

# Spin polarization and electronic structure of ferromagnetic Mn<sub>5</sub>Ge<sub>3</sub> epilayers

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Germanium-based alloys hold great promise for future spintronics applications, due to their potential for integration with conventional Si-based electronics. High-quality single phase Mn<sub>5</sub>Ge<sub>3</sub>(0001) films, grown by solid-phase epitaxy on Ge(111) and GaAs(111), exhibit strong ferromagnetism up to the Curie temperature  $T_c \sim 296$  K. Point Contact Andreev Reflection (PCAR) measurements on Mn<sub>5</sub>Ge<sub>3</sub> epilayers reveal

a spin-polarization  $P = 42 \pm 5\%$  for both substrates. We also calculate the spin polarization of bulk Mn<sub>5</sub>Ge<sub>3</sub> in the diffusive and ballistic regimes using density-functional theory (DFT). The measured spin polarization exceeds the theoretical estimates of PDFT =  $35 \pm 5\%$  and  $10 \pm 5\%$  for the diffusive and ballistic limits, respectively.

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Semiconductor spintronics has recently been recognized for its potential to combine the spin selectivity and non-volatility of ferromagnetic compounds with the ability to fabricate hybrid thin-film devices naturally integrated with conventional semiconductors [1]. Yet in order to succeed in technological applications one has to be able to introduce *room-temperature* spin-polarized materials that are compatible with, and preferably lattice-matched to, mainstream GaAs- and/or Si-based electronic materials. Ga<sub>1-x</sub>Mn<sub>x</sub>As epilayers, fabricated by the molecular beam epitaxy (MBE) technique, satisfy some of these requirements. However, in spite of considerable progress in increasing the Curie temperature of this alloy [2], it has yet to exceed 200 K. Another potential problem for Ga<sub>1-x</sub>Mn<sub>x</sub>As is the intrinsic disorder of Mn on the Ga sublattice due to its non-stoichiometric composition, which limits the hole mobility and spin transport in these compounds. Some reports on (Ga,Mn)N and other dilute magnetic semiconductors with smaller lattice constants and larger effective valence-band masses suggest the possibility of higher Curie temperatures; however, transport properties in these materials are likely to suffer even more than in (Ga, Mn)As.

Zeng et al. [3] reported the first measurements of a novel ferromagnetic Mn<sub>5</sub>Ge<sub>3</sub> epitaxial film grown on Ge(111) sub-

strate with the Curie temperature  $T_c = 296$  K. The film has sufficiently good crystalline quality, surface topography, and thermal stability to allow the growth of germanium-based heterostructures. Recently, we have grown high quality Mn<sub>5</sub>Ge<sub>3</sub> on GaAs substrates as well. In addition to having high Curie temperature, sufficiently high spin polarization,  $P$ , is essential for Mn<sub>5</sub>Ge<sub>3</sub> to be useful in a spintronics device.

In this Letter we report measurements of  $P$  for Mn<sub>5</sub>Ge<sub>3</sub> epilayers grown on both Ge and GaAs substrates using Point Contact Andreev Reflection spectroscopy (PCAR), and calculations of spin polarization for bulk Mn<sub>5</sub>Ge<sub>3</sub> in the ballistic and diffusive regimes using density-functional theory (DFT).

Spin polarization in the ballistic and diffusive limits is given by the expression

$$P_n = \frac{\langle N_{\uparrow}(E_F) v_{F\uparrow}^n \rangle - \langle N_{\downarrow}(E_F) v_{F\downarrow}^n \rangle}{\langle N_{\uparrow}(E_F) v_{F\uparrow}^n \rangle + \langle N_{\downarrow}(E_F) v_{F\downarrow}^n \rangle},$$

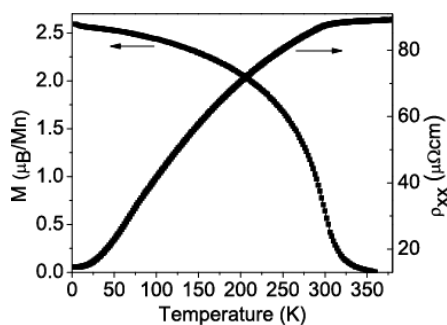
with  $n = 1$  and  $2$ , respectively. Here,  $N_{\uparrow}(E_F)$  and  $N_{\downarrow}(E_F)$ ,  $v_{F\uparrow}$  and  $v_{F\downarrow}$  are the densities of states (DOS) and the Fermi velocities for majority and minority spin sub-bands.  $P_{1,2}$  can be measured by the Andreev reflection technique [4, 5], particu-

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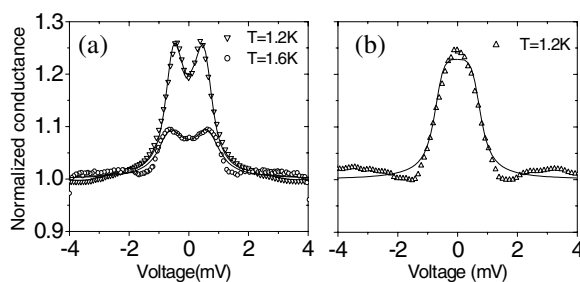
larly in the point contact configuration (PCAR) [4]. In spite of the success of the PCAR technique, which demonstrated very high  $P_C$  in a number of magnetic compounds such as CrO<sub>2</sub> [4, 6] and La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> [7], there are some theoretical issues concerning the rigorous description of the Andreev process, especially related to interface scattering [8]. While the technique has been successfully applied in the ballistic regime to high-mobility In<sub>1-x</sub>Mn<sub>x</sub>Sb epilayers [9], the presence of inelastic scattering in low-mobility dilute magnetic semiconductors such as Ga<sub>1-x</sub>Mn<sub>x</sub>As [10, 11] is likely to lead to unconventional behavior [11], which makes the analysis more difficult. From this perspective, the Mn<sub>5</sub>Ge<sub>3</sub> system has a very important advantage: It is a *stoichiometric* material, so its Mn sublattice is well ordered, while its low residual resistivity indicates high mobility. The fact that Mn<sub>5</sub>Ge<sub>3</sub> is a stoichiometric compound also makes it possible to use DFT to determine the DOS, Fermi velocities, and spin polarization – thereby allowing a direct comparison between theoretical and experimental results.

Mn<sub>5</sub>Ge<sub>3</sub> films with a typical thickness of ~50 nm were grown by depositing Mn onto bulk Ge(111) and subsequently annealing between 300 °C and 650 °C for several minutes, a technique known as solid-phase epitaxy (see Ref. [3]) and, more recently, by depositing a thin Ge(111) buffer layer on top of GaAs(111), followed by co-deposition of Mn and Ge in stoichiometric amounts at a substrate temperature of 330 °C and a growth rate of ~6 Å/min. X-ray diffraction  $\theta$ - $2\theta$  scans indicate a high-quality epitaxial film: all diffraction peaks can be indexed according to the Mn<sub>5</sub>Ge<sub>3</sub>(0001) structure. The intermetallic compound Mn<sub>5</sub>Ge<sub>3</sub> has the hexagonal crystal structure with the unit-cell parameters at room temperature  $a = 7.184$  Å and  $c = 5.053$  Å. The stoichiometry of 0.375 Mn, corresponding to the Mn<sub>5</sub>Ge<sub>3</sub> structure, was obtained from Rutherford backscattering (see Ref. [3]). Transport measurements indicate an excellent quality film with  $\rho_{4K} \sim 5$ – $10$   $\mu\Omega$  cm and  $\rho_{300K}/\rho_{4K} \sim 10$  (see Fig. 1). The temperature dependence of the saturation magnetization (Fig. 1) demonstrates conventional magnetic behavior (the easy axis of the film is in-plane due to shape anisotropy). The Curie temperature is ~296 K for both substrates, practically identical to that of bulk Mn<sub>5</sub>Ge<sub>3</sub>.

Mechanically sharpened Sn superconductor tips were used for all point-contact measurements. A contact was established between the sample and the Sn tip along the [001] direction of Mn<sub>5</sub>Ge<sub>3</sub>. The conductance was measured by the standard four-terminal technique with lock-in detection (see

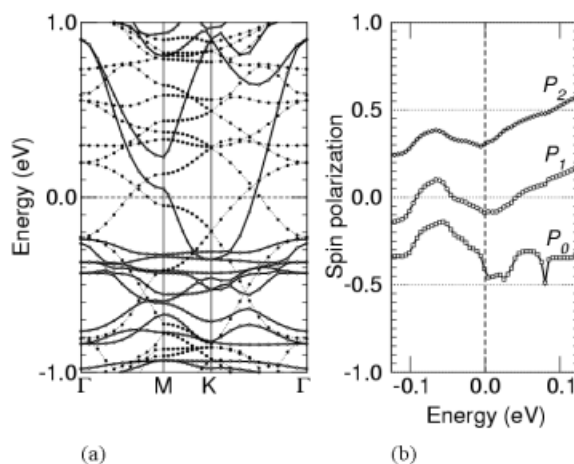


**Figure 1** Saturation magnetization (in the field  $H = 1$  T) and resistivity of a 48 nm thick epitaxial Mn<sub>5</sub>Ge<sub>3</sub>(0001) film on GaAs(111). The Curie temperature is ~296 K.



**Figure 2** Sn contacts with Mn<sub>5</sub>Ge<sub>3</sub> epitaxial film (a) grown on Ge(111): minimum (top curve) and maximum (bottom curve) measured values of spin polarization: fitting parameters:  $Z = 0.2$ ,  $P = 33\%$ ; and  $Z = 0.1$ ,  $P = 46\%$  respectively; (b) grown on GaAs(111):  $Z \sim 0$ ,  $P = 42\%$ .

Ref. [12]). A series of measurements in all of the Sn/Mn<sub>5</sub>Ge<sub>3</sub> point contacts in several different samples (grown both on Ge and GaAs substrates) demonstrate conventional behavior, with the superconducting gap close to the bulk value of Sn,  $\Delta(0) \sim 0.55$  meV, and dimensionless interfacial scattering parameter,  $Z$  close to zero, indicating a low interface barrier. The gap at higher temperatures was consistently obtained from the BCS  $\Delta(T)$  dependence. As we will show below, all the measurements are done in the ballistic limit and the point contacts have low  $Z$  values. This allowed us to fit the conductance curves using the modified Blonder–Tinkham–Klapwijk (BTK) model [13] using just two fitting parameters,  $P$  and  $Z$ , and to obtain the spin polarization for each individual fit with an accuracy of  $\pm 1\%$ . The values of  $P$  and  $Z$  were found to be very similar for the films grown directly on Ge and those grown on Ge/GaAs(111). Representative  $dI/dV$  curves for three different contacts are shown in Fig. 2 (a, b). The spin polarization of Mn<sub>5</sub>Ge<sub>3</sub>, obtained by averaging over many different contacts and temperatures, was found to be  $P \sim 42 \pm 5\%$ . A fairly large difference in the minimum and maximum measured spin polarization (see Fig. 2a) is likely to be due to strong crystallographic anisotropy, leading to a directional dependence of  $P$ . The value of  $P$  does not change ap-



**Figure 3** (a) Calculated band structure of Mn<sub>5</sub>Ge<sub>3</sub> for the theoretical hexagonal crystal structure. Open circles and solid curves denote majority bands; filled circles and dotted curves denote minority bands. (b) Spin polarization for the DOS ( $P_0$ ), ballistic case ( $P_1$ ), and diffusive case ( $P_2$ ).

preciably if we take the limit of  $Z = 0$  (see Ref. [6]), since in the case of  $\text{Mn}_3\text{Ge}_3$  all of the measured contacts have very low  $Z$  ( $0 < Z < 0.2$ ). The theoretical calculations were carried out within the generalized-gradient approximation (GGA) to DFT, using the projector-augmented wave (PAW) method and a plane-wave basis [14]. All the calculations used an energy cut-off of 337 eV; the structural optimization and DOS calculations used  $4 \times 4 \times 6$  and  $12 \times 12 \times 14$   $\Gamma$ -centered samplings, respectively, of the  $\text{Mn}_5\text{Ge}_3$  hexagonal Brillouin zone. The resulting equilibrium lattice parameters,  $a = 7.092$  Å and  $c = 4.984$  Å, are in good agreement with our experimental results, and the two equilibrium internal parameters,  $x(\text{Mn}) = 0.244$  and  $x(\text{Ge}) = 0.606$ , are very close to experimental values reported earlier for  $\text{Mn}_3\text{Ge}_3$ ,  $x(\text{Mn}) = 0.2397$  and  $x(\text{Ge}) = 0.6030$  [15].

The hexagonal  $\text{Mn}_3\text{Ge}_3$  band structure is shown in Fig. 3a. Based on this band structure, the spin polarization was calculated according to the definitions given earlier, using the linear tetrahedron method. For the  $z$ -direction (perpendicular to the hexagonal plane) we obtain  $P_{\perp} = -9\%$  and  $P_{\parallel} = +35\%$  (see Fig. 3b). We estimate the overall numerical uncertainty in these values to be roughly 5 to 10%. Interestingly, when we repeat the calculations using the experimental lattice and internal parameters (which differ by 1–2% from the theoretical values) we obtain very different spin polarizations,  $P_{\perp} = +15\%$  and  $P_{\parallel} = +50\%$ , indicating a surprisingly large sensitivity of the polarization to the details of the crystal structure. These results are consistent with values obtained recently using a different DFT method [16]. Such sensitivity is not surprising for materials with complicated Fermi surfaces, and even suggests a role for materials where strong coupling between strain and spin polarization is desirable. Crystallographic anisotropy may also be important: using the theoretical lattice parameters, the in-plane ballistic spin polarization,  $P_{\parallel} = 10\%$  is very different from that along the  $z$ -direction,  $P_{\perp} = -9\%$ . We note, however, that this anisotropy is much reduced if one uses the experimental lattice parameters [16]. Thus, we consider uncertainty in the lattice parameters to be the primary source of uncertainty in the calculated spin polarization.

Using,  $\sigma_i = e^2 \langle N(E_F) v_{Fi}^2 \rangle \tau$  and the known conductance of the  $\text{Mn}_3\text{Ge}_3$  film, we can estimate the mean free path  $L$ . From the calculated values of  $\langle N(E_F) v_{Fz\uparrow}^2 \rangle + \langle N(E_F) v_{Fz\downarrow}^2 \rangle = 8.1$  eV Å<sup>2</sup> and  $\langle v_{Fz\uparrow} \rangle \sim 1.7 \times 10^7$  cm/s,  $\langle v_{Fz\downarrow} \rangle = 2.0 \times 10^7$  cm/s, we find the relaxation time  $\tau = L / \langle v_F \rangle \sim 4.5 \times 10^{-13}$  s, yielding  $L \sim 85$  nm. The contact size  $d$  can be estimated from the Sharvin formula  $R_c \sim 4\rho L / 3\pi d^2 + \rho / 2d$ , where  $R_c$  is the contact resistance. For the typical values of  $R_c \sim 30$  Ω, we obtain  $d \sim 25$  nm, indicating that our measurements were done in the ballistic regime,  $L \gg d$ .

In summary, we have measured the spin polarization of epitaxial  $\text{Mn}_3\text{Ge}_3$  films with room temperature  $T_C$ , grown on Ge(111) and on GaAs(111). A compendium of X-ray, transport, magnetic, and RBS data attest to homogeneity and high structural uniformity of the  $\text{Mn}_3\text{Ge}_3$  epilayers. All the PCAR measurements are done in the ballistic regime for high-transparency junctions with small  $Z$ , and thus can be analyzed with a conventional BTK weak-coupling theory [13]. The spin

polarization of  $\text{Mn}_3\text{Ge}_3$  along the [001] direction grown on both Ge(111) and GaAs(111) was measured to be  $42 \pm 5\%$ , much higher than the  $P_{\text{DFT}} = 10\text{--}15\%$  in the ballistic limit, but fairly close to the  $P_{\text{DFT}} = 35\text{--}50\%$  in the diffusive limit; the latter agreement is likely to be coincidental. We attribute the discrepancy between the experiment and the theory to the extreme sensitivity of the DFT calculations to the values of the lattice parameters for  $\text{Mn}_3\text{Ge}_3$ . Such effects may be interesting in their own right, when strong coupling between strain and spin polarization is desired. These films have high mobility and room Curie temperature, and  $P$  higher than that theoretically predicted – comparable to the spin polarization of 3d metals as well as MnAs [12], indicating high potential for this novel material in a variety of spintronics applications.

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## References

- [1] H. Munekata et al., Phys. Rev. Lett. **63**, 1849 (1989).
- [2] A. M. Nazmul et al., J. Cryst. Growth **251**, 303 (2003).
- [3] C. Zeng et al., Appl. Phys. Lett. **83**, 5002 (2003).
- [4] R. J. Soulen, Jr., J. M. Byers, M. S. Osofsky, B. Nadgorny, T. Ambrose, et al., Science **282**, 85–88 (1998).
- [5] S. K. Upadhyay, A. Palanisami, R. N. Louie, and R. A. Buhrman, Phys. Rev. Lett. **81**, 3247–3250 (1998).
- [6] A. Anguelouch et al., Phys. Rev. B **64**, 180408 (R) (2001).
- [7] B. Nadgorny, I. I. Mazin, M. Osofsky, R. Soulen, et al., Phys. Rev. B **63**, 184433 (2001).
- [8] K. Xia, P. J. Kelly, G. E. W. Bauer, and I. Turek, Phys. Rev. Lett. **89**, 166603 (2002).
- [9] R. P. Panguluri, B. Nadgorny, T. Wojtowicz, W. L. Lim, X. Liu, and J. K. Furdyna, Appl. Phys. Lett. **84**, 4947 (2004).
- [10] J. G. Braden, J. S. Parker, P. Xiong, S. H. Chun, and N. Samarth, Phys. Rev. Lett. **91**, 056602 (2003).
- [11] R. P. Panguluri, K. C. Ku, T. Wojtowicz, X. Liu, J. K. Furdyna, Y. Lyanda-Geller, N. Samarth, and B. Nadgorny, preprint.
- [12] R. P. Panguluri, G. Tsoi, B. Nadgorny, S. H. Chun, N. Samarth, and I. I. Mazin, Phys. Rev. B **68**, 201307 (2003).
- [13] I. I. Mazin, A. A. Golubov, and B. Nadgorny, J. Appl. Phys. **89**, 7576 (2001).
- [14] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993). G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
- [15] J. B. Forsyth and P. J. Brown, J. Phys.: Condens. Matter **2**, 773 (1990).
- [16] S. Picozzi, A. Continenza, and A. J. Freeman, Phys. Rev. B **70**, 235205 (2004).