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Magnetic and electronic properties of $D0_{22}$-Mn_3Ge (001) films

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Oriented thin films of Mn_3Ge with the tetragonal $D0_{22}$ structure, grown on strontium titanate substrates, exhibit a low magnetization $M_s = 73\,\text{kA m}^{-1}$ combined with high uniaxial anisotropy $K_u = 0.91\,\text{MJ m}^{-3}$ at 300 K, making them potentially useful for thermally stable sub-10 nm spin torque memory elements. The highly ordered epitaxial Mn_3Ge (001) films show 46% diffusive spin polarization at the Fermi level, measured by point contact Andreev reflection. Density functional calculations show that the compounds are ferrimagnetic, with anisotropic spin polarization at the Fermi level. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4754123]

Since the advent of perpendicular magnetic recording and spin torque switching, there is growing interest in magnetic thin film materials with positive uniaxial anisotropy K_u, which have a magnetic easy axis normal to the film surface. Such materials are needed to realize energy-efficient, scalable spin torque memories,[1,2] high-density magnetic recording media,[3] spin logic with integrated memory,[4] and efficient circularly-polarized light emission from spin light-emitting diodes (spin-LEDs).[5,6]

The advantage in the case of spin torque memory arises from the relationship between the critical switching current density j_c and magnetic anisotropy energy $(K_u\text{-}1/2\mu_0 M_s^2)V$ that is directly proportional to the thermal stability.[1] There is no need to overcome an extra shape anisotropy energy barrier during magnetization reversal, and large values of K_u allow for high density scaling. Such devices utilize the transfer of angular momentum carried by spin-polarized conduction electrons to switch the magnetization of the free layer in a nanoscale spin valve (SV) or magnetic tunnel junction (MTJ). The high spin polarization of cubic $L2_1$ Heusler alloys such as Co_2MnSi, Co_2MnGe, and $Co_2Fe(Ge_{0.5}Ga_{0.5})$ has been used to improve spin transfer toque efficiency, and it leads to high magnetoresistance ratios in both SVs and MTJs.[7–13]

Recently, there has been growing interest in manganese-based compounds with the tetragonal $D0_{22}$ structure, which can be regarded as a severely distorted variant of the cubic $L2_1$ structure.[14,15] Alloys in the $Mn_{3-x}Ga$ series with $0 \le x \le 1$ exhibit uniaxial anisotropy, and density-functional calculations indicate a high spin polarization.[16,17] Oriented thin films have been grown, which exhibit perpendicular anisotropy with substantial coercivity,[18–22] useful spin polarization,[22] and low damping[23] which are promising for spin torque magnetic random access memories. Here, we present magnetic and electronic properties of $D0_{22}$-Mn_3Ge (001) epitaxial thin films with perpendicular anisotropy.

Mn-Ge binary compounds can crystallize in as many as eleven different structures with very different magnetic properties.[24,25] Mn_3Ge, the compound of interest here, crystallizes in either the hexagonal $D0_{19}$ structure (ε phase) or the tetragonal $D0_{22}$ structure (ε_1 phase). The high-temperature hexagonal phase is obtained by annealing the material at 700 °C, and quenching. The low-temperature tetragonal phase is obtained by annealing the hexagonal material for 1–2 weeks at 450 °C.[26] Several other non-equilibrium Mn_3Ge structures were also reported, including a cubic α-Mn type solid solution,[27] a cubic $L1_2$ phase,[28,29] and another complex tetragonal phase.[30] The crystal and magnetic structures of the $D0_{19}$ and $D0_{22}$ phases have been determined by Kádár and Krén[26] and Yamada[24,31] using powder neutron diffraction in an off-stoichiometric material of composition $Mn_{3.1}Ge_{0.9}$, which helps to stabilize a single tetragonal $D0_{22}$ phase.[32,33] The lattice parameters of tetragonal $D0_{22}$ unit cell are $a = 3.816$ Å and $c = 7.261$ Å.[26] The magnetic structure determined from the neutron scattering experiments reveals a collinear c-axis ferrimagnetic structure as shown in the inset of Figure 1. The magnetic moments of Mn atoms in 2b and 4d positions are aligned with c-axis and couple antiferromagnetically. Their magnitudes at room temperature were determined to be either $\mu_{2b} = -3.4 \pm 0.3\ \mu_B$ and $\mu_{4d} = 1.9 \pm 0.2\ \mu_B$[26] or $\mu_{2b} = -2.6 \pm 0.3\ \mu_B$ and $\mu_{4d} = 1.8 \pm 0.2\ \mu_B$,[24,31] which give a net magnetization of 0.4 or 1.0 μ_B per formula unit,

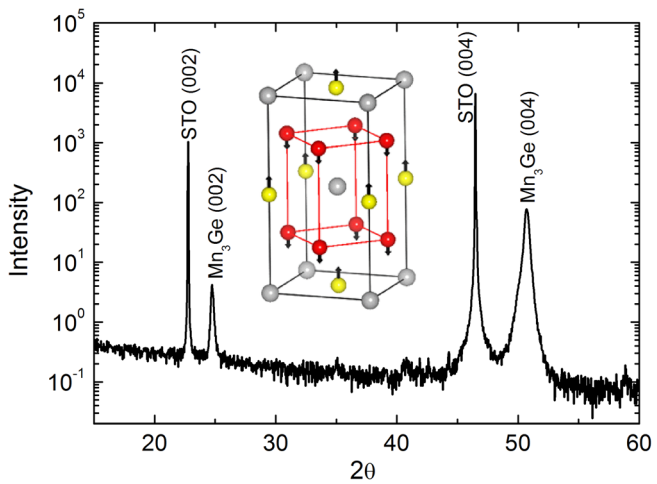

FIG. 1. X-ray diffraction pattern of an epitaxial $D0_{22}$-Mn_3Ge film grown on a $SrTiO_3$ (001) substrate. The inset shows the $D0_{22}$ unit cell of Mn_3Ge. Ge (gray) atoms in 2a positions order in a body-centred tetragonal structure, and Mn atoms occupy 2b (yellow) and 4d (red) sites, which couple antiferromagnetically.

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respectively; 1 μ_B per formula unit corresponds to a magnetization of 175 kA m^{-1} (emu cc^{-1}). The net ferrimagnetic moment is particularly sensitive to any occupancy of the Ge 2*a* site by Mn. For example, exchange of 0.05 atoms per formula unit of the ideal structure from 4*d* to 2*a* sites will reduce the net moment per formula unit by 0.3 μ_B.[24] The $D0_{22}$-Mn_3Ge was found to undergo a structural phase change to the $D0_{19}$ structure at 850 K before reaching its extrapolated the Curie temperature, which is estimated to be 920 K.[26]

We have grown epitaxial $D0_{22}$-Mn_3Ge thin films on $SrTiO_3$ (001) substrates at 450 °C by dc-magnetron sputtering from a Mn_3Ge target. The lattice mismatch between $SrTiO_3$ ($a = 3.905$ Å) and the *a* parameter of tetragonal Mn_3Ge is 2.3%, which allows epitaxial growth of *c*-axis films, as shown by the x-ray diffraction in Figure 1. The lattice parameters obtained from reciprocal space mapping are $a = 3.85 \pm 0.03$ Å and $c = 7.185 \pm 0.007$ Å. Compared to the lattice parameters of the bulk alloy, the unit cell expands in the *ab* plane to facilitate epitaxial growth on the $SrTiO_3$ (001) substrate while shrinking along *c*-axis. The atomic order parameter *S* is defined as the square root of the measured intensity ratio of (101) to (204) reflections, divided by the calculated ratio. It is 0.57 for the as-grown film and 0.82 for the film after annealing at 450 °C for 1 day.

Magnetization measurements on the thin films (Figure 2) show that the crystallographic *c*-axis is the easy axis; the films exhibit substantial coercivity, $\mu_0 H_c = 2.3$ T, and the anisotropy field $\mu_0 H_k$ estimated from room temperature magnetization curves measured in fields of up to 14 T is 25 T. The magnetization of the films is 73 kA m^{-1}, and the anisotropy constant K_u calculated as $\mu_0 H_k M_s/2$ is 0.91 MJ m^{-3}. As in oriented Mn_3Ga films,[22] there is an unusual soft in-plane ferromagnetic component of magnetization, 8 kA m^{-1}, which saturates in a magnetic field of ~60 mT. The soft moment is not seen when the field is applied in the perpendicular direction, and it is therefore not due to a soft ferromagnetic impurity phase present in the films. It may be accounted for by a small, in-plane component of the magnetization of Mn_3Ge, 0.044 μ_B fu^{-1}, which is free to rotate in the basal plane.

The sign of the direct exchange coupling between Mn atoms depends on the interatomic distance; it is usually antiferromagnetic below 2.9 Å.[24] In $D0_{22}$-Mn_3Ge, the distances from a Mn_{4d} atom to the four nearest and two second nearest neighbour Mn_{4d} atoms are 2.698 Å and 3.630 Å, respectively, leading to antiferromagnetic and ferromagnetic coupling. The Mn_{2b}-Mn_{2b} separations are 3.816 Å for the nearest four neighbors and 4.523 Å for the eight second nearest neighbours, which are both ferromagnetic. The short Mn_{2b}-Mn_{4d} distance 2.633 Å (8 nearest neighbors) leads to the strongest antiferromagnetic coupling, which overcomes the antiferromagnetic coupling between nearest neighbor Mn_{4d} spins, and results in the overall ferrimagnetic structure as shown in Figure 1. The small in-plane moment may be a consequence of frustration of some of the exchange bonds.

The spin polarization of the films was measured by point contact Andreev reflection (PCAR)[34,35] at 2 K using a shear-cut Nb tip. The data and the corresponding fit using a modified Blonder-Tinkham-Klapwijk model[36] are shown in Fig 3. Despite the appreciable barrier parameter $Z = 0.36(3)$, the refined value of the spin polarization obtained from measurements on a dozen contacts all agree to yield a spin polarization of the annealed film of 46(2)%, which is greater than that of Fe or Co, but less than we had found previously in $D0_{22}$ Mn_3Ga.[22] A 5.5 K discrepancy between the electronic and lattice temperatures is associated with the high *Z* value.

Electronic structure and magnetic properties of bulk $D0_{22}$ Mn_3Ge were calculated using the full-potential linearized augmented plane-wave (FLAPW) method as implemented in FLEUR code,[36] while the supercell's electronic structures are evaluated using the VASP[37,38] plane-wave based code. In both calculations, we used the Perdew-Burke-Ernzerhof parametrization of the generalized gradient approximation (GGA).[39] The calculated spin-polarized density of states is shown in Fig. 4(a) for the stoichiometric composition (blue lines), and a Mn-rich composition with some Mn on Ge sites (black lines). The net magnetization and spin polarization in the two cases are 177 kA m^{-1} and 75% and 110 kA m^{-1} and 39%, respectively. The latter fits the experimental data quite well, which suggests that the thin films, like the bulk material, are Mn-rich. In addition, the spin polarized Fermi surface for both spin channels, presented in Figs. 4(b) and 4(c), show that

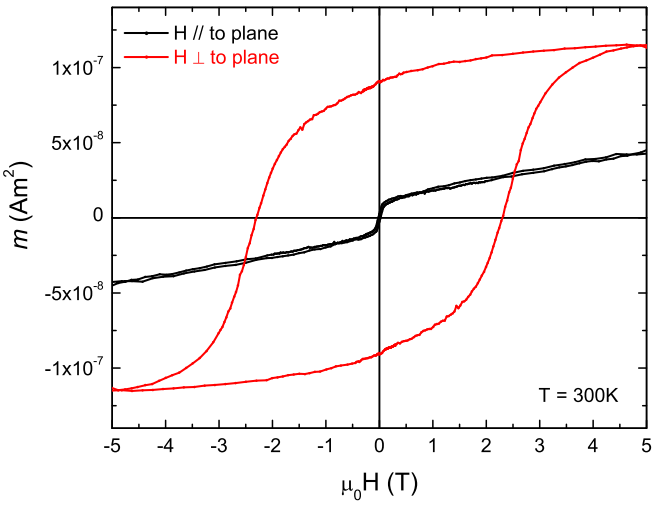

FIG. 2. Magnetization curves for a film of Mn_3Ge at room temperature. The film dimensions are 4.12 mm × 4.18 mm × 100 nm.

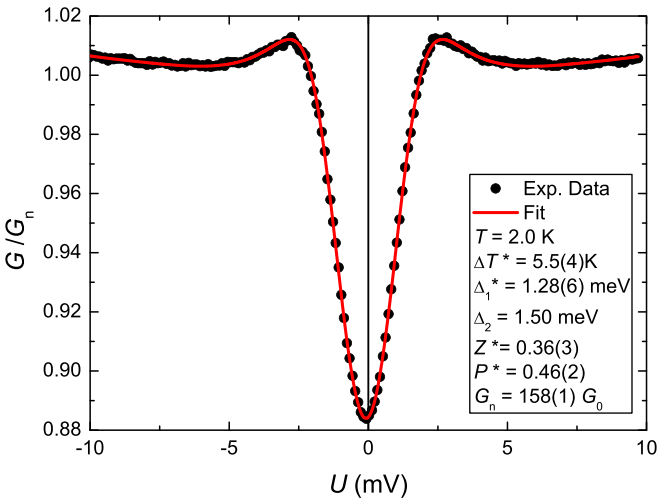

FIG. 3. Point contact Andreev reflection spectroscopy for a *c*-axis oriented $D0_{22}$ Mn_3Ge (001) film. The fitted parameters in the modified BTK model are designated by an asterix.

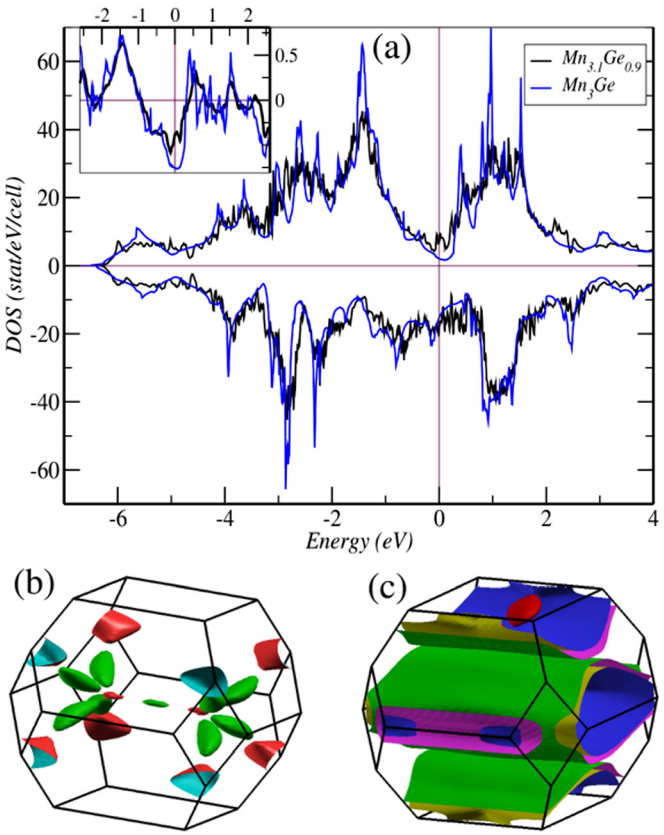

FIG. 4. Top: (a) Spin polarized density of states for $D0_{22}$ Mn_3Ge (blue) and $Mn_{3.1}Ge_{0.9}$ (black). (b) Majority spin and (c) minority spin polarized Fermi surfaces for Mn_3Ge.

Fermi velocity, and therefore the effective spin polarization in Andreev reflection is highly anisotropic. The calculated diffusive Andreev spin polarization (P_2) ranges from 44% to 77% depending on the probing direction. The inclusion of the spin-orbit coupling allows us to calculate the magnetocrystalline anisotropy and we found that $D0_{22}$ Mn_3Ge has a uniaxial anisotropy of the order of 0.8 meV per formula, which corresponds to uniaxial anisotropy constant of 2.4 MJ m^{-3}, which is higher than the measured one. The magnetic and electronic properties are robust against lattice strain.

In conclusion, the large uniaxial anisotropy and useful spin polarization make Mn_3Ge films potential candidates for spin-torque memory applications. The *c*-axis films can be grown directly on $SrTiO_3$ substrates or lattice matching seed layers such as Pd. The stability condition $K_uV/k_BT \geq 60$ is satisfied at room temperature for elements as small as $V = 10 \times 10 \times 2.7\ nm^3$. The magnetization is tunable by varying the manganese stoichiometry, and the small co-existing in-plane moment may facilitate spin torque switching.

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