magnified plots of XMCDD spectra in Co L$_2$-edge region.
showing that the effect of the $T_z$ term was small. The tendency for the spin moment of Co to increase for the thinner samples was common for $\theta=0^\circ$ and $54.7^\circ$. The orbital moment for $\theta=0^\circ$, $m_{\text{orb}}^0(\text{Co})$, was about $0.10 \mu_B$ for all the samples. The CMS film-thickness-dependent XMCD studies and first principles calculations by Saito et al. revealed that the $m_{\text{spin}}(\text{Co})$ of CMS was enhanced for CMS thicknesses ($t_{\text{CMS}}$) < 4 ML. This enhancement was explained by an Fe/Co interfacial effect at the lower side interface. They reported that the MnSi termination with MnO bond at the upper side interface was energetically stable regardless of $t_{\text{CMS}}$. As a consequence, the lower side Fe/Co interface was also favored for $t_{\text{CMS}}$ = 1 ML. Since the layer structure of the CMS/MgO heterostructures was quite similar to that of the present CMS/MgO heterostructures, the enhanced $m_{\text{spin}}(\text{Co})$ for the CMS/MgO ultrathin samples could also be due to the Fe/Co interfacial effect at the lower side interface.

IV. DISCUSSION

We discuss the oxidation of the Mn in the nonstoichiometric CMS ultrathin films facing an MgO barrier. Saito et al. reported in their XMCD study on CMS/MgO that the $m_{\text{spin}}(\text{Mn})$ of intentionally oxidized CMS was almost zero and Mn $L_{2,3}$-edge XAS clearly showed an MnO-like Mn$^{3+}$ multiplet structure. In contrast, the Co $L_{2,3}$-edge XAS of intentionally oxidized CMS showed no multiplet structure, and the Co $L_{2,3}$-edge XAS was similar to that of unoxidized CMS. They concluded that, in CMS, Mn atoms were easily oxidized compared with Co atoms, which is consistent with our result that the Co atoms, even in the 1- and 2-ML samples, were highly stable against oxidation compared with the Mn atoms.

FIG. 5. (Color online) Film-thickness dependences of (a) Co spin magnetic moment ($m_{\text{spin}}$) for $\theta=0^\circ$ and 54.7$^\circ$ (magic angle) and (b) Co orbital magnetic moment ($m_{\text{orb}}$) for $\theta=0^\circ$. These were determined using the spin and orbital sum rules (Refs. 23 and 24). The theoretical spin-moment value for bulk CMG was taken from Ref. 27.

Figure 6 shows the O $K$-edge XAS spectra ($B=0$ T) of the 1- and 10-ML samples. The strong peaks observed for $h\nu>535$ eV originate from oxygen in the CMS capping layer and AlO$\text{c}$ capping layer. Interestingly, pre-edge structures were clearly observed for the 1-ML sample at $530 \text{ eV} < h\nu < 535 \text{ eV}$. It is known that neither MgO nor AlO$_x$ exhibit such pre-edge features but MnO does show them in O $K$-edge XAS, in sharp contrast to the main peaks for $h\nu > 535 \text{ eV}$. Thus, these features could be attributed uniquely to MnO formed at the interfaces. The existence of the pre-edge structures for the 1-ML sample also supports again our view of oxidized Mn atoms.

Sicot et al. reported x-ray photoemission, XAS, and XMCD studies of Co, Fe, and Mn metals facing MgO. They revealed that Co and Fe metals were not oxidized after MgO growth on them but that Mn metal was oxidized, particularly at the interfacial region, which is consistent with the present results for the 1- and 2-ML samples. Furthermore, the enthalpy of formation of MnO ($\sim 92$ kcal/mol) is lower than that of CoO ($\sim 57$ kcal/mol). Saito et al. reported that the calculated $m_{\text{spin}}(\text{Mn})$ and $m_{\text{spin}}(\text{Co})$ for CMS/MgO in the case of MnSi termination (MnSi/MgO interface) with Mn-O bonds well explained their experimental results in contrast to the case of Co termination (Co/MgO interface). In this context, for the present 1-ML CMS sample, a MnGe termination, i.e., a layer structure of (Fe underlayer)/(Co layer)/(MnGe layer)/MgO with Mn-O bonds, should be energetically more stable. We therefore conclude that the interfacial Mn atoms in the ultrathin CMS samples were easily oxidized while the Co atoms were highly stable against oxidation. Comparing $m_{\text{total}}(\text{Mn})=m_{\text{spin}}(\text{Mn})+m_{\text{orb}}(\text{Mn})$ for the 1-ML sample with $m_{\text{total}}(\text{Mn})$ for the 10-ML sample, we estimated that about 70% of the Mn atoms in the 1-ML sample were oxidized. Here, we assumed that all the Mn atoms in the 10-ML sample were not oxidized.

To confirm the validity of our estimation, we subtracted 30% of the Mn $L_{2,3}$-edge XAS for the 10-ML sample, which would correspond to the contribution of the unoxidized Mn in the 1-ML sample as discussed above, from that for the 1-ML one. The result is shown in Fig. 7. The subtraction-deducted spectrum is very similar to the Mn $L_{2,3}$-edge XAS...
the observed oxidation of Mn in the ultrathin 1- and 2-ML samples. The observed oxidation of Mn in the ultrathin CMG/MgO samples is in contrast to the absence of that in the CMS/MgO samples. It should be noted that the present CMG film composition was Mn-deficient and highly Ge-deficient (Co$_2$Mn$_{0.77}$Ge$_{0.42}$), in contrast to the slightly Mn- and Si-deficient film composition of the CMS film (Co$_2$Mn$_{0.91}$Si$_{0.93}$) in the CMS/MgO samples. In accordance with the chemical composition model for Mn- and Ge-deficient CMG films, developed by taking into consideration the formation energies of various kinds of defects, the chemical composition for nonstoichiometric Co$_2$Mn$_{0.77}$Ge$_{0.42}$ film is estimated to be Co$_2$[Mn$_{0.49}$Co$_{0.51}$][Ge$_{0.53}$Mn$_{0.47}$], where [Mn$_{0.49}$Co$_{0.51}$] and [Ge$_{0.53}$Mn$_{0.47}$] represent the nominal Mn and Ge sites, respectively. Similarly, the chemical composition for the slightly Mn- and Si-deficient CMS film of Co$_2$Mn$_{0.91}$Si$_{0.93}$ is estimated to be Co$_2$[Mn$_{0.92}$Co$_{0.08}$][Si$_{0.97}$Mn$_{0.03}$]. Thus, the degrees of order of the nominal Mn and Ge sites in Co$_2$Mn$_{0.77}$Ge$_{0.42}$ films should be significantly lower than those in the nominal Mn and Si sites in Co$_2$Mn$_{0.91}$Si$_{0.93}$. Furthermore, the degree of structural order would be lower for ultrathin CMG (CMS) films with 1- and 2-ML thicknesses, resulting in increased disorder between the nominal Mn-Ge (Mn-Si) plane and the nominal Co plane. The decreased degree of structural order in the ultrathin CMG films along with the highly disordered nominal Mn and Ge sites would be a possible reason of the observed oxidation of Mn in the 1- and 2-ML samples.

Next, we discuss the effects of antisites defects in the nonstoichiometric CMG/MgO thin films. The deduced $m_{\text{spin}}$(Co) for all the CMG samples was obviously larger than a theoretical value of −1 $\mu_B$ (Ref. 27) and the experimental XMCD value of 1.04 $\mu_B$ for the bulk samples reported by Miyamoto et al. Note that their XMCD study was done at $B=1.4$ T and $T=45$ K and that they scraped the bulk CMG samples to obtain clean surfaces and used a Co 3d hole number of 3.0. Picozzi et al. investigated theoretically the effect of antisite defects in CMG and CMS. They reported that $m_{\text{spin}}$(Co) of the Co antisites in CMG, Co$_{0.74}$Mn$_{0.26}$Ge$_{0.42}$, was 1.35 $\mu_B$, which was larger than 1.06 $\mu_B$ for Co at the regular Co site, Co$_{\text{reg}}$. Here, the Co antisites mean Co atoms occupying Mn sites in regular CMG. The present large $m_{\text{spin}}$(Co) of 1.40–1.77 $\mu_B$ therefore indicates the possibility of the existence of Co$_{\text{Mn}}$. We confirmed by in situ RHEED that the present CMG samples on which we measured XMCD had the disorder-free L$_2$$_1$ structure. However, since the film composition was Co$_{0.49}$Mn$_{0.51}$Ge$_{0.53}$Mn$_{0.47}$ deviating from 2:1:1, some Co atoms possibly occupy the Mn site. The calculated total DOS for each of the majority- and minority-spin bands of CMG was reported, and in-gap states were found to exist within the minority-spin gap only when Co$_{\text{Mn}}$ existed. The possible existence of Co$_{\text{Mn}}$ in CMG may lead to a decrease in the spin polarization. This consideration is consistent with the spin polarization of Co-rich CMG estimated from the TMR ratio at 4.2 K for CMG/MgO/CoFe MTJs assuming Jullière’s model, $P_{\text{CMG}}$, was as low as 0.74.

It was reported that the $m_{\text{spin}}$(Co) of Co-rich CMS/MgO was 1.16 $\mu_B$ for a sample with $t_{\text{CMS}}=50$ nm, and 1.25 $\mu_B$ for a sample with $t_{\text{CMS}}=1.1$ nm (4 ML), both being larger than a theoretical value of 1.06 $\mu_B$. The CMS film composition of Co$_{0.49}$Mn$_{0.51}$Ge$_{0.53}$Mn$_{0.47}$ was comparable to the Co-rich CMG that we have studied here. Consequently, the Co-rich CMS might have had more or less the same amount of Co$_{\text{Mn}}$ as in Co-rich CMG. Picozzi et al. reported that in-gap states could theoretically exist within the minority-spin gap for CMS with Co$_{\text{Mn}}$. The spin polarization of Co-rich CMS estimated from the TMR ratio at 4.2 K for CMS/MgO/CoFe MTJs assuming Jullière’s model, $P_{\text{CMS}}$, was as low as 0.75. The comparison between Co-rich CMG and Co-rich CMS can be summarized as follows: (i) the deviation in composition from 2:1:1 for CMG is larger than that for CMS, (ii) the $P_{\text{CMS}}$ of 0.74 (Ref. 6) is comparable to the $P_{\text{CMS}}$ of 0.75, and (iii) the difference in $m_{\text{spin}}$(Co) between the present XMCD results and the theories for CMG is larger than that for CMS.

The spin polarization at $E_F$ and the spin moment would be influenced by nonstoichiometry in CMG thin films. To reduce the minority-spin in-gap DOS and to improve the TMR ratio, appropriate control of the film composition is critical. A promising method is to prepare CMG films by cosputtering from CMG, Mn, and Ge targets to appropriately control the CMG film composition. In fact, high TMR ratios of 650% at 4.2 K and 220% at RT have been demonstrated for CMG/MgO/CMG MTJs with Mn-rich Co$_2$Mn$_{0.49}$Ge$_{0.38}$...
electrodes prepared by cosputtering from CMG and Mn targets. In addition, theoretical studies have revealed that Mn antisites (located at the regular Co sites) in Mn-rich CMS do not affect the half-metallic gap.

V. CONCLUSION

We studied the magnetic and electronic states of Co$_2$MnGe/MgO magnetic tunnel junctions by CMG film-thickness dependent XMCD measurements. The XAS and XMCD spectral shapes for thick samples ($t_{CMG}$ $\geq$ 4 ML) were similar to those for bulk CMG, and neither the Mn nor Co atoms were oxidized. We have found that about 70% of the Mn atoms in the 1-ML sample were oxidized. The lattice distortions and disorder in the ultrathin samples would be related to oxidation. In contrast, Co atoms in the ultrathin samples were not oxidized and more strongly spin polarized. The enhanced $m^{\text{spin}}_{\text{Co}}$ for the ultrathin samples could be due to the Fe/Co interfacial effect as in CMS/MgO heterostructures. The existence of Co antisites is suggested by considering theories on Co antisites and the observed $m^{\text{spin}}_{\text{Co}}$ of 1.40–1.77 $\mu_B$, which was larger than theoretical values for ideal compounds.

The nonstoichiometry of the Co-rich CMG samples is also consistent with the existence of Co antisites. In-gap states have been predicted to exist within the Co minority-spin band gap when Co antisites are present. The consideration is consistent with the experimental results that the TMR ratios at both 4.2 K and RT of CMG/MgO/CMG MTJs with Co-rich CMG electrodes were considerably lower than those of CMG/MgO/CMG MTJs with Mn-rich CMG electrodes. CMG-composition and temperature-dependent XMCD studies would be desirable in the near future to fully understand the electronic states of CMG with an MgO barrier. Spin-resolved photoemission studies would also be desirable to directly observe the half-metallic nature of Heusler alloys.

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