Effects of nonstoichiometry on the half-metallic character of Co$_2$MnSi investigated through saturation magnetization and tunneling magnetoresistance ratio.
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We investigated the effect of nonstoichiometry on the half-metallic character of the Heusler alloy Co$_2$MnSi (CMS) through the Mn composition ($\alpha$) dependence of the saturation magnetization per formula unit ($\mu_s$) of Co$_{2-x}$Mn$_x$Si$_y$ thin films and the tunneling magnetoresistance (TMR) ratio of CMS/MgO/CMS magnetic tunnel junctions (CMS MTJs) having Co$_{2}$Mn$_{x}$Si$_{y}$ electrodes. As a basis for understanding the effect of nonstoichiometry in CMS, we developed a generalized form of the site-specific formula unit (SSFU) composition model, which assumes the formation of only antisite defects, not vacancies, to accommodate nonstoichiometry. The $\alpha$ dependence of $\mu_s$ was well explained by density functional calculations with the coherent potential approximation based on the SSFU composition model for $\alpha$ up to a certain critical value ($\alpha_c$) $> 1.0$. The $\mu_s$ data for Mn-deficient films deviated from the Slater-Pauling predicted data for half-metals due to Co atoms at the nominal Mn sites (Co$_{0.56}$). The theoretical spin polarizations, obtained from only the s- and p-orbital components, were found to qualitatively explain the $\alpha$ dependence of the TMR ratio except for $\alpha > \alpha_c$. This is in contrast to the theoretical spin polarizations obtained from the s-, p-, and d-orbital components, $P_{0\alpha}(spd)$. A decrease in the TMR ratio observed for CMS MTJs having Mn-deficient electrodes was ascribed to small s- and p-orbital components of the local density of minority-spin in-gap states at the Fermi level that appeared for both antisite Co$_{0.56}$ atoms and Co atoms at the regular sites.

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I. INTRODUCTION

Spintronic devices, which are based on the manipulation of the spin degree of freedom of the electron, have attracted much interest as future-generation electron devices [1] because of their potential advantages of nonvolatility, decreased power consumption, and reconfigurable logic function capabilities. A highly efficient spin source is essential for spintronic devices. Among the Co$_2$YZ family, CMS has been one of the materials most extensively applied to MTJs [5–11,26–28] and GMR devices [13,15,16]. This is because of (1) its theoretically predicted half-metallic nature, with a large energy gap of 0.81 eV [22] for its minority-spin band; (2) its high Curie temperature of 985 K [24]; and (3) the existence of coherent tunneling in epitaxial CMS/MgO heterostructures [31,32]. On the other hand, nonstoichiometry is inevitable, to various degrees, in Co$_2$YZ thin films prepared by magnetron sputtering or molecular beam epitaxy, leading to structural defects. Thus, the clarification of the influence of structural defects on the half-metallicity of Co$_2$YZ is critical for spintronic device applications [33–36]. Picozzi et al. [33] theoretically predicted that Co$_{0.56}$ antisites in CMS and Co$_2$MnGe, where a Mn site is replaced by a Co atom, cause minority-spin in-gap states at $E_F$ and thus are detrimental to the half-metallicity of CMS and Co$_2$MnGe. Similarly, Miura et al. [34] theoretically predicted a Co$_2$YZ thin film and a MgO tunnel barrier [7–11,25–30] or consisting of a Co$_2$YZ thin film and a thin nonmagnetic metal layer such as Ag have been prepared [13–16]. Furthermore, in epitaxial Co$_2$YZ/MgO heterostructures having a Co$_2$YZ electrode such as Co$_2$MnSi (CMS) and Co$_2$MnGe that have $\Delta_1$ states in the majority spin band at $E_F$, coherent tunneling is dominant [31,32], leading to an enhancement of the tunneling spin polarization.

Among the Co$_2$YZ family, CMS has been one of the materials most extensively applied to MTJs [5–11,26–28] and GMR devices [13,15,16]. This is because of (1) its theoretically predicted half-metallic nature, with a large energy gap of 0.81 eV [22] for its minority-spin band; (2) its high Curie temperature of 985 K [24]; and (3) the existence of coherent tunneling in epitaxial CMS/MgO heterostructures [31,32]. On the other hand, nonstoichiometry is inevitable, to various degrees, in Co$_2$YZ thin films prepared by magnetron sputtering or molecular beam epitaxy, leading to structural defects. Thus, the clarification of the influence of structural defects on the half-metallicity of Co$_2$YZ is critical for spintronic device applications [33–36]. Picozzi et al. [33] theoretically predicted that Co$_{0.56}$ antisites in CMS and Co$_2$MnGe, where a Mn site is replaced by a Co atom, cause minority-spin in-gap states at $E_F$ and thus are detrimental to the half-metallicity of CMS and Co$_2$MnGe. Similarly, Miura et al. [34] theoretically predicted a Co$_2$YZ thin film and a MgO tunnel barrier [7–11,25–30] or consisting of a Co$_2$YZ thin film and a thin nonmagnetic metal layer such as Ag have been prepared [13–16]. Furthermore, in epitaxial Co$_2$YZ/MgO heterostructures having a Co$_2$YZ electrode such as Co$_2$MnSi (CMS) and Co$_2$MnGe that have $\Delta_1$ states in the majority spin band at $E_F$, coherent tunneling is dominant [31,32], leading to an enhancement of the tunneling spin polarization.
that disorder between Co sites and Cr sites in Co$_2$CrAl leads to a significant reduction in the spin polarization at $E_F$, while the disorder between Cr sites and Al sites does not significantly decrease the spin polarization. Some of us recently showed that the tunneling magnetoresistance (TMR) ratios at 4.2 K and at RT for epitaxial CMS/MgO/CMS MTJs (CMS MTJs) [8–10] and (from the bottom) Co$_{21}$Si$_{22}$MgO/CMS MTJs [11] increased as the Mn composition in CMS was increased from Mn-deficient to Mn-rich. We demonstrated markedly high TMR ratios of 1995% at 4.2 K and 354% at RT for CMS MTJs with Mn-rich CMS electrodes [10]. The higher TMR ratios for MTJs with Mn-rich CMS electrodes were qualitatively explained by the suppression of the theoretically predicted Co$_{Mn}$ antisites [8,9]. These results also demonstrated that a wide range of Mn-rich CMS films retain half-metallicity in terms of their Mn composition, which is also favorable for applying Co$_2$YZ thin films to spintronic devices. In this context, further understanding of the effect of nonstoichiometry on the electronic properties of CMS is important for extending the application of Heusler alloy films to spintronic devices.

The purpose of the present study was to elucidate the effect of nonstoichiometry on the half-metallic character of CMS. To do this, we investigated how the structural properties, the saturation magnetization per formula unit ($\mu_s$), and the TMR ratio of CMS MTJs depend on the Mn composition in nonstoichiometric CMS thin films. Expressed as Co$_2$Mn$_{\alpha}$Si$_{\beta}$, the films had compositions with various Mn compositions $\alpha$ and a constant $\beta$ for each film series. The structural properties of the films were experimentally investigated using the x-ray diffraction (XRD) intensity ratios of I(002)/I(111) and I(004)/I(111). As a basis for theoretically analyzing these experimental results, we developed a generalized form of the site-specific formula unit (SSFU) composition model [9], which assumes the formation of only antisite defects, not vacancies, to accommodate nonstoichiometry, resulting in the preservation of a 2:1:1 stoichiometry in terms of the $L2_1$ site occupation regardless of film nonstoichiometry in terms of the Co:Mn:Si atomic ratio.

The XRD intensity ratios of I(002)/I(111) and I(111)/I(112) provide insight into the site occupancy through a comparison with kinematical XRD theory calculations based on the SSFU compositions. The theoretical total spin magnetic moment per formula unit and the tunneling spin polarization at $E_F$ for nonstoichiometric and stoichiometric Co$_2$Mn$_{\alpha}$Si$_{\beta}$ were calculated by first-principles calculations based on the SSFU composition. The experimental dependence of the XRD intensity ratios, $\mu_s$, and the TMR ratio on $\alpha$ were consistently explained by the theoretical calculations for $\alpha$ ranging from that for a Mn-deficient composition to that for a certain Mn-rich composition, indicating the validity of the SSFU model based on the antisite formation for understanding the effect of nonstoichiometry in CMS.

This paper is organized as follows. Section II presents our experimental and computational methods, including the SSFU composition model. Section III presents the results and discussion. Section III A describes the structural properties of nonstoichiometric Co$_2$Mn$_{\alpha}$Si$_{\beta}$ films investigated through XRD and high-resolution atomic number (Z)-contrast scanning transmission electron microscopy (STEM). Section III B describes the $\alpha$ dependence of $\mu_s$ of Co$_2$Mn$_{\alpha}$Si$_{\beta}$ thin films. Section III C describes the $\alpha$ dependence of the TMR ratios of CMS MTJs. In combination with the results of density functional theory calculations with coherent potential approximation (CPA), the experimental dependence of $\mu_s$ and the TMR ratio on $\alpha$ is discussed in terms of the effect of defects associated with nonstoichiometry on the half-metallic character of CMS. Section III C also describes the experimental dependence on $\alpha$ of the degree of temperature dependence of the TMR ratio of CMS MTJs and its origin. Section IV summarizes our results and concludes the paper.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. Experimental method

In order to investigate the effect of nonstoichiometry on the structural and magnetic properties of CMS thin films, we prepared Co$_2$Mn$_{\alpha}$Si$_{\beta}$ films having various values of $\alpha$ and a constant value of $\beta$ for each film series. The sample layer structure we prepared for the magnetization measurements and structural characterization by XRD and STEM was as follows: (from the substrate side) MgO buffer (10 nm)/CMS (~30 nm)/MgO barrier (2 nm)/AlO$_x$ cap layer (1 nm), grown on a MgO(001) substrate, as shown in Fig. 1. This layer structure corresponds to half of an MTJ. We used a MgO barrier to protect the CMS surface because we had previously confirmed that the CMS layer is not oxidized by MgO deposition by means of x-ray absorption spectroscopy and x-ray magnetic circular dichroism [37] and because of the demonstrated high quality of the CMS/MgO interface [10,11].

The CMS thin film was deposited at RT using radio-frequency magnetron cosputtering from a nearly...
FIG. 2. (Color online) A typical low-angle x-ray reflectivity scan for a layer structure consisting of MgO(001) substrate/MgO buffer (10 nm)/Co₂Mn₁₃₂Si₀₈₈ thin layer/MgO barrier (2 nm)/AlOₓ cap layer (1 nm). The solid and dotted lines represent the experimental and fitted curves as a function of angle 2θ. A fit of the oscillatory x-ray reflectivity intensity for a 2θ range from 1.4 to 5.6° (dotted line) using the Parratt formalism [38] yielded a Co₂Mn₁₃₂Si₀₈₈ layer thickness of 32.34 nm for this film. This method was used to determine the thickness of each Co₂MnₐSiₜ layer.

The lattice constants in the plane, a, and perpendicular to the plane, c, also had to be determined for the films in order to obtain μ₂, α and c were measured by making x-ray θ-2θ Bragg scans with a four-axis x-ray diffractometer (Bruker AXS D8 Discover Hybrid) with a scintillation counter. Tables I and II show the measured values of α for Co₂MnₐSi₁₀ films and Co₂MnₐSi₀₈₈ films, respectively. For the Co₂MnₐSi₁₀ films, α increased from α = 0.564 nm for α = 0.69 to α = 0.567 nm for α = 1.44 (0.5% increase in α), while c was almost constant and showed only an increase within 0.1% for a range of α from 0.69 to 1.44 (Table I). The measured α = (0.5664 nm) and c = (0.5649 nm) for a stoichiometric Co₂Mn₁₀Si₁₀ film (Table I) are in good agreement with the α = (0.5654 nm) reported for a polycrystalline CMS bulk sample [24]. The measured α and c for the Co₂MnₐSi₀₈₈ films showed a similar dependence on α (Table II).

To investigate the site occupancies of the nonstoichiometric Co₂MnₐSiₜ films, we measured the ratio of the 002 peak intensity with respect to the 004 peak intensity, I(002)/I(004), and the ratio of the 111 peak intensity to the 022 peak intensity, I(111)/I(022), in XRD. The 002 peak is characteristic of the B2 (or Lₐ) structure, the 111 peak is characteristic of the L₂₁ structure, and the 004 and 022 peaks are characteristic to the fundamental A2 structure. For these measurements, we used a two-dimensional position-sensitive proportional counter (two-dimensional detector) in the four-axis x-ray diffractometer. The sample rotation angle (ϕ), tilt angle (χ), incident angle (ω), and detection angle (or diffraction angle) (2θ) were fixed in the diffraction intensity measurement using the two-dimensional detector. However, the intensity profiles along χ and 2θ were included in the measured intensities due to the use of the two-dimensional detector. In XRD intensity ratio measurements, the x-ray irradiation area, which depends on the incident angle of the x rays, must be smaller than the sample size for any diffraction angles to be investigated. An x-ray collimator having a beam diameter of 0.5 mm was used for the measurements using the two-dimensional detector, thereby ensuring this condition was met for all 002, 004, 111, and 022 reflections.

<table>
<thead>
<tr>
<th>α in Co₂MnₐSi₁₀</th>
<th>SSFU composition</th>
<th>Type no.</th>
<th>a (nm)</th>
<th>c (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.69</td>
<td>Co₂[Mn₀.₃⁷Co₀.₆₃]Si₀₈₆</td>
<td>I</td>
<td>0.5643</td>
<td>0.5648</td>
</tr>
<tr>
<td>0.85</td>
<td>Co₂[Mn₀.₃₈Co₀.₆₂]Si₀₈₄</td>
<td>I</td>
<td>0.5658</td>
<td>0.5647</td>
</tr>
<tr>
<td>1.00</td>
<td>Co₂MnSi</td>
<td>–</td>
<td>0.5664</td>
<td>0.5649</td>
</tr>
<tr>
<td>1.15</td>
<td>[Co₀.₉₇Mn₀.₀₃]Si₀₈₆Mn₀.₀₄</td>
<td>III</td>
<td>0.5670</td>
<td>0.5647</td>
</tr>
<tr>
<td>1.29</td>
<td>[Co₀.₈₆Mn₀.₁₄]Si₀₈₆Mn₀.₀₇</td>
<td>III</td>
<td>0.5672</td>
<td>0.5653</td>
</tr>
<tr>
<td>1.44</td>
<td>[Co₀.₈₆Mn₀.₂₈]Si₀₈₆Mn₀.₁₀</td>
<td>III</td>
<td>0.5674</td>
<td>0.5654</td>
</tr>
</tbody>
</table>
TABLE II. SSFU compositions, formula unit type, and measured lattice parameters $a$ and $c$ for $\sim$30-nm-thick epitaxial Co$_2$Mn$_x$Si$_{0.88}$ films with various Mn compositions $\alpha$ grown on MgO(001) substrates.

<table>
<thead>
<tr>
<th>$\alpha$ in Co$_2$Mn$<em>x$Si$</em>{0.88}$</th>
<th>SSFU composition</th>
<th>Type no.</th>
<th>$a$ (nm)</th>
<th>$c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.72</td>
<td>Co$<em>2$[Mn$<em>0.76$Co$</em>{0.22}$][Si$</em>{0.98}$Mn$_{0.02}$]</td>
<td>II</td>
<td>0.5642</td>
<td>0.5652</td>
</tr>
<tr>
<td>1.00</td>
<td>Co$<em>2$[Mn$<em>0.94$Co$</em>{0.06}$][Si$</em>{0.91}$Mn$_{0.09}$]</td>
<td>II</td>
<td>0.5657</td>
<td>0.5655</td>
</tr>
<tr>
<td>1.15</td>
<td>[Co$<em>{0.90}$Mn$</em>{0.10}$][Mn]Si$<em>{0.88}$Mn$</em>{0.12}$</td>
<td>III</td>
<td>0.5667</td>
<td>0.5655</td>
</tr>
<tr>
<td>1.32</td>
<td>[Co$<em>{0.90}$Mn$</em>{0.10}$][Mn]Si$<em>{0.84}$Mn$</em>{0.16}$</td>
<td>III</td>
<td>0.5666</td>
<td>0.5651</td>
</tr>
<tr>
<td>1.37</td>
<td>[Co$<em>{0.86}$Mn$</em>{0.14}$][Mn]Si$<em>{0.83}$Mn$</em>{0.17}$</td>
<td>III</td>
<td>0.5672</td>
<td>0.5654</td>
</tr>
<tr>
<td>1.53</td>
<td>[Co$<em>{0.81}$Mn$</em>{0.19}$][Mn]Si$<em>{0.80}$Mn$</em>{0.20}$</td>
<td>III</td>
<td>0.5680</td>
<td>0.5660</td>
</tr>
<tr>
<td>1.68</td>
<td>[Co$<em>{0.75}$Mn$</em>{0.25}$][Mn]Si$<em>{0.77}$Mn$</em>{0.23}$</td>
<td>III</td>
<td>0.5673</td>
<td>0.5659</td>
</tr>
<tr>
<td>1.84</td>
<td>[Co$<em>{0.60}$Mn$</em>{0.40}$][Mn]Si$<em>{0.75}$Mn$</em>{0.25}$</td>
<td>III</td>
<td>0.5672</td>
<td>0.5657</td>
</tr>
</tbody>
</table>

B. Computational method

To investigate the effect of $\alpha$ on the electronic properties, we performed density functional calculations on the basis of the Korringa-Kohn-Rostoker (KKR) method [40,41] with the CPA to determine the total magnetic moments per formula unit, $m_{\text{spins}}$, and the spin-resolved, local density of states (LDOS). In this method, the space is divided into nonoverlapping muffin-tin spheres. We used a scalar relativistic calculation, in which the spin-orbit interaction was neglected. For the Brillouin zone (BZ) integration, we included 8000 points in the full BZ. The unit cell of the full-Heusler alloy $X_2YZ$ with the $L2_1$ structure consists of four different fcc sublattices. Each has an atom basis as follows: $X$ element at (1/4,1/4,1/4) and (3/4,3/4,3/4), $Y$ at (0,0,0), and $Z$ at (1/2,1/2,1/2). We used the generalized gradient approximation for the exchange and correlation term [42]. We used the experimental lattice constants $a$ described above for both Co$_2$Mn$_x$Si$_{1.0}$ films (Table I) and Co$_2$Mn$_x$Si$_{0.88}$ films (Table II), but we ignored the small difference between $a$ and $c$ and assumed a cubic CMS lattice with the experimental $a$ value for each film. The KKR-CPA calculations were based on the SSFU composition model assuming antisite formation rather than vacancy formation to accommodate nonstoichiometry, as described in Sec. II C.

C. Formula unit composition model

In our previous paper [9], we proposed a model of the SSFU composition for nonstoichiometric Co$_2$Mn$_x$Si$_{\beta}$. In this section, we describe the model from a more generalized point of view. This model emphasizes the occupancy at each site in the $L2_1$ lattice, rather than simply describing the compositions of Co, Mn, and Si atoms included in the formula unit. Most importantly, we assumed the formation of antisite defects, not vacancies, to accommodate nonstoichiometry. This is because of the theoretically predicted higher formation energies of vacancies at the nominal Co, Mn, and Si sites compared with various kinds of antisites for CMS [33,36]. In this model, each site in the $L2_1$ structure is occupied, either by the nominal atom (Co, Mn, or Si) for that site or by an antisite defect atom, so the total number of atoms included in the formula unit, $N_{\text{AP}}$, is always four, even though the film is nonstoichiometric in terms of the Co:Mn:Si atomic ratio. Thus, this model preserves a generalized 2:1:1 stoichiometry in terms of the site occupancy. We call this SSFU composition model the antisite-based SSFU composition model.

Given this model, we showed three types of SSFU compositions, summarized in Table III, which cover all the formula unit compositions of the films that we investigated in this paper. These films include Co$_2$Mn$_{x}$Si$_{1.0}$ with a Co:Si ratio of 2:1 and Si-deficient Co$_2$Mn$_x$Si$_{\beta}$ with $\beta < 1.0$, both over a range of $\alpha$ from a Mn-deficient composition ($\alpha < 2 - \beta$) to a Mn-rich one ($\alpha > 2 - \beta$).

Let us first consider Co$_2$Mn$_{x}$Si$_{1.0}$ ($\beta = 1.0$). For $\alpha < 1$ (Mn deficient), some of the Mn sites are filled by surplus Co and Si atoms, creating Co$_{\text{Mn}}$ and Si$_{\text{Mn}}$ antisites, both of which have lower calculated formation energy than Mn vacancies [33,36]. The resulting SSFU composition is Co$_2$[Mn$_{1-\alpha}$Co$_{\alpha}$Si$_{\beta}$], which we call a type I SSFU composition. [Mn$_{1-\alpha}$Co$_{\alpha}$Si$_{\beta}$]

<table>
<thead>
<tr>
<th>Type no.</th>
<th>General expression for SSFU composition</th>
<th>$x$</th>
<th>$y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Co$<em>2$[Mn$</em>{1-\alpha}$Co$<em>{\alpha}$]Z$</em>{\beta}$</td>
<td>$2\alpha$ &amp; $2\alpha + \beta$</td>
<td>$2\alpha$ &amp; $2\alpha + \beta$</td>
</tr>
<tr>
<td>II</td>
<td>Co$<em>2$[Mn$</em>{1-\alpha}$Co$<em>{\alpha}$][Z$</em>{\beta}$Mn$_{\alpha}$]</td>
<td>$2\alpha$ &amp; $2\alpha + \beta$</td>
<td>$2\alpha$ &amp; $2\alpha + \beta$</td>
</tr>
<tr>
<td>III</td>
<td>[Co$<em>2$Mn$</em>{1-\alpha}$]Mn$<em>{\alpha}$Z$</em>{\beta}$</td>
<td>$2\alpha$ &amp; $2\alpha + \beta$</td>
<td>$2\alpha$ &amp; $2\alpha + \beta$</td>
</tr>
</tbody>
</table>
is the composition on the nominal Mn site. For \( \alpha > 1 \) (Mn-rich), the excess Mn atoms occupy nominal Co and Si sites, creating CoMn and MnSi antisites, both of which have lower calculated formation energy than either a Co or Si site vacancy [33,36]. The resulting SSFU composition is \([Co_{2-x}Mn_x][MnSi_{1-y}Mn_y]\), which we call type III. \([Co_{2-x}Mn_x]\) and \([Si_{1-y}Mn_y]\) are the compositions of the nominal Co and Si sites, respectively.

Next, let us consider Si-deficient Co\(_2\)Mn\(_x\)Si\(_\beta\) (\(\beta < 1\)). Again, there are two cases, determined by the Co atomic ratio in the formula unit, \(r_{Co}\). The ratio \(r_{Co}\) is given by \(2/N = 2/(2 + \alpha + \beta)\), where the number of Co atoms included in one unit of Co\(_2\)Mn\(_x\)Si\(_\beta\), \(N\), is divided by the total number of atoms included in one unit of Co\(_2\)Mn\(_x\)Si\(_\beta\), \(N = N_{f.u.} = 4\) for \(\alpha + \beta = 2\). If \(r_{Co} > 1/2\) (i.e., \(\alpha + \beta < 2\)), some of the Si sites are filled by Mn atoms, creating MnSi antisites, which have lower predicted formation energy than CoSi antisites [36], and some of the Mn sites are filled by Co atoms, creating CoMn antisites, which have lower formation energy than Mn vacancies [36]. This results in a type II SSFU composition of Co\(_2\)[Mn\(_{1-x}\)Co\(_x\)][Si\(_{1-y}\)Mn\(_y\)]. If \(r_{Co} < 1/2\) (i.e., \(\alpha + \beta > 2\)), which is the case for Mn-rich Co\(_2\)Mn\(_x\)Si\(_\beta\) with \(2 - \beta > \beta\) and \(\beta < 1\), the SSFU composition is of type III.

The parameters \(x\) and \(y\) in the SSFU composition are determined as functions of \(\alpha\) and \(\beta\) from the requirement that the Co:Mn:Si atomic ratio in the resulting formula unit must be equal to the film composition expressed as Co\(_2\)Mn\(_x\)Si\(_\beta\) with given \(\alpha\) and \(\beta\). Furthermore, the boundaries of the respective regions of the type I to type III SSFU compositions in the \(\alpha-\beta\) plane are determined from the requirements that the parameters \(x\) and \(y\) should be in the range of 0 \(<\ x <\ 1\) and 0 \(<\ y <\ 1\) (Fig. 3). The boundary given by \(\alpha + \beta = 2\) corresponds to the SSFU composition, where \(r_{Co}\) is 1/2. Similarly, the boundary given by \(\beta = (2 + \alpha)/3\) corresponds to the SSFU composition, where the Si atomic ratio in the formula unit, \(r_{Si}\), is 1/4. Thus, the Co atomic ratio in the formula unit for the type I and type II regions in the \(\alpha-\beta\) plane is larger than 1/2 and that for the type III region is smaller than 1/2.

The calculated SSFU compositions of the samples are listed in Table I for \(\beta = 1.0\) and in Table II for \(\beta = 0.88\). We used these compositions to model various experiment results, including structural properties, EDS, and TMR ratios, in order to test whether the underlying assumption of dominant antisite defects is true and to explore the effect of such antisite defects on the half-metallic character of Co\(_2\)Mn\(_x\)Si\(_\beta\).

### III. RESULTS AND DISCUSSION

#### A. Structural properties

First, we describe the effects of nonstoichiometry on the structural properties of Co\(_2\)Mn\(_x\)Si\(_\beta\) films having various \(\alpha\) values with a fixed \(\beta\) for each series. RHEED observations of these nonstoichiometric CMS films showed 1/2-order superlattice reflections (or 11* streak lines) along the [110] CMS direction for both the Mn-deficient and Mn-rich compositions, as has been shown for a Mn-deficient Co\(_2\)Mn\(_{0.91}\)Si\(_{0.09}\) film [26] and for a Mn-rich Co\(_2\)Mn\(_{1.20}\)Si\(_{1.0}\) film [11], indicating \(L_{21}\) order at the surface of the prepared nonstoichiometric CMS films regardless of whether their composition was Mn-rich or Mn-deficient. The electron diffraction patterns for both a Mn-deficient CMS film having a film composition of Co\(_2\)Mn\(_{0.90}\)Si\(_{0.10}\) [43] and a Mn-rich CMS film having that of Co\(_2\)Mn\(_{1.20}\)Si\(_{1.0}\) [9] showed 111 spots, indicating the existence of the \(L_{21}\) structure in both the films.

Figures 4(a) and 4(b) show the measured intensity ratios \(I(002)/I(004)\) and \(I(111)/I(022)\) for four samples of Co\(_2\)Mn\(_{0.9}\)Si\(_{0.88}\) films with \(\alpha = 0.72\), 1.0, 1.37, and 1.84. The respective SSFU compositions for these four samples are shown in Table II.

I(002)/I(004) decreased monotonically with increasing \(\alpha\). Furthermore, I(111)/I(022) for \(\alpha = 1.0, 1.37, \) and 1.84 were clearly lower than that for \(\alpha = 0.72\). The atomic scattering factors of the Mn atom (the atomic number 25) and Co atom (27) are close, but that of the Si atom (14) is about half that of Mn and Co, so the 002 peak intensity for CMS in the XRD mainly depends on the occupation ratio of Si in the MnSi plane (\(\gamma_{L}\)). According to the SSFU compositions for Co\(_2\)Mn\(_{0.9}\)Si\(_{0.88}\), \(\gamma_{1}\) decreases with increasing \(\alpha\) from \(\gamma_{1} = 0.98/2\) for \(\alpha = 0.72\) to \(\gamma_{1} = 0.75/2\) for \(\alpha = 1.84\). Thus, the observed decrease in I(002)/I(004) can be ascribed to the decrease in the occupation of Si in the MnSi plane with increasing \(\alpha\), as shown by the SSFU compositions. Similarly, the 111 peak intensity for CMS mainly depends on the occupation of Si at the nominal Si site (\(\gamma_{2}\)), and the \(\gamma_{2}\) values for \(\alpha = 1.0, 1.37,\) and 1.84 ranging from \(\gamma_{2} = 0.91\) for \(\alpha = 1.0\) to \(\gamma_{2} = 0.75\) for \(\alpha = 1.84\) are definitely lower than the \(\gamma_{2} = 0.98\) for \(\alpha = 0.72\). Thus, the observed I(111)/I(022) being lower for \(\alpha = 1.0, 1.37,\) and 1.84 than for \(\alpha = 0.72\) can also be attributed to the lower occupation of Si.
For I(111)/I(022), which is related to the order between the nominal Mn site and the nominal Si site in the MnSi plane, the observed lower intensity ratios for \( \alpha = 1.0, 1.37, \) and 1.84 compared with that for \( \alpha = 0.72 \) were reproduced by the calculation, indicating that the proposed SSFU compositions are basically valid regarding the order between the nominal Mn site and the nominal Si site. In more detail, the experimental I(111)/I(022) decreased with \( \alpha \) increasing from 0.72 to 1.0, in agreement with the calculation. In contrast, the experimental I(111)/I(022) increased with \( \alpha \) increasing from 1.0 to 1.37 and 1.84, which is in disagreement with the calculation. To identify the possible origin of this increase, we should note that the experimental \( \mu_s \) for Co\(_2\)Mn\(_{0.78}\)Si\(_{0.88}\) films showed a distinct decrease with \( \alpha \) increasing beyond 1.53, as will be shown in Fig. 6(a) in Sec. III B and that the TMR ratio at 290 K for CMS MTJs having \( \beta = 0.88 \) CMS electrodes showed a decrease with \( \alpha \) increasing beyond 1.48, as will be discussed in Sec. III C. Furthermore, the decrease in \( \mu_s \) and the TMR ratio for \( \alpha \) larger than a certain critical value, \( \alpha_c, \) was also observed for other \( \beta \) series. These decreases in the experimental \( \mu_s \) and TMR ratios with increasing \( \alpha > \alpha_c \) can be explained by the appearance of a second phase that is a nonmagnetic or antiferromagnetic material and is not a half-metal. One possible candidate for the second phase is antiferromagnetic Mn\(_3\)Si with a Néel temperature of 25 K \[44\]. Furthermore, Mn\(_3\)Si is theoretically predicted not to be a half-metal \[45\]. Thus, the assumption of the appearance of Mn\(_3\)Si as the second phase can explain the decrease in the experimental \( \mu_s \) and TMR ratios with increasing \( \alpha > \alpha_c \). Regarding the structural properties, Mn\(_3\)Si crystallizes in a DO\(_3\) structure having lattice constant \( a = 0.5722 \) nm \[44\], which is close to the values for CMS films (Tables I and II), and its crystal structure has the same basic unit cell as the \( L_2_1 \) structure of Heusler alloy CMS.

If Mn\(_3\)Si appeared as the second phase, the SSFU composition of the CMS matrix would shift to a reduced Mn composition with respect to Co and Si. The occupation of Si at the nominal site, \( \gamma_S, \) would thus increase in the CMS matrix, resulting in an increase in the 111 peak intensity. Since the \( \alpha = 1.84 \) film (Co\(_2\)Mn\(_{0.78}\)Si\(_{0.88}\)) is obviously in the range of \( \alpha > \alpha_c, \) the increase in the experimental I(111)/I(022) and the decrease in the experimental \( \mu_s \) for the \( \alpha = 1.84 \) film of the \( \beta = 0.88 \) CMS film series can be consistently explained. To sum up, although we could not get a full understanding of the origin of the increase in the experimental I(111)/I(022) for \( \alpha = 1.37 \) and 1.84, we propose that Mn\(_3\)Si, which is antiferromagnetic and not half-metallic, appears as a second phase, to explain the increased I(111)/I(022) for \( \alpha = 1.84. \)

To further characterize the structural properties, we directly observed lattice images of Mn-deficient and Mn-rich CMS films at atomic resolution using aberration-corrected Z-contrast STEM. Figures 5(a) and 5(b) show typical Z-contrast STEM images for a Mn-deficient Co\(_2\)Mn\(_{0.78}\)Si\(_{0.88}\) film (SSFU composition Co\(_2\)[Mn\(_{0.78}\)Co\(_{0.22}\)]Si\(_{0.8}\) and a Mn-rich Co\(_2\)Mn\(_{0.9}\)Si\(_{0.98}\) film (Co\(_{0.18}\)Mn\(_{0.82}\)) shown in Figs. 4(a) and 4(b), decreased with increasing \( \alpha. \) Thus, we found a fairly good agreement between the experimental and calculated dependences of I(002)/I(004), indicating the validity of the proposed SSFU compositions, in particular, regarding the order between the nominal Co plane and the nominal MnSi plane.

In the MnSi plane for \( \alpha = 1.0, 1.37, \) and 1.84, as shown by the SSFU compositions.

We also calculated I(002)/I(004) and I(111)/I(022) for Co\(_2\)Mn\(_{0.78}\)Si\(_{0.88}\) as a function of \( \alpha \) using kinematical XRD theory and the SSFU compositions. Although the main factor in the calculation is the structure factor that depends on the site occupations, we also took into account (1) the Lorentz factor proportional to \( 1/\sin(2\theta) \) for a single-crystalline film, (2) the polarization factor proportional to \( 1+\cos^22\theta \), and (3) the absorption factor proportional to \( (1-\exp(-2\mu t/\sin\theta)) \), where \( t \) is a film thickness smaller than the effective x-ray penetration depth, and \( \mu \) is the line absorption coefficient of the film. The calculated I(002)/I(004) and I(111)/I(022), shown in Figs. 4(a) and 4(b), decreased with increasing \( \alpha. \) Thus, we found a fairly good agreement between the experimental and calculated dependences of I(002)/I(004), indicating the validity of the proposed SSFU compositions, in particular, regarding the order between the nominal Co plane and the nominal MnSi plane.

**FIG. 4.** Mn composition \((\alpha)\) dependence in Co\(_2\)Mn\(_{0.78}\)Si\(_{0.88}\) films of the experimental (solid circles) and calculated (open circles) ratios of XRD intensity of (a) 002 peak with respect to that of 004 peak, I(002)/I(004) and (b) 111 peak with respect to that of 022 peak, I(111)/I(022). The calculated ratios were obtained using the kinematical XRD theory and formula unit compositions given in Table II.
are consistent with the lower Si occupation ratio at the nominal Si site in the proposed SSFU composition for the Mn-rich film with $\alpha = 1.37$ relative to that for the Mn-deficient film with $\alpha = 0.72$.

In summary, the experimental findings regarding the structural properties observed for both the XRD intensity ratios and HRSTEM images support the proposed SSFU compositions.

B. Saturation magnetization per formula unit composition

We now describe how the experimental saturation magnetization per formula unit $\mu_s$ of nonstoichiometric Co$_2$Mn$_{\alpha}\text{Si}_\beta$ ($\beta = 0.88$ and 1.0) films varied with $\alpha$. We will compare the experimental $\mu_s$ with the theoretically calculated total spin magnetic moments per formula unit, $m_{\text{spin}}$, and with the Slater-Pauling rule for half-metallic Co$_2$YZ alloys, $Z_{\alpha-24}$ ($\mu_{\text{B}}/\text{f.u.}$) [23], where $Z_{\alpha}$ is the total number of valence electrons per formula unit provided by the SSFU composition and $\mu_{\text{B}}$ is the Bohr magneton. Figure 6(a) plots $\mu_s$ at 10 K and $m_{\text{spin}}$ for Co$_2$Mn$_{\alpha}\text{Si}_{\beta}$ films with $\alpha$ ranging from 0.72 (Mn-deficient CMS) to 1.84 (Mn-rich CMS), while Fig. 6(b) compares $m_{\text{spin}}$ with $Z_{-24}$. As shown in Fig. 6(a), $\mu_s$ is in good agreement with $m_{\text{spin}}$ over a wide range of $\alpha$ from 0.72 to 1.37. For a strongly Mn-deficient composition ($\alpha = 0.72$), $\mu_s$ was markedly lower than $Z_{-24}$. However, $\mu_s$ increased with an increase in $\alpha$ over $\alpha = 0.72$, growing closer to $Z_{-24}$ and was very close to $Z_{-24}$ for $\alpha = 1.15$ to 1.37. The $\mu_s$ was appreciably lower than $m_{\text{spin}}$ for $\alpha = 1.53$, and it decreased significantly with a further increase in $\alpha$. We estimated the critical value $\alpha_c$ over which $\mu_s$ decreased to be $\alpha_c = 1.53$ for $\beta = 0.88$, midway between 1.37 and 1.68.

As shown in Fig. 6(b), $m_{\text{spin}}$ for $\alpha = 0.72$ was distinctly lower than the half-metallic value, $Z_{-24}$. However, $m_{\text{spin}}$ increased with increasing $\alpha$, growing closer to $Z_{-24}$. Note that the Co atomic ratio at the nominal Mn site decreased with $\alpha$ increasing from 0.72 in accordance with the SSFU composition model (Table II). The two values are in good agreement for $\alpha = 1.15$ ($\{(\text{Co}_{0.69}\text{Mn}_{0.31})\text{Si}_{0.84}\text{Mn}_{0.16}\}$) to 1.84 ($\{(\text{Co}_{1.60}\text{Mn}_{0.40})\text{Si}_{0.75}\text{Mn}_{0.25}\}$), where the Co$_{\text{Mn}}$ antisites are suppressed.

To confirm the reproducibility of these features for the $\alpha$ dependence of $\mu_s$, we also investigated $\mu_s$ values for the $\beta = 1.0$ film series (Co$_2$Mn$_{\alpha}\text{Si}_{1.0}$). Figure 6(c) plots $\mu_s$ at 10 K and $m_{\text{spin}}$ for Co$_2$Mn$_{\alpha}\text{Si}_{1.0}$ films with $\alpha$ ranging from 0.69 to 1.44, while Fig. 6(d) compares $m_{\text{spin}}$ with $Z_{-24}$. As shown in Fig. 6(c), the dependence of $\mu_s$ on $\alpha$ was well reproduced by $m_{\text{spin}}$ for a wide range of $\alpha$ from 0.69 to 1.29, although we observed a small scattering of $\mu_s$ for $\beta = 1.0$ as a function of $\alpha$ for $\alpha = 0.85$ to 1.29. This small scattering of $\mu_s$ was probably due to experimental errors and not to an intrinsic factor because common features for the $\alpha$ dependence of $\mu_s$ were observed for both $\beta = 0.88$ and 1.0 and because a more continuous change in $\mu_s$ with respect to $\alpha$ was observed for $\beta = 0.88$. For a strongly Mn-deficient composition ($\alpha = 0.69$), $\mu_s$ was markedly lower than $Z_{-24}$. However, $\mu_s$ increased with an increase in $\alpha$ over $\alpha = 0.69$ and was close to $Z_{-24}$ for $\alpha = 1.0$ to 1.29. With an even further increase in $\alpha$, $\mu_s$ decreased significantly. Thus, the characteristic dependence of $\mu_s$ on $\alpha$ observed in the $\beta = 0.88$ films was also observed in the $\beta = 1.0$ films. As shown in Fig. 6(d), the dependence of $m_{\text{spin}}$ on
FIG. 6. (Color online) (a) Experimental $\mu_s$ values at 10 K and theoretical $m_{\text{spin}}$ values obtained by KKR-CPA calculations as a function of $\alpha$ for Co$_2$Mn$_{\alpha}$Si$_{0.88}$. (b) Theoretical $m_{\text{spin}}$ values and $Z_t-24$, where $Z_t$ is the total valence electron number/formula unit provided by the SSFU compositions as a function of $\alpha$ for Co$_2$Mn$_{\alpha}$Si$_{0.88}$. (c) Experimental $\mu_s$ values at 10 K and theoretical $m_{\text{spin}}$ values as a function of $\alpha$ for Co$_2$Mn$_{\alpha}$Si$_{1.0}$. (d) Theoretical $m_{\text{spin}}$ values and $Z_t-24$ as a function of $\alpha$ for Co$_2$Mn$_{\alpha}$Si$_{1.0}$.

For $\beta = 1.0$ was similar to that for $\beta = 0.88$. The $m_{\text{spin}}$ for $\alpha = 0.69$ was distinctly lower than $Z_t-24$ [Fig. 6(d)], but $m_{\text{spin}}$ increased with increasing $\alpha$, growing closer to $Z_t-24$. The two values are in good agreement for $\alpha = 1.0$ to 1.44.

There was good agreement between $\mu_s$ and $Z_t-24$ for $\alpha = 1.15$ to 1.37 for Co$_2$Mn$_{\alpha}$Si$_{0.88}$ films, as shown in Figs. 6(a) and 6(b), and for $\alpha = 1.0$ to 1.29 for Co$_2$Mn$_{\alpha}$Si$_{1.0}$ films, as shown in Figs. 6(c) and 6(d). These observations indicate that Co$_2$Mn$_{\alpha}$Si$_{0.88}$ films with $\alpha$ ranging from 1.15 to 1.37 and Co$_2$Mn$_{\alpha}$Si$_{1.0}$ films with $\alpha$ ranging from 1.0 to 1.29 are close to half-metals.

To clarify the origin of the decrease in $\mu_s$ with respect to $Z_t-24$ for Mn-deficient CMS films (Mn deficiency generally corresponds to $\alpha < 2 - \beta$ for the expression of Co$_2$Mn$_{\alpha}$Si$_{\beta}$), we calculated by KKR-CPA the $\alpha$ dependence of the Co and Mn spin magnetic moments, $m_{\text{spin}}$(Co) and $m_{\text{spin}}$(Mn), at the respective regular site and antisite. The calculated $m_{\text{spin}}$(Co) and $m_{\text{spin}}$(Mn) are shown for Co$_2$Mn$_{\alpha}$Si$_{0.88}$ films in Figs. 7(a) and 7(b). In Fig. 7, the KKR-CPA calculations indicate that the spin magnetic moment of Co at the nominal Mn site, $m_{\text{spin}}$(Co$_{\text{Mn}}$), is much smaller than that of Mn at the nominal Mn site, $m_{\text{spin}}$(Mn$_{\text{Mn}}$) ($m_{\text{spin}}$(Co$_{\text{Mn}}$) = 1.89 $\mu_B$ in contrast to $m_{\text{spin}}$(Mn$_{\text{Mn}}$) = 3.29 $\mu_B$ for $\alpha = 0.72$). This results in $\mu_s$ being lower than $Z_t-24$ with decreasing $\alpha < 2 - \beta$. Thus, the loss of the half-metallicity in Mn-deficient CMS films, shown by $\mu_s$ being lower than $Z_t-24$, originates from the Co$_{\text{Mn}}$ antisite defects.

The good agreement between the experimental $\mu_s$ and theoretical $m_{\text{spin}}$ values for both Co$_2$Mn$_{\alpha}$Si$_{0.88}$ films with $\alpha = 0.72$ to 1.37 and Co$_2$Mn$_{\alpha}$Si$_{1.0}$ films with $\alpha = 0.69$ to 1.29 supports the validity of the SSFU composition model based on the formation of antisites rather than
electrodes, including the MgO-buffered $\beta = 1.0$ MTJs [8] and CoFe-buffered $\beta = 0.96$ MTJs [10], previously reported, and the CoFe-buffered $\beta = 0.88$ MTJs investigated in this study. Then, we theoretically investigate the $\alpha$ dependence of the spin polarization by using KKR-CPA calculations based on the SSFU composition model. We show that the $\alpha$ dependence of the theoretical spin polarization, $P_{\text{th}}(\alpha)$, for Mn-deficient compositions in Co$_2$Mn$_{\alpha}Si_y$ electrodes differs significantly from that of $P_{\text{b}}(\alpha)$, where $P_{\text{b}}(\alpha)$ is determined by considering all the contributions from $s$-, $p$-, and $d$-like electrons for the majority- and minority-spin density of states (DOS) at $E_F$ and where $P_{\text{b}}(\alpha)$ is determined by considering only the contributions from $s$- and $p$-like electrons. By comparing the $\alpha$ dependence of the TMR ratio with that of $P_{\text{th}}(\alpha)$ and $P_{\text{b}}(\alpha)$, we show that the $\alpha$ dependence of the TMR ratio can be qualitatively explained by $P_{\text{th}}(\alpha)$ for an $\alpha$ range from a Mn-deficient composition to a critical Mn-rich composition, $\alpha_c$. Then, we show that the decrease in $P_{\text{b}}(\alpha)$ with decreasing $\alpha$ in the Mn-deficient compositions is caused by a small amount of itinerant $s$- and $p$-orbital components of the local density of minority-spin in-gap states at $E_F$ of Co at the nominal Mn site (Co$_{\text{Mn}}$) and at the regular site (Co$_{\text{Co}}$). We also show that $\alpha_c$ increases with decreasing $\beta$, suggesting a correlation between $\alpha_c$ and the SSFU composition.

Figures 8(a) and 8(b) show the TMR ratios at 290 and 4.2 K of CMS MTJs having Co$_2$Mn$_{\alpha}Si_y$ electrodes as a function of $\alpha$ for $\beta = 0.88$, 0.96, and 1.0. The data for $\beta = 0.96$ and 1.0 MTJs were previously presented [10,8]. The $\beta = 0.88$ and 0.96 MTJs were prepared on CoFe-buffered MgO(001) substrates, but the $\beta = 1.0$ MTJs were prepared on MgO-buffered MgO(001). The TMR ratios of the CoFe-buffered $\beta = 0.88$ and 0.96 MTJs were significantly higher than those of the MgO-buffered $\beta = 1.0$ MTJs as a result of the enhanced coherent tunneling caused by the increased misfit dislocation spacing at the lower and upper MgO barrier interfaces [10]. Although the TMR ratios of CoFe-buffered CMS MTJs were much higher than those of MgO-buffered CMS MTJs, the dependences of their TMR ratios at 4.2 and 290 K on $\alpha$ were almost identical. In all three cases, the TMR ratio for the CMS MTJ series significantly increased with $\alpha$ increasing from a Mn-deficient composition up to a certain Mn-rich composition, $\alpha_c$, beyond which it decreased.

For each CMS MTJ series, we estimated $\alpha_c$ as the value midway between the $\alpha$ for the maximum TMR ratio at 290 K and the next $\alpha$. The $\alpha_c$ values for $\beta = 1.0$, 0.96, and 0.88 were 1.34, 1.42, and 1.48, respectively, which are the same as those determined from the TMR ratio at 4.2 K. The $\alpha_c$ values from the TMR ratio are, thus, in good agreement with those from $\mu_s$ (Sec. III B).

The $\alpha_c$ value increased with decreasing $\beta < 1.0$ (larger Si deficiency). This suggests a correlation between $\alpha_c$ and the SSFU compositions. The SSFU compositions were type III, [Co$_{2-x}$Mn$_x$]Mn[Si$_{1-y}$Mn$_y$], for $\alpha \approx \alpha_c$. If we determine the critical values of $x$ for the type III SSFU compositions, $x_c$, from $\alpha_c$ by following Table III, we obtain an almost identical value, $x_c = 0.17 \pm 3\%$, for $\beta = 1.0, 0.96$, and 0.88. This suggests that there is an upper limit for Mn at Co sites. We suspect that films having $\alpha > \alpha_c$ contain a second phase that is nonmagnetic or antiferromagnetic and is not half-metallic, thereby explaining the decrease in $\mu_s$ and the TMR ratio for
FIG. 8. (Color online) Mn composition dependence of the TMR ratios at (a) 290 K and (b) 4.2 K obtained for three series of Co$_2$Mn$_{\alpha}$Si$_{\beta}$/MgO/Co$_2$Mn$_{\alpha}$Si$_{\beta}$ MTJs (CMS MTJs) as a function of $\alpha$, including MgO-buffered MTJs with Co$_2$Mn$_{\alpha}$Si$_{1.0}$ electrodes [9] (open rectangles), CoFe-buffered MTJs with Co$_2$Mn$_{\alpha}$Si$_{0.86}$ electrodes [10] (solid triangles), and CoFe-buffered MTJs with Co$_2$Mn$_{\alpha}$Si$_{0.45}$ electrodes (open diamonds).

$\alpha > \alpha_c$. One possible candidate for the second phase is Mn$_1$Si, as discussed in Sec. III A.

Figure 9 shows two kinds of theoretical spin polarization, $P_{th}(spd)$ and $P_{th}(sp)$, calculated for Co$_2$Mn$_{\alpha}$Si$_{1.0}$ for various $\alpha$ values ranging from $\alpha = 0.69$ to 1.44. The $P_{th}(spd)$ value was determined by considering all the contributions from $s$-, $p$-, and $d$-like electrons for the majority- and minority-spin DOS at $E_F$, $D_M(spd)$ and $D_m(spd)$, respectively. It is defined as

$$P_{th}(spd) = \frac{D_M(spd) - D_m(spd)}{D_M(spd) + D_m(spd)} \quad (1)$$

The $P_{th}(sp)$ value was determined by considering only the contributions from $s$- and $p$-like electrons for the majority- and minority-spin DOS at $E_F$, $D_M(sp)$ and $D_m(sp)$, respectively. It is defined as

$$P_{th}(sp) = \frac{D_M(sp) - D_m(sp)}{D_M(sp) + D_m(sp)} \quad (2)$$

As shown in Fig. 9, the values for $P_{th}(sp)$ and $P_{th}(spd)$ for Co$_2$Mn$_{\alpha}$Si$_{1.0}$ with $\alpha \geq 1.13$ were almost half-metallic: $P_{th}(sp) = 0.995$ and $P_{th}(spd) \geq 0.99$. The values for $P_{th}(spd)$ (0.81) and $P_{th}(sp)$ (0.96) for $\alpha = 1.0$ (stoichiometric CMS) were lower than 1.0, the value for half-metals, due to the atomic sphere approximation in the KKR-CPA calculation, which assumes a spherically symmetric potential in each atomic sphere. First-principles calculations performed using a full potential method showed half-metallicity for stoichiometric CMS [31,32].

Note that the $\alpha$ dependence of $P_{th}(spd)$ for the Mn-deficient region differed markedly from that of $P_{th}(sp)$. $P_{th}(spd)$ decreased pronouncedly with $\alpha$ for $\alpha < 1.0$ and became negative for a strongly Mn-deficient composition ($\alpha = 0.69$). If the tunneling current in CMS MTJs was dominantly determined by $P_{th}(spd)$, the TMR ratio for $\alpha < 1.0$ would significantly decrease with $\alpha$, become almost zero one time for $P_{th}(spd) \approx 0$, and then increase again to a certain positive value. However, the $\alpha$ dependence of the TMR ratio showed a monotonic decrease with $\alpha$ for $\alpha < 1.0$, in obvious disagreement with the $\alpha$ dependence of $P_{th}(spd)$. On the other hand, $P_{th}(sp)$ for $\alpha < 1.0$ was positive and increased with $\alpha$ from $P_{th}(sp) = 0.850$ for $\alpha = 0.69$ to 0.945 for $\alpha = 0.93$. Thus, the $\alpha$ dependence of $P_{th}(sp)$, in contrast to that of $P_{th}(spd)$, was found to qualitatively explain the $\alpha$ dependence of the TMR ratio except for $\alpha > \alpha_c$. This suggests that tunneling in CMS/MgO-based MTJs is mainly due to itinerant $s$- and $p$-like electrons and the contribution to tunneling from localized $d$-like electrons is negligible. This picture is essentially the same as the one
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FIG. 10. (Color online) LDOS for (a) Co at the regular site (CoCo) and (b) Co at the nominal Mn site (CoMn) for Co2MnSi1.0 for various α as a function of energy E relative to the Fermi level (E_F). Inset shows a magnification of the LDOS of the nominal site Co near E_F. Majority spin states are shown as positive LDOS and minority spin states as negative.

Next, we describe the correlation of the degree of T dependence of the TMR ratio with the Mn composition α in Co2MnSi_β electrodes. If we use parameter γ = TMR(4.2 K)/TMR(290 K) to represent the degree of T dependence of the TMR ratio, the γ values for the CMS MTJs were higher than those for CoFeB/MgO/CoFeB MTJs. For example, the γ value for the CoFe-buffered CMS MTJ with α = 1.37 in Co2MnSi_{0.96} electrodes, which showed TMR ratios of 1910% at 4.2 K and 354% at 290 K [10], was 5.4, which is much larger than the 2.0 reported for a CoFeB/MgO/CoFeB MTJ, which showed TMR ratios of 1144% at 5 K and 576% at 300 K [47]. It is, however, beyond the scope of this paper to speculate on the origin of the strong T dependence of the TMR ratio of CMS MTJs, and it will be discussed in a subsequent report [48].

Here, we focus on the Mn composition dependence of γ for CMS MTJs. As a typical result, Fig. 11(a) plots γ for CoFe-buffered CMS MTJs having Co2MnSi_{0.96} electrodes as a function of α. The γ value increased with α up to α = 1.37, from γ = 3.6 for α = 0.72 (TMR ratio at 4.2 K = 640%) to γ = 5.4 for α = 1.37 (TMR ratio at 4.2 K = 1910%). It subsequently decreased with a further increase in α beyond 1.37 accompanying the decrease in the TMR ratio at 4.2 K. We call the first region, from α = 0.72 to 1.37, α-region I and the second one, α > 1.37 (particularly including α = 1.47 and 1.57), α-region II.

As shown previously for a CMS MTJ with Mn-deficient CMS electrodes [49], and as will be separately shown for CMS MTJs with various Mn compositions [50], R_p (= 1/G_p) of these MTJs was mostly independent of T from
Given that the $G_{AP}(T)$ values of the CoFe-buffered CMS MTJs were well fitted by Eq. (3) [50], we will discuss the behavior of $γ_{AP}$ on the basis of the Zhang et al. model. Approximating $G_{AP}(4.2 \text{ K})$ in the expression $γ_{AP} = G_{AP}(290 \text{ K})/G_{AP}(4.2 \text{ K})$ by $G_{AP}(T = 0)$ and $TMR(T = 0)$ in Eq. (5) by $TMR(4.2 \text{ K})$, we obtain an approximate expression for $γ_{AP}$ from Eq. (3):

$$\frac{G_{AP}(T)}{G_{AP}(T = 0)} = \left\{1 + \frac{2S}{E_m}k_B T \cdot f(T)\right\}, \quad (3)$$

$$f(T) = -\ln(1 - \exp(-E_s/k_BT)) \quad (f(T) > 0), \quad (4)$$

where $\frac{Q = 1/\left(|T^d|^2/|T^f|^2 + 2S^2\right)}{2D_sD_m/(D_s^2 + D_m^2) = (1 - P^2)/(1 + P^2)}$, $P$ is the tunneling spin polarization at $E_F$, and $D_s$ and $D_m$ are the majority-spin and minority-spin DOS at $E_F$, respectively. Other parameters, including $T^d, T^f, S, E_s$, and $E_m$ are given elsewhere [51]. The quantity $1/ξ$ is related to $G_{P}(T = 0)$ and $G_{AP}(T = 0)$ [51]:

$$\frac{1}{ξ} = \frac{G_{P}(T = 0)}{G_{AP}(T = 0)} = TMR(T = 0) + 1. \quad (5)$$

Given that the $G_{AP}(T)$ values of the CoFe-buffered CMS MTJs having $Co_{2}MnSi_{0.96}$ electrodes as a function of $η = TMR(4.2 \text{ K}) + 1$, including $α$-regions I and II. It clearly shows that $γ_{AP}$ increased almost linearly with $η$, particularly for $α$-region I, which means that the product of the coefficients $Q, 2S/E_m$ and $f(290 \text{ K})$, where the latter includes a factor $E_s$, was almost independent of $α$ for $α$-region I for the CoFe-buffered CMS MTJs and that $η \approx 1/ξ = (1 + P^2)/(1 - P^2)$ was a dominant factor determining $γ_{AP}$. Furthermore, the $γ_{AP}$ values for both $α$-regions showed a similar linear dependence on $η$ even though those of $α$-region II were slightly lower than the linear approximation of those of $α$-region I. The linear dependence of $γ_{AP}$ on $η$, particularly for $α$-region I, suggests that the observed increase in the degree of $T$ dependence of the TMR ratio represented by $γ$ with $α$ is an intrinsic property explained by the model of Zhang et al. Thus, we experimentally clarified that the degree of $T$ dependence of the TMR ratio of CMS MTJs from 4.2 K to RT increased with an increase in the tunneling spin polarization or equivalently with that of the TMR ratio at 4.2 K. From a more qualitative point of view, the increase in $γ_{AP}$, with an increase in the tunneling spin polarization, is reasonable given that $G_{AP}$ at 4.2 K decreases with a
The decrease in $D_m$, while the increase in $G_{AP}$ at finite temperatures from $G_{AP}(4.2 \, K)$, $\delta G_{AP}$, is proportional to $D_{m}^2 + D_{p}^2 \approx D_{m}^2$ (for high spin polarizations), according to the Zhang et al. model [51]. A similar dependence of the concentration in thin films was further reduced by an antisite concentration of thin films prepared by sputtering et al. [50].

The linear increase in $\gamma_{AP}$ with $\eta \approx 1/\xi = (1 + P^2)/(1 - P^2)$ is also consistent with our understanding that the dominant factor leading to the increase in the TMR ratio with increasing $\eta$ up to the respective Mn-rich $\alpha$ values for MgO-buffered and CoFe-buffered CMS MTJs is the increase in the tunneling spin polarization arising from the decrease in CoMn antisites. This means that although the coherent tunneling contribution for both MgO-buffered and CoFe-buffered CMS MTJs is evident and the degree of the contribution is significantly larger for the latter [10], the degree is mostly independent of $\alpha$ in $Co_2MnSi_\beta$ electrodes of the MgO-buffered CMS MTJs and the CoFe-buffered MTJs.

Finally, note that the TMR ratios at both 4.2 and 290 K still increased in the Mn-rich region defined by $\alpha > 2 - \beta$ of the $Co_2MnSi_\beta$ electrodes up to $\alpha = \alpha_c$ and that $\gamma_{AP}$ for CMS MTJs having $Co_2MnSi_{0.96}$ electrodes also increased almost linearly with $\eta$ in the Mn-rich region, $\alpha > 2 - \beta$, particularly for $\alpha = 1.17$ and 1.37. These results indicate that there is a slight difference between the CoMn antisite concentration of thin films prepared by sputtering and the nominal concentration given by the SSFU model and that the concentration in thin films was further reduced by an increase in $\alpha$ even in the Mn-rich region up to $\alpha = \alpha_c$.

IV. CONCLUSION

The effect of nonstoichiometry on the half-metallic character of $Co_2MnSi$ (CMS) was experimentally investigated through the Mn composition ($\alpha$) dependence of the saturation magnetization per formula unit ($\mu_s$) of $Co_2MnSi_\beta$ thin films and the TMR ratio of CMS/MgO/CMS MTJs (CMS MTJs) having $Co_2MnSi_\beta$ electrodes with various values of $\alpha$ and $\beta = 1.0, 0.96$, or 0.88. Experimental $\mu_s$ and TMR ratios were compared with KKR-CPA calculations based on the SSFU composition model, which assumes the formation of only antisite defects, not vacancies, to accommodate nonstoichiometry. The $\alpha$ dependence of $\mu_s$ was in good agreement with the KKR-CPA results. In particular, the decrease in $\mu_s$ for Mn-deficient films was explained by the smaller spin magnetic moment of Co at the nominal Mn site ($Co_{Mn}$) in comparison with Mn at the nominal Mn site. The $\alpha$ dependence of the TMR ratio of CMS MTJs having $Co_2MnSi_\beta$ electrodes was qualitatively explained by the theoretical spin polarizations obtained from the $s$- and $p$-orbital components of the DOS at $E_F$ in the KKR-CPA results. It was shown that minority-spin in-gap states around $E_F$ were induced for not only antisite CoMn atoms but also Co atoms at the regular sites ($Co_{Co}$) in Mn-deficient CMS films. The decrease in the TMR ratio observed for CMS MTJs having Mn-deficient electrodes was ascribed to small $s$- and $p$-orbital components of the local density of minority-spin in-gap states at $E_F$ that appeared for both the antisite CoMn and regular-site CoCo. In conclusion, these findings demonstrate the presence of harmful CoMn antisites in Mn-deficient CMS and the effectiveness of preparing CMS thin films with a Mn-rich composition to retain the half-metallic character of CMS.

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