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**Magnetic states of Mn and Co atoms at Co$_2$MnGe/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 Co$_2$MnGe Heusler alloy thin films facing an MgO barrier were studied by means of soft x-ray magnetic circular dichroism (XMCD). In particular, the Co$_2$MnGe film-thickness dependence of the Mn and Co magnetic moments was investigated. With a decrease in the Co$_2$MnGe film thickness from 1 to 2 monolayers (MLs), the spin magnetic moment of Mn decreased and the Mn $L_{2,3}$-edge x-ray absorption spectra (XAS) showed a Mn$^{2+}$-like multiplet structure in MnO, in contrast to samples with thicknesses of 4 ML, indicating that the Mn atom of the 2 ML sample was oxidized. The Co spin magnetic moment increased slightly with decreasing thickness. A Co$^{2+}$-like multiplet structure in CoO was not observed in all the Co $L_{2,3}$-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 $1.40 \pm 0.17$ $\mu_B$ larger than the theoretical value for ideal stoichiometric Co$_2$MnGe ($\sim 1 \mu_B$) 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 $\Delta_1$ band that is conserving the 1-band electrons of the half-metallic ferromagnetic electrodes. Fully epitaxial Fe/MgO/Fe MTJs, in which Fe electrodes feature a half-metallic nature for the $\Delta_1$ band electrons, have experimentally shown a TMR ratio of 180% (Ref. 1) at room temperature (RT) owing to coherent tunneling of the $\Delta_1$-band electrons. This value is much higher than that in conventional MTJs consisting of polycrystalline electrodes and an amorphous AlO$_x$ tunnel barrier.

Co-based full Heusler alloys Co$_2$YZ such as Co$_2$MnGe (CMG) and Co$_2$MnSi (CMS) are also promising candidates for ferromagnetic electrodes in MTJs, because some theories have predicted that they are ideal half metals. 1-5 In fact, TMR ratios of several hundred percent in Co-based full Heusler alloys with an MgO tunnel barrier have recently been reported. 6-10 Here, the TMR ratio is defined as $[\text{TMR ratio}] = (R_{AP} - R_0) / R_0$ in terms of the resistances for the parallel ($R_P$) and antiparallel ($R_{AP}$) geometries. 11 The (anti) parallel geometry means that electrode 1 is (anti) ferromagnetically coupled with electrode 2 across the thin non-magnetic tunnel barrier. Assuming ideal half metals without interface state (Jullière’s model), 12 the formula can be written as $[\text{TMR ratio}] = 2P_1P_2/(1 - P_1P_2)$, where $P_1$ and $P_2$ are the spin polarizations at the Fermi level ($E_F$) of electrodes 1 and 2, respectively. 12 In this model, if Co-based full Heusler alloys are perfectly half metallic, i.e., if $P_1$ and $P_2$ are equal to 1, the TMR ratio given by Jullière’s formula 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 $X_2YZ$ full Heusler alloy has the L2$_1$ 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 L2$_1$ to B2 or A2 is one of the possible reasons to reduce the spin polarizations at $E_F$. A numerical study 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, 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 \((t_{\text{CMG}}) = 1.1 \) 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)/AlO\(_x\) (1 nm) capping layer, grown on a MgO(001) single-crystal substrate [type-1 layer structure, Fig. 1(a)].

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)/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 Co\(_2\)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 \( 6 \times 10^{-7} \) Pa.

Figure 2(a) shows the photon-flux-normalized polarization dependent XAS (\( \mu_+ \) and \( \mu_- \)) 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 (\( \Delta \mu = \mu_+ - \mu_- \)) spectra. Here, \( \mu_+ \) and \( \mu_- \) stand for the absorption coefficients for the photon helicity \((h)\) parallel and antiparallel to the Mn 3d majority spin.
MAGNETIC STATES OF Mn AND Co ATOMS AT Co-rich CMG samples with various CMG thicknesses. 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 3d majority spin, respectively. The XAS and XMCD spectra of the 172-ML sample reflect the bulk electronic structure in addition to the interfacial one of the CMG/MgO barrier (the upper side CMG/MgO interface). Except 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(−tCMG/λ) (~0.80, 0.71, and 0.56 for 4, 6, and 10 ML), where λ (≤5 nm) 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. The theoretical spin-moment value for bulk CMG was taken from Ref. 27. The small difference between mspin and mspin,0.74~ represents the effect of the Tz term.

The theoretical spin-moment value for bulk CMG was taken from Ref. 27. The small difference between mspin and mspin,0.74~ represents the effect of the Tz term. Thus, the reduction of the Mn spin magnetic moment (mspin) for θ=0° and 54.7° (magic angle) and (b) Mn orbital magnetic moment (morb) for θ=0°. 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. The small difference between mspin and mspin,0.74~ represents the effect of the Tz term.

The signiﬁcance even if it existed. The XMCD signal was reduced from the lower side interface was not significant even if it existed. The XMCD signal was reduced from the lower side interface.
difference between \( m_{\text{spin}}^{0\circ}(\text{Mn}) \) and \( m_{\text{spin}}^{4.5\circ}(\text{Mn}) \), i.e., the \( T_z \) term, is small even for the thin samples. The considerably reduced \( m_{\text{spin}}^{0\circ}(\text{Mn}) \) and \( m_{\text{spin}}^{4.5\circ}(\text{Mn}) \) 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, \( m_{\text{spin}}^{0\circ}(\text{Mn}) \) did not show any clear film-thickness dependence. For all the samples, \( m_{\text{spin}}(\text{Mn}) \) and \( m_{\text{orb}}(\text{Mn}) \) had the same sign, indicating that the Mn 3d state was more than half filled, with an electron occupation number of \( n_3(\text{Mn}) > 5 \), which was consistent with the theoretical Mn 3d hole number of \( n_3(\text{Mn}) = 4.5 \) (Ref. 26) used for the sum rules.

Saito et al.\(^{28} \) reported CMS-film-thickness-dependent XMCD and theoretical studies on slightly Co-rich \( \text{Co}_2\text{Mn}_{0.91}\text{Si}_{0.93}\text{MgO} \) 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 XMCD results. The \( m_{\text{spin}}(\text{Mn}) \) of CMS was reduced only for the 1-ML sample but the XAS and XMCD spectra for the 1-ML sample did not show any Mn\(^{5+} \)-like multiplet structure indicating the absence of oxidation.\(^{28} \) On the other hand, the present experimental results on the Co-rich CMS/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 XMCD**

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 XMCD spectra. For all the samples, a shoulder, which is common to bulk samples,\(^{20} \) was observed in the higher energy region of the Co \( L_2 \)-edge XAS. The XMCD 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\(^{20} \) 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 XMCD between the 4-ML samples with and without Fe were not so large.

We determined the Co magnetic moments by using the sum rules\(^{23,24} \) 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 XMCD at the magic angle of \( \theta=54.7\circ \) in order to accurately determine the spin moment. We used a theoretical Co 3d 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 the 1-ML sample and 1.77 \( \mu_B \) for the 172-ML sample. For all the samples, \( m_{\text{spin}}^{0\circ}(\text{Co}) \) was larger than the theoretical value of 0.98 \( \mu_B \).\(^{27} \) The spin moment for the magic angle of \( \theta \) =54.7\circ without any contribution from \( T_z \), \( m_{\text{spin}}^{0\circ}(\text{Co}) \), is also shown as a function of \( I_{\text{CMG}} \) 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, but

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<th>Thickness</th>
<th>1 ML</th>
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<th>4 ML</th>
<th>4 ML</th>
<th>6 ML</th>
<th>10 ML</th>
<th>172 ML</th>
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<td>( m_{\text{spin}}^{0\circ}(\text{Mn}) ) (( \mu_B ))</td>
<td>1.15</td>
<td>2.74</td>
<td>2.85</td>
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<td>3.76</td>
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<td>( m_{\text{spin}}^{0\circ}(\text{Mn}) ) (( \mu_B ))</td>
<td>0.06</td>
<td>0.05</td>
<td>0.07</td>
<td>0.11</td>
<td>0.04</td>
<td>0.05</td>
<td>0.16</td>
</tr>
<tr>
<td>( m_{\text{spin}}^{4.5\circ}(\text{Mn}) ) (( \mu_B ))</td>
<td>1.19</td>
<td>2.56</td>
<td>2.80</td>
<td>2.89</td>
<td>4.71</td>
<td>3.53</td>
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<tr>
<td>( m_{\text{spin}}^{0\circ}(\text{Co}) ) (( \mu_B ))</td>
<td>1.77</td>
<td>1.46</td>
<td>1.26</td>
<td>1.47</td>
<td>1.27</td>
<td>1.38</td>
<td>1.40</td>
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<tr>
<td>( m_{\text{spin}}^{0\circ}(\text{Co}) ) (( \mu_B ))</td>
<td>0.14</td>
<td>0.06</td>
<td>0.16</td>
<td>0.13</td>
<td>0.13</td>
<td>0.09</td>
<td>0.16</td>
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<tr>
<td>( m_{\text{spin}}^{4.5\circ}(\text{Co}) ) (( \mu_B ))</td>
<td>1.58</td>
<td>1.61</td>
<td>1.21</td>
<td>1.40</td>
<td>1.49</td>
<td>1.30</td>
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**FIG. 4.** (Color online) Normal-incidence (\( \theta=0\circ \)) Co \( L_{2,3} \)-edge XAS and XMCD of Co-rich Co\(_2\)MnGe samples with various CMG thicknesses. (a) XAS measured at 300 K and \( B=\pm 3 \) T. \( \mu_+ \) and \( \mu_− \) are the absorption coefficients for photon helicity parallel and anti-parallel to the Co 3d majority spin, respectively. (b) XMCD spectra given by \( \Delta \mu=\mu_+−\mu− \). (c) Magnified plots of XMCD spectra in Co \( L_{2,3} \) edge region.
MAGNETIC STATES OF Mn AND Co ATOMS AT Co...  PHYSICAL REVIEW B 82, 184419 (2010)

The small difference between \( m_{\text{spin}} \) and \( m_{\text{spin}}^{54.7°} \) represents the effect of the \( T_z \) term.

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 \( \theta=0° \) and 54.7°. The orbital moment for \( \theta=0° \), \( m_{\text{orb}}^{0°}(\text{Co}) \), 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.\textsuperscript{28} revealed that the \( m_{\text{spin}}(\text{Co}) \) of CMS was enhanced for CMS thicknesses \( t_{\text{CMS}} \leq 4 \text{ ML} \). 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 \( t_{\text{CMS}} \).\textsuperscript{28} As a consequence, the lower side Fe/Co interface was also favored for \( t_{\text{CMS}}=1 \text{ ML} \). Since the layer structure of the CMS/MgO heterostructures\textsuperscript{28} 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.\textsuperscript{16} 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\(^{2+}\) 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 \( \theta=0° \) and 54.7° (magic angle) and (b) Co orbital magnetic moment \( (m_{\text{orb}}) \) for \( \theta=0° \). These were determined using the spin and orbital sum rules (Refs. 23 and 24).

**FIG. 6.** (Color online) O \( K\)-edge XAS spectra \((B=0 \text{ T})\) of the 1- and 10-ML samples. The strong peaks observed for \( h\nu>535 \text{ eV} \) originate from oxygen in the MgO barrier\textsuperscript{30} and AlO\(_x\) capping layer. Interestingly, pre-edge structures were clearly observed for the 1-ML sample at 530 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\textsuperscript{21,31} 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.\textsuperscript{32} 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\(\sim 92 \text{ kcal/mol}\) is lower than that of CoO\(\sim 57 \text{ kcal/mol}\).\textsuperscript{33} Saito et al.\textsuperscript{28} 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.
of MnO.\textsuperscript{21,34–36} Because MnO is a paramagnetic insulator at RT and an antiferromagnetic insulator below $T_N \sim 120$ K,\textsuperscript{37} a large number (~70\%) of oxidized Mn atoms in the 1-ML sample did not contribute to the ferromagnetism.

Here, we discuss possible origins of 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.\textsuperscript{28} In accordance with the chemical composition model for Mn- and Ge-deficient CMG films\textsuperscript{38} developed by taking into consideration the formation energies of various kinds of defects,\textsuperscript{39} 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$_{0.93}$]$_3$ 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.\textsuperscript{40,41} 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.\textsuperscript{40,41} Picozzi et al.\textsuperscript{42} 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$_{0.91}$Mn$_{0.93}$, was 1.35 $\mu_B$, which was larger than 1.06 $\mu_B$ for Co at the regular Co site, Co$_{0.93}$. 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$_{0.91}$Mn$_{0.93}$ in CMG. We confirmed by in situ RHEED that the present CMG samples on which we measured XMCD had the disorder-free L$_2^\text{I}$ structure. However, since the film composition was Co:Mn:Ge=2:0.77:0.42 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,\textsuperscript{42} and in-gap states were found to exist within the minority-spin gap only when Co$_{0.91}$Mn$_{0.93}$ existed. The possible existence of Co$_{0.91}$Mn$_{0.93}$ 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.\textsuperscript{4}

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),\textsuperscript{43} both being larger than a theoretical value of 1.06 $\mu_B$.\textsuperscript{27} The CMS film composition of Co:Mn:Si=2:0.91:0.93 was Co-rich similar to the present CMG that we have studied here. Consequently, the Co-rich CMS might have had more or less the same amount of Co$_{0.91}$Mn$_{0.93}$ as in Co-rich CMG. Picozzi et al.\textsuperscript{42} reported that in-gap states could theoretically exist within the minority-spin gap for CMS with Co$_{0.93}$. 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.\textsuperscript{7} 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 $P_{\text{CMG}}$ value of 0.74 (Ref. 6) is comparable to the $P_{\text{CMS}}$ of 0.75,\textsuperscript{7} 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.\textsuperscript{27}

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.\textsuperscript{38,44} 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 Co₂MnGe/MgO magnetic tunnel junctions by CMG film-thickness dependent XMCD measurements. The XAS and XMCD spectral shapes for thick samples (f_CMG=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 mspin(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 mspin(Co) of 1.40–1.77 μB, 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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29. T. J. Regan, H. Ohldag, C. Stamm, F. Nolting, J. Lüning, J.