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## Research articles

Structural and antiferromagnetic characterization of noncollinear  $DO_{19}$   $Mn_3Ge$  polycrystalline filmTakahiro Ogasawara<sup>a,b</sup>, Jun-young Kim<sup>c,\*</sup>, Yasuo Ando<sup>a,d,e,\*</sup>, Atsufumi Hirohata<sup>b</sup><sup>a</sup> Department of Applied Physics, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan<sup>b</sup> Department of Electronic Engineering, University of York, Heslington YO10 5DD, United Kingdom<sup>c</sup> Department of Physics, University of York, Heslington YO10 5DD, United Kingdom<sup>d</sup> Center for Science and Innovation in Spintronics (Core Research Cluster) Organization for Advanced Studies, Japan<sup>e</sup> Center for Spintronics Research Network, Tohoku University, Sendai 980-8579, Japan

## A B S T R A C T

Distorted Heusler compound of  $DO_{19}$   $Mn_3Ge$  polycrystalline films were studied in terms of their crystalline structures and antiferromagnetic behavior by varying annealing temperature and Mn-Ge composition. Although low temperature growth for 30 nm  $Mn_3Ge$  showed no diffraction peaks in X-ray diffraction patterns, high temperature growth over 773 K with Mn-rich composition is found to promote the (0001) orientation of  $DO_{19}$   $Mn_3Ge$  which resulted in the emergence of an exchange bias effect in  $Co_{0.6}Fe_{0.4}$  ferromagnetic layer at 120 K. The exchange bias field of 12 Oe in  $Mn_{3.16}Ge$  film grown at 773 K were improved to 61 Oe by enriching Mn composition to  $Mn_{3.97}Ge$ . The average blocking temperature was measured to be at 150 K which is not as high as its reported Néel temperature of 390 K in the bulk state, however, further improvements are expected by doping additional transition elements.

Exchange bias effect induced at the interface between antiferromagnetic and ferromagnetic layers has played an important role as a building block of the spintronic devices to pin the magnetization of ferromagnetic layer. After the first discovery of the exchange bias effect from CoO [1], many antiferromagnetic materials have been found such as IrMn which has been most commonly used as an antiferromagnetic material for the device applications such as a spin-valve structure [2]. However, new antiferromagnetic materials should be developed for the replacement of IrMn due to the depletion of Ir being identified as a critical raw metal [3]. From this view point, antiferromagnetic binary Heusler alloys such as the  $DO_{19}$   $Mn_3Z$  ( $Z = Ga$  [4–7],  $Ge$  [8] and  $Sn$  [9]) have been studied on their structural and magnetic properties. As an  $Mn_3Ge$  binary alloy is taken as an example, it allows two stable crystalline structures of the tetragonal  $DO_{22}$  and hexagonal  $DO_{19}$  structures which is distorted from the basic full-Heusler  $L2_1$  structures along the (0 0 1) and (1 1 1) direction, respectively [10]. As a result of different crystalline structures, the  $DO_{22}$  or  $DO_{19}$  structure exhibits different magnetic anisotropy such as ferrimagnet with perpendicular magnetic anisotropy and low saturation magnetization [11,12] or antiferromagnet with noncollinear magnetic moments in which exchange bias effect [8] or giant anomalous hall effect [13,14] are appeared. In the bulk state, the  $DO_{19}$  phases are formed by high temperature annealing according to the Mn-Ge phase diagram [15,16]. Fig. 1 shows the crystalline structure of  $DO_{19}$   $Mn_3Ge$  with 6 Mn and 2 Ge atoms in a unit cell.

Lattice constants are calculated to be  $a = 5.28 \text{ \AA}$  and  $c = 4.22 \text{ \AA}$  [10], and experimentally measured to be  $a = 5.34 \text{ \AA}$  and  $c = 4.32 \text{ \AA}$  [8], respectively. In the  $ab$  plane, Kagome lattice, *i.e.*, triangular configuration of Mn atoms, are formed [17]. This sublattice results in geometrical frustration of magnetic moments, which are stabilized by the Dzyaloshinskii-Moriya interaction [17–19]. Consequently, each Mn magnetic moment is aligned triangular  $120^\circ$  direction along the  $ab$  plane and shows antiferromagnetic behavior with the Néel temperature,  $T_N$  of 390 K [20] at which antiferromagnetic order disappears. Owing to this noncollinear configuration of magnetic moment, weak ferromagnetism with the Currie temperature  $T_c$ , at 365 K [21] and a magnetic moment of  $0.005\text{--}0.008 \mu_B$  per Mn atom, where  $\mu_B$  denotes Bohr magneton, are demonstrated by previous experiments [13,14]. Although  $DO_{19}$   $Mn_3Ge$  has been studied in the bulk state, for the further understandings and spintronic applications, its structural and magnetic characterizations in the thin film form are necessary. Therefore, we focus on the exchange bias effect induced from antiferromagnetic  $Mn_3Ge$  thin films. Successfully we demonstrate to grow  $DO_{19}$   $Mn_{3.16}Ge$  films with substrate heating which exhibits the exchange bias up to 13 Oe at 120 K. In addition, the exchange bias is found to be improved by doping additional Mn atoms up to 64 Oe because of the improved (0001) orientation of  $Mn_3Ge$ .

All the polycrystalline samples were fabricated using a Plasma Quest high target utilization sputtering (HiTUS) system with a base

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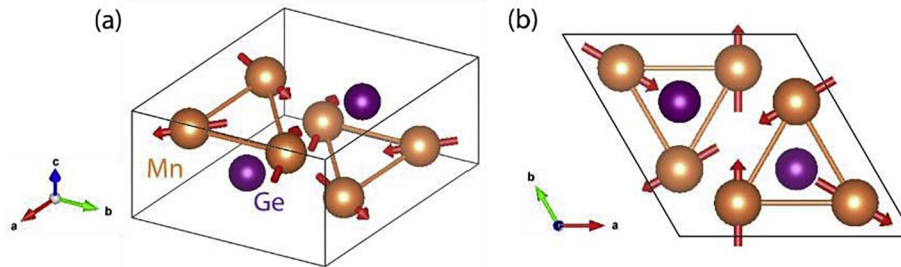
E-mail addresses: [takahiro.ogasawara.p3@dc.tohoku.ac.jp](mailto:takahiro.ogasawara.p3@dc.tohoku.ac.jp) (T. Ogasawara), [junyoung.kim@york.ac.uk](mailto:junyoung.kim@york.ac.uk) (J.-y. Kim), [ando@mlab.apph.tohoku.ac.jp](mailto:ando@mlab.apph.tohoku.ac.jp) (Y. Ando), [atsufumi.hirohata@york.ac.uk](mailto:atsufumi.hirohata@york.ac.uk) (A. Hirohata).<https://doi.org/10.1016/j.jmmm.2018.10.035>

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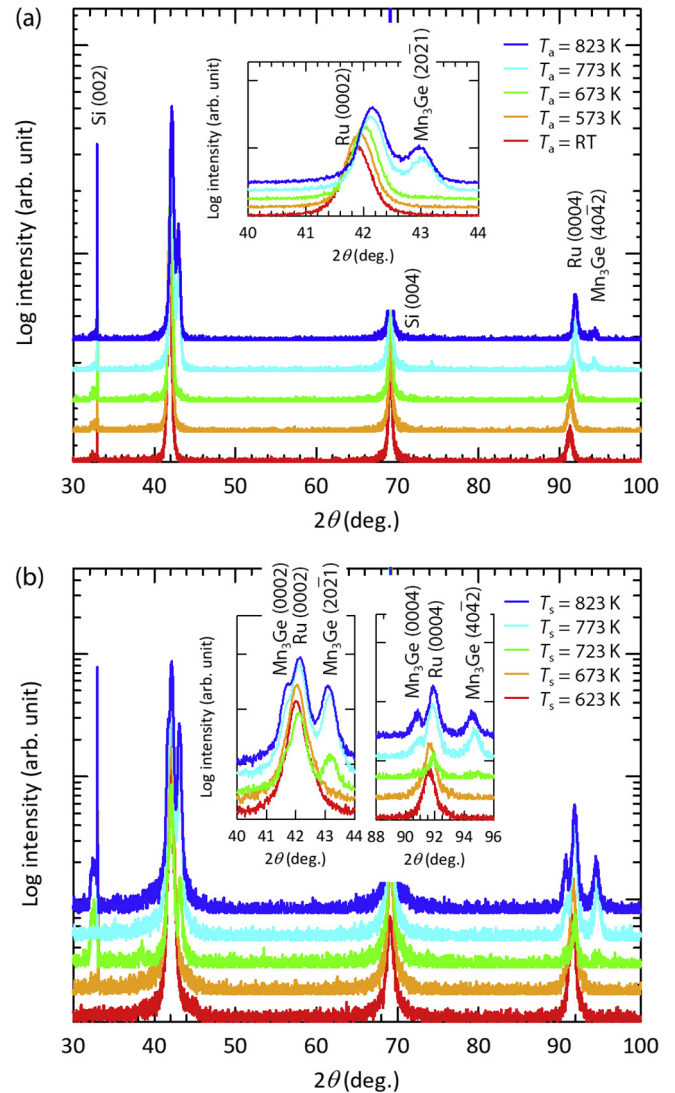
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**Fig. 1.** Illustration of the  $D0_{19}$   $Mn_3Ge$  structure. Red arrows describe expected Mn moment directions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

pressure less than  $5 \times 10^{-5}$  Pa. The stacking structures of Ta (5)/Ru (35)/ $Mn_3Ge$  (30)/ $Co_{0.6}Fe_{0.4}$  (0 or 3.3)/Ta (5) (thickness in nm) were grown onto Si (0 0 1) substrate in 1.86 mbar Ar atmosphere with a bias voltage of  $-900$  V to maximize grain volume [22] (hereinafter refer to  $Co_{0.6}Fe_{0.4}$  as CoFe). The sputtering rate of  $Mn_3Ge$  is ca.  $0.8 \text{ \AA/s}$ . For the film growth, different heating treatments were carried out such as substrate heating for the growth of  $Mn_3Ge$  at  $T_s$  or *ex-situ* post-annealing at  $T_a$  in a range of 573–823 K by using heater lamp located above a substrate in the chamber. The Mn-Ge compositions were also controlled from  $Mn_{2.67}Ge$  to  $Mn_{3.97}Ge$ , respectively by adding Mn pegs into  $Mn_3Ge$  target. The compositions were measured using energy dispersive X-ray spectroscopy (EDX). The crystalline structures and magnetic properties were characterized by X-ray diffraction (XRD; Rigaku, Smart Lab) at room temperature (RT) and vibrating sample magnetometer (VSM; ADE, Model 10) between 100 and 300 K.

Fig. 2(a) shows XRD spectra of  $2\theta$  scan for the films with the stacking of Ta (5)/Ru (35)/ $Mn_{3.80}Ge$  (30)/CoFe (3.3)/Ta (5) (thickness in nm) post-annealed at various  $T_a$ . For the films post-annealed at the temperature range between RT and 673 K, there is no peak associated with  $Mn_3Ge$  appeared in the XRD spectra. It should be noted that the sharp peaks shown at  $2\theta = ca. 33^\circ$  are originated from misalignment of a Si substrate. However, as increasing  $T_a$  above 773 K, the films exhibit  $D0_{19}$   $Mn_3Ge$  (2021) and (4042) peaks. This behavior may be caused by the formation of the  $D0_{19}$  phase of  $Mn_3Ge$  which is the higher temperature phase than the  $D0_{22}$  phase in the bulk state. Also, the (2021) peak intensity is the highest in accordance with calculated and experimental results as previously reported [8]. On the other hand, as shown in Fig. 2(b), a substrate-heated sample during  $Mn_3Ge$  deposition shows a different crystalline orientation. The films with the stacking of Ta (5)/Ru (35)/ $Mn_{3.16}Ge$  (30)/CoFe (3.3)/Ta (5) (thickness in nm) grown at  $T_s$  below 573 K show no peak similarly to Fig. 2(a). However, the peaks from  $D0_{19}$   $Mn_3Ge$  (0002) and (0004) planes as well as (2021) and (4042) planes are visible with  $T_s$  over 723 K. Although they are overlapped with the Ru (0002) peak, the presence of diffractions at a higher angle confirms the peak identification. As a result, it suggests the films with  $T_s$  over 723 K are crystallized with the mixture of the (0001) and (2021) orientations normal to the film plane. The (0001) orientation of  $D0_{19}$   $Mn_3Z$  is favorable to induce the exchange bias as previously reported [5,7,9], indicating that the substrate-heated samples are advantageous than the post-annealed samples for this purpose. The lattice constants of the  $Mn_{3.16}Ge$  with  $T_s = 773$  and 823 K are estimated to be  $a = 5.53 \text{ \AA}$  and  $c = 4.32 \text{ \AA}$ , and  $a = 5.54 \text{ \AA}$  and  $c = 4.33 \text{ \AA}$ , respectively, from clearly distinctive (0004) and (2021) peaks. This minor distortion in the  $ab$  plane is associated with the lattice mismatch of 1.3% with the Ru buffer layer. The magnetization curve of 30-nm-thick  $Mn_{3.16}Ge$  at  $T_s = 773$  K measured at RT is shown in Fig. 3. The weak ferromagnetic behavior is shown similarly to previous bulk studies [13,14]. The hysteresis in this figure indicates the spin chirality switching of triangular Mn atoms [23]. The small saturation magnetization  $M_s$  is estimated to be  $34 \text{ emu/cm}^3$  which value is approximately the same with previous work of  $Mn_3Sn$  film [9]. However, the magnetic



**Fig. 2.** XRD spectra of the  $2\theta$  scans for the 30-nm-thick (a)  $Mn_{3.80}Ge$  films with *ex-situ* post-annealing at  $T_a$ , and (b)  $Mn_{3.16}Ge$  films with substrate heating at  $T_s$ .

moment per Mn in this film is estimated to be  $0.06 \mu_B$ , which is almost 10 times higher than that in the  $Mn_3Ge$  bulk state with  $0.005$ – $0.008 \mu_B$  [13,14]. In general, such a small net magnetic moment of  $Mn_3Ge$  is associated with the formation of the Kagome lattice with 3 Mn atoms which leads canting of Mn moments [13,14]. However, once Mn atoms occupy Ge sites, the triangular moment configuration cannot be formed which results in a larger net moment. Therefore, this increase of magnetic moment is attributed to excess Mn atoms which occupy Ge sites randomly. Another possible reason is random grain orientations owing

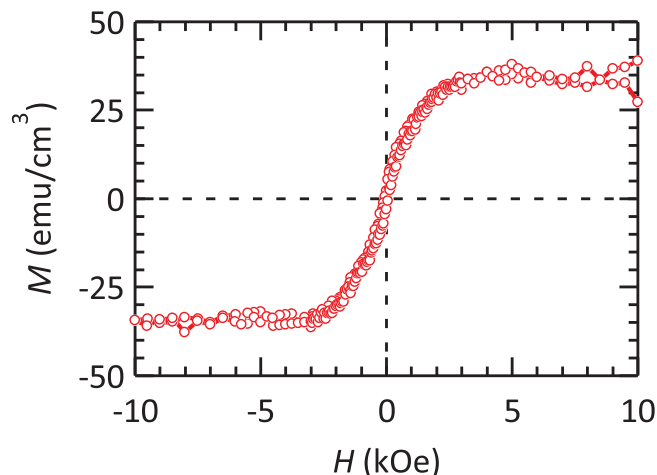


Fig. 3. In-plane magnetization curve of the 30-nm-thick  $\text{Mn}_{3.16}\text{Ge}$  film grown at  $T_s = 773$  K measured at RT.

to the polycrystalline nature of our films which causes less interactions of triangular Mn moments at the grain boundaries.

The exchange bias,  $H_{\text{ex}}$ , originated at the interface between  $\text{Mn}_{3.16}\text{Ge}/\text{CoFe}$  was measured from the shift of hysteresis loop.  $H_{\text{ex}}$  was induced by field cooling down to 100 or 120 K after the samples were annealed at 500 K for 30 mins with an external in-plane magnetic field of  $-6$  kOe. Fig. 4 displays magnetization curves of  $\text{Mn}_{3.16}\text{Ge}/\text{CoFe}$  bilayers grown at  $T_s = 773$  K measured at 100 and 120 K. Both curves show positive horizontal shift which indicates the existence of exchange coupling at the interfaces and  $H_{\text{ex}}$  is estimated to be at 28 and 12 Oe at 100 and 120 K, respectively. The observed exchange bias in this film is lower than the other  $\text{Mn}_3\text{Z}$  films ( $Z = \text{Ga}$  [5,7] and  $\text{Sn}$  [9]) due to the mixture of the (0001) and (2021) crystalline orientations. In addition, Fig. 5 shows the results of X-ray reflectivity (XRR) of the  $\text{Mn}_{3.16}\text{Ge}/\text{CoFe}$  (3.3) film. Sample information such as thickness and density is used for fitting of the measured reflectivity which results in Ta ( $3.4 \pm 0.3$ )/Ru ( $35.7 \pm 0.6$ )/ $\text{Mn}_{3.16}\text{Ge}$  ( $30.7 \pm 1.9$ )/CoFe ( $3.73 \pm 1.1$ )/Ta ( $4.0 \pm 0.2$ ) (thickness in nm). This large roughness in the  $\text{Mn}_{3.16}\text{Ge}$  layer is also one of the possible reasons to decrease the exchange bias.

Next, we studied the Mn-Ge composition effect on the film growth and exchange bias effect. Fig. 6 shows XRD diffraction patterns of Ta (5)/Ru (35)/ $\text{Mn}_x\text{Ge}$  (30)/CoFe (3.3)/Ta (5) (thickness in nm) with  $T_s = 773$  K. In this graph, a large Mn composition increases the

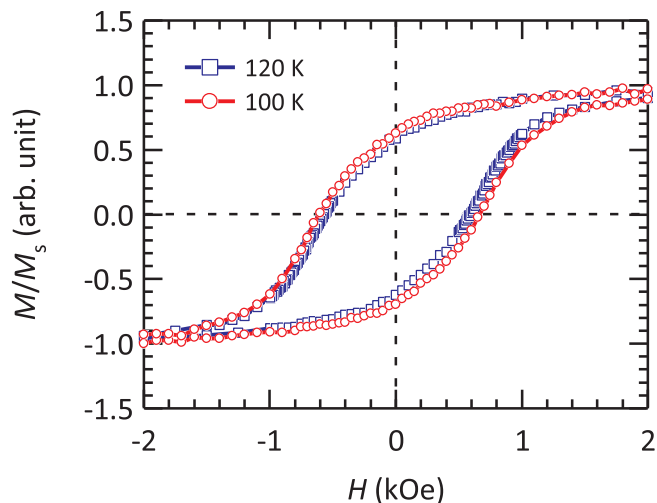


Fig. 4. In-plane magnetization curves of the  $\text{Mn}_{3.16}\text{Ge}$  (30)/CoFe (3.3) film measured at 100 K and 120 K after field cooling.

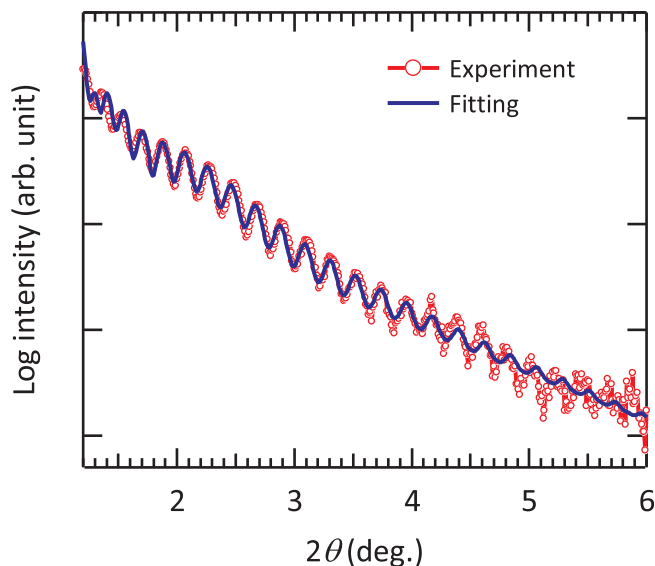


Fig. 5. X-ray reflectivity of the  $\text{Mn}_{3.16}\text{Ge}$  (30)/CoFe (3.3) film grown at  $T_s = 773$  K.

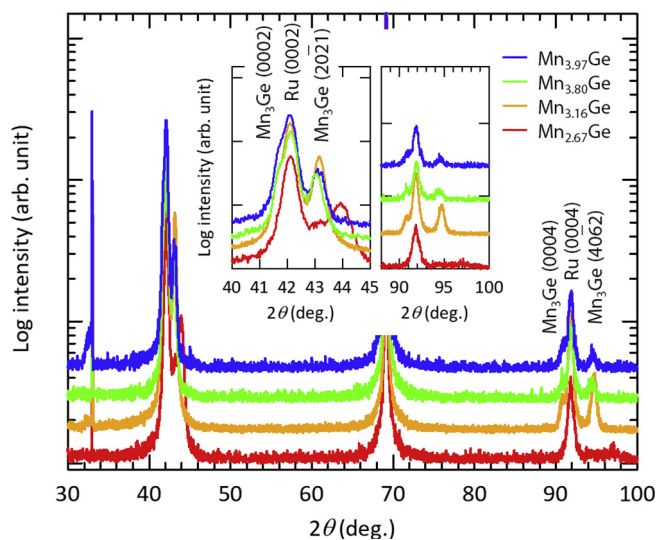


Fig. 6. XRD spectra of the  $2\theta$  scans for the 30-nm-thick  $\text{Mn}_x\text{Ge}$  films grown at  $T_s = 773$  K.

intensity of the (0002) peak while that of the (2021) peak is suppressed. The lattice constant of  $\text{Mn}_{3.97}\text{Ge}$  is determined to be  $a = 5.53$  Å and  $c = 4.32$  Å, respectively, which is the same with the  $\text{Mn}_{3.16}\text{Ge}$  film as described above. However, the atomic radius of Mn, 1.27 Å is larger than that of Ge, 1.22 Å, and hence, the large Mn compositions increase the in-plane lattice constant of  $\text{Mn}_3\text{Ge}$ . Therefore,  $\text{Mn}_{3.97}\text{Ge}$  may experience less frustration than  $\text{Mn}_{3.16}\text{Ge}$  during the growth onto the (0001) plane of the Ru buffer layer, resulting in the promotion of the  $D0_{19}$  (0001) orientation. In order to confirm the antiferromagnetic behavior, the exchange bias were measured in these structures. Fig. 7(a) displays magnetization curves of  $\text{Mn}_x\text{Ge}$  (30)/CoFe (3.3) layered film measured at 120 K and, while Fig. 7(b) shows  $H_{\text{ex}}$  dependent on the Mn composition,  $x$ . Horizontal shift of magnetization curves are shown for the film of  $\text{Mn}_x\text{Ge}$  with  $x$  above 3.16.  $\text{Mn}_{2.67}\text{Ge}$  does not have the (0001) orientation as shown in Fig. 6. Hence, the exchange bias are almost zero. With increasing Mn composition, the exchange bias is found to be increased gradually up to 61 Oe in the film of  $\text{Mn}_{3.97}\text{Ge}$ , while the (0001) orientation of  $D0_{19}$   $\text{Mn}_3\text{Ge}$  becomes dominant as compared with the (2021) orientation. It should be noted that the

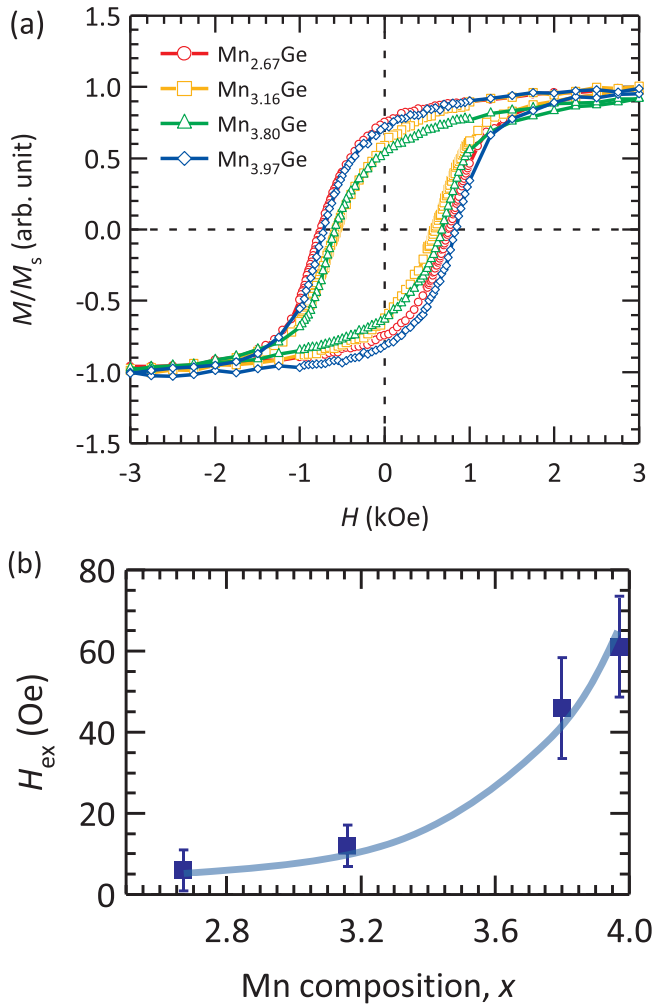


Fig. 7. (a) In-plane magnetization curves of  $\text{Mn}_x\text{Ge}$  (30)/CoFe (3.3) films grown at  $T_s = 773$  K measured at 120 K. (b)  $H_{\text{ex}}$  dependence on Mn composition,  $x$ . The line is guide to eyes.

vertical magnetization shift of  $27 \text{ emu/cm}^3$  from the saturated magnetization,  $M_s$ , of  $1180 \text{ emu/cm}^3$  is observed in a  $\text{Mn}_{3.97}\text{Ge}/\text{CoFe}$  bilayer, which is more than twice larger than that for  $\text{Mn}_{3.16}\text{Ge}$ ,  $12 \text{ emu/cm}^3$ . This vertical shift is associated with increased interfacial uncompensated spins [24], which can also contribute to the enhancement of the exchange bias.

In the thin films with antiferromagnet/ferromagnet bilayer, the temperature at which the exchange bias field becomes zero, *i.e.*, blocking temperature,  $T_B$ , is basically lower than  $T_N$  because of a finite size effect [25,26]. Accordingly the experimental determination of  $T_B$  is one of the important studies for antiferromagnetic films. Especially for the polycrystalline films, grain size of an antiferromagnet is distributed which results in that each grain with different sizes shows different  $T_B$ . According to the earlier study on the correlation between the exchange bias and the grain volume [27], the grain volume of a polycrystalline antiferromagnetic film predominantly controls the exchange bias properties. A polycrystalline film is formed by a large number of fine crystals, hence, the grain volume are varied following lognormal distribution. There are two critical volumes for the magnitude of exchange bias in such grain distribution. The first one is critical volume,  $V_c$ , below which the exchange bias cannot be set in grains below because they are thermally unstable. The second one is  $V_{\text{set}}$ , above which anisotropy energy is too high to induce the exchange bias. Therefore, the exchange bias can be set only in medium-sized grains between  $V_c$  and  $V_{\text{set}}$  [27,28]. Therefore, we carried out our  $T_B$  measurement by following

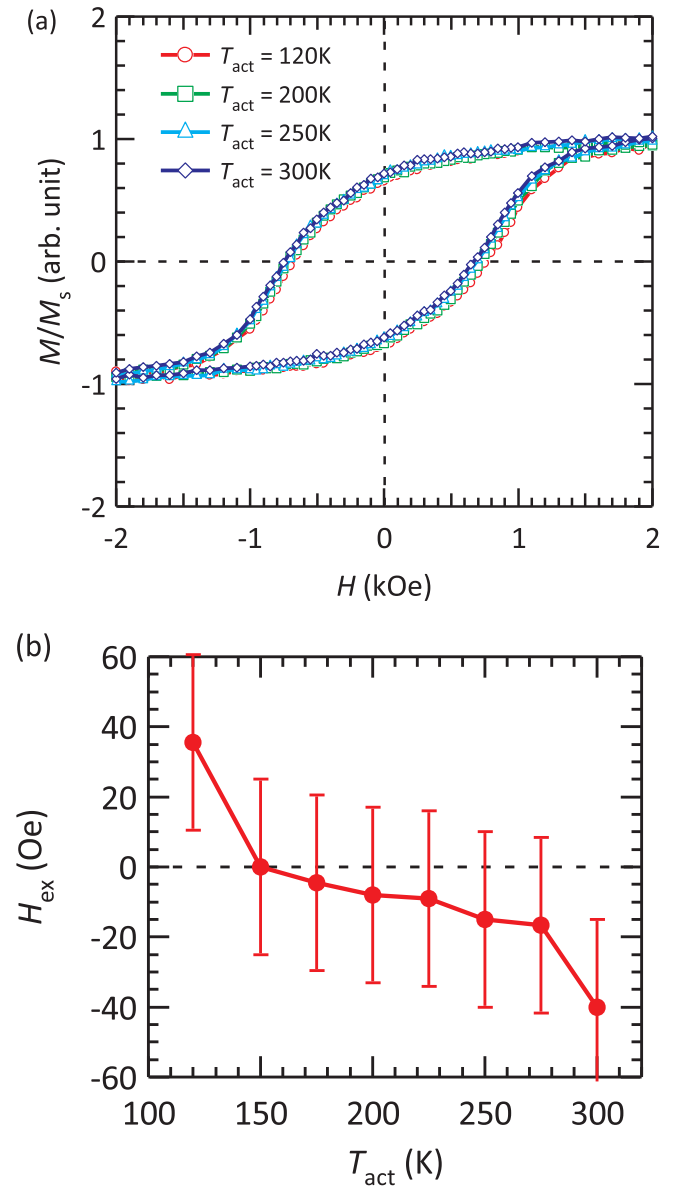


Fig. 8. (a) In-plane magnetization curves of  $\text{Mn}_{3.97}\text{Ge}$  (30)/CoFe (3.3) with different activation temperature,  $T_{\text{act}}$  from 120 to 300 K measured at 120 K. (b)  $H_{\text{ex}}$  dependence as a function of  $T_{\text{act}}$ .

the York Protocol [28] which allowed us to determine average blocking temperature ( $T_B$ ) among all of the grains. In this study, the samples were set at  $T_{\text{set}} = 500$  K for 90 mins under an external magnetic field of  $-6$  kOe to induce the exchange bias. Afterwards, the samples were heated at different activation temperature,  $T_{\text{act}}$ , for 30 mins with a reversed magnetic field of 6 kOe.  $T_{\text{act}}$  was elevated from 120 to 300 K at each thermal activation process. This process reverses the antiferromagnetic ordering of some distributed grains depending on  $T_{\text{act}}$ . As  $T_{\text{act}}$  becomes higher, larger antiferromagnetic grains are reversed owing to the thermal activation with a reversed magnetic field which are caused by elevated thermal energy exceeding energy barrier of  $\Delta E$  standing for the stability of the antiferromagnetic grains [27,28]. Just after completing the thermal activation at each  $T_{\text{act}}$ , the samples were cooled back to 120 K, where the corresponding magnetization curve was measured to detect the modification of the exchange bias due to thermal activation process. Fig. 8(a) shows magnetization curves of a  $\text{Mn}_{3.97}\text{Ge}$  (30)/CoFe (3.3) (thickness in nm) bilayer measured at 120 K after elevating activation temperature by following the procedure of the York Protocol. At  $T_{\text{act}} = 120$  K, positive shift of the magnetization

is shown in the film because of the field cooling with a negative magnetic field. The exchange bias is shifted towards the negative field direction with increasing  $T_{\text{act}}$  since elevated  $T_{\text{act}}$  can reverse the antiferromagnetic ordering of some grains, which is *i.e.* thermal activation. As a result,  $H_{\text{ex}}$  dependent on  $T_{\text{act}}$  shows a gradual change as shown in Fig. 8(b). When  $T_{\text{act}}$  is around 150 K, a half of the antiferromagnetic ordering of set grains are reversed, which brings  $T_{\text{act}}$  to zero. This temperature is called the average blocking temperature of ( $T_{\text{B}}$ ). When  $T_{\text{act}}$  is 300 K, as the absolute value of the exchange bias becomes almost the same as the initial measurement of 120 K, it suggests that almost all set grains are reversed. This experimental ( $T_{\text{B}}$ ) of 150 K is much lower than  $T_{\text{N}}$  of bulk  $\text{Mn}_3\text{Ge}$  as high as 390 K [20]. This seems to be caused by excess Mn atoms occupying Ge site randomly. Moreover, from structural viewpoints, a polycrystalline film shows no in-plane texture, so that the (0001) oriented grains are grown without in-plane ordering. The  $\text{Mn}_3\text{Ge}$  film also consists of both the (0001) and (2021) oriented antiferromagnetic grains. These two facts implying that the interactions between the Kagome lattices become almost random at the boundary of the grains results in low ( $T_{\text{B}}$ ). Even so, it is expected to be improved by doping transition elements into  $\text{Mn}_3\text{Ge}$  which enables to engineer the lattice constant with maintaining the crystalline structure [29,30], achieving long-distance in-plane magnetic ordering. In addition, recent study reveals that high pressure induces spin canting along c-axis of the  $\text{DO}_{19}$   $\text{Mn}_3\text{Ge}$ , which brings the transformation of the spin configuration to noncoplanar [31]. In our case, a lattice mismatch between Ru and  $\text{Mn}_3\text{Ge}$  possibly induces the pressure to the  $\text{Mn}_3\text{Ge}$  layer. However, our films are polycrystalline with an average grain size of 17.7 nm calculated from distinctive (2021) peak, suggesting that the magnitude of the induced pressure from the mismatch may be small. Even so, such pressure may also be a possible reason to explain low exchange bias and ( $T_{\text{B}}$ ).

In summary, we studied polycrystalline  $\text{DO}_{19}$   $\text{Mn}_3\text{Ge}$  films grown on a Ru buffer layer. It was found that post-annealing and substrate heating induce (2021) and (0001) orientations, respectively. These structural characterizations are greatly useful for studying an antiferromagnetic films for device applications such as the exchange bias effect and the giant anomalous Hall effect. Mn-rich  $\text{Mn}_3\text{Ge}$  films show the improvement of the (0001) orientation and result in large  $H_{\text{ex}}$  up to 61 Oe at 120 K. Although the measured ( $T_{\text{B}}$ ) of 150 K is lower than room temperature, however, further improvements can be expected by doping an additional transition metal to control the lattice constant.

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