Large zero-field cooled exchange-bias in bulk Mn$_2$PtGa

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We report a large exchange-bias (EB) effect after zero-field cooling the new tetragonal Heusler compound Mn$_2$PtGa from the paramagnetic state. The first-principle calculation and the magnetic measurements reveal that Mn$_2$PtGa orders ferrimagnetically with some ferromagnetic (FM) inclusions. We show that ferrimagnetic (FI) ordering is essential to isothermally induce the exchange anisotropy needed for the zero-field cooled (ZFC) EB during the virgin magnetization process. The complex magnetic behavior at low temperatures is characterized by the coexistence of a field induced irreversible magnetic behavior and a spin-glass-like phase. The field induced irreversibility originates from an unusual first-order FI to antiferromagnetic transition, whereas, the spin-glass like state forms due to the existence of anti-site disorder intrinsic to the material.

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The class of Ni$_2$Mn$_{1+x}$Z$_{1-x}$ based Heusler alloys exhibit a structural transition from a high temperature cubic austenite phase to a low temperature tetragonal/orthorhombic martensitic phase, whereas, a magnetic ordering transition takes place in the cubic phase. The existence of a first-order structural transition with strong magneto-structural coupling leads to the observation of various functional properties $^{11-14}$. In these off-stoichiometric Mn rich alloys the extra Mn replaces the Z atoms. The Mn-Mn exchange interaction is ferromagnetic (FM) within the regular Mn sublattices while it is antiferromagnetic (AFM) between the Mn atoms occupying the regular Mn sublattice and Z sublattice $^{15-18}$. The tetragonal/orthorhombic distortion in the martensitic phase enhances this AFM interaction due to the decrease in the Mn-Mn distance, which also results in a large degree of magnetic frustration. Furthermore, many Heusler alloys also display anti-site disorder $^{19}$. All these factors contribute to a complex magnetic state in the low temperature regime. The observations of spin-glass behavior $^{11}$ and the exchange-bias (EB) phenomenon $^{11}$ are direct evidence of this complex magnetic state.

A new class of Mn$_2$YZ based binary and ternary Heusler compounds stabilize in the cubic/tetragonal crystal structure with high Curie temperatures ($T_C$). These materials are attractive candidates for spin-torque transfer devices $^{12,13}$. The magnetic interaction in most of these compounds is found to be ferrimagnetic (FI) in nature $^{13,16}$. The magnetic circular dichroism in x-ray absorption (XMCD) measurements in Mn$_3-x$Co$_x$Ga compounds show direct evidence of the FI ordering $^{17}$. In a recent work it is found that Mn$_2$PtIn, which crystallizes in a tetragonal structure with FI ordering, exhibits an inhomogeneous magnetic state at low temperature and shows a weak conventional EB effect $^{18}$. In this Letter, we report a large unconventional EB effect obtained after zero-field cooling the Heusler compound Mn$_2$PtGa from its paramagnetic state. To further elucidate the microscopic origin of the EB behavior we carried out a theoretical investigation on the magnetic structure. Based on our experimental and theoretical results we propose a phenomenological model for the large zero-field cooled (ZFC) EB.

Polycrystalline ingots of Mn$_2$PtGa were prepared by arc melting stoichiometric amounts of the constituent elements and subsequent annealing for one week at 1273 K. The samples were structurally characterized by X-ray powder diffraction. The details of the structural analysis is given in the supplementary material $^{19}$. The physical quantities were investigated utilizing Quantum Design measurement systems. The pulsed magnetic field experiments were performed at the Dresden High Magnetic Field Laboratory. We have also performed a calculation to map out the magnetic structure using the PYA-LMTO program package $^{20}$.

Mn$_2$PtGa undergoes a paramagnetic (PM) to FM(FI) transition at $T_C = 230$ K as exemplified in the magnetization, $M(T)$, and ac-susceptibility, $\chi(T)$, data in Fig. 1a and b. With further decreasing temperature $M(T)$ exhibits a sudden drop at 150 K. To probe the nature of this transition we have measured field cooled (FC) and field heated (FH) $M(T)$ curves that show a significant hysteresis. The presence of such a thermal hysteresis between the FC and FH curves is a strong evidence for the first-order nature of a phase transition $^{21}$. Therefore, we argue that Mn$_2$PtGa undergoes a first-order FM(FI) to AFM transition at 150 K. However, the existence of a small irreversibility between ZFC and FC curves suggests that the low temperature phase is not perfectly AFM in nature. This irreversibility mainly originates from the presence of anti-site disorder that gives rise to a magnetically inhomogeneous state. We note that the
an AFM to a FI phase, which will be addressed later.

$M(H)$ measured in pulsed fields does not show any saturation up to 60 T (see Fig. 2). The sample shows a magnetization of $0.8 \mu_B$/f.u. in 7 T at 1.9 K and $1.6 \mu_B$/f.u. in 60 T at 4.2 K. The small value of the magnetization and the still increasing $M(H)$ indicates the presence of FI ordering in Mn$_2$PtGa. At 275 K, which is above $T_C$, we find paramagnetic behavior. Interestingly, the $M(H)$ curve at 4.2 K displays a similar shift as that observed in the low field ZFC $M(H)$ data. This evidences that a field of 60 T is too small to affect the exchange anisotropy produced in the sample during the initial magnetization process. The temperature dependence of the EB field ($H_{EB}$) and the coercive field ($H_C$) deduced from the ZFC and FC hysteresis loops are shown in Fig. 2b. In FC mode the sample was cooled in 7 T from 300 K to the desired temperature. $H_{EB}$ and $H_C$ are calculated using $H_{EB} = |H_1+H_2|/2$ and $H_C = |H_1-H_2|/2$, where $H_1$ and $H_2$ are the lower and upper cut-off fields. At 1.9 K, $H_{EB}$ possesses a maximum value of around 0.17 T in ZFC mode and 0.16 T in FC mode. $H_{EB}(T)$ and $H_C(T)$ exhibit a monotonic decrease upon increasing temperature, which is for $H_C(T)$ interrupted by a local maximum around 40 K. The origin of this anomaly will be discussed later.

We will now turn our focus to the details of the magnetic phase diagram of Mn$_2$PtGa. Figure 3 displays the ZFC $M(H)$ loops at various temperatures. The 10 K $M(H)$ loop shows a similar behavior as that at 1.9 K (Fig. 1b) with a reduction of the field required to induce the metamagnetic transition. Interestingly, the metamagnetic transition is only observed in the virgin curve for $T \leq 15$ K. However, at 17.5 K the loop shows a signature of the metamagnetic transition in the negative field path. Upon increasing temperature this signature becomes more pronounced for negative as well as positive fields. The presence of the virgin curve outside the envelope loop and the incomplete metamagnetic transition results in an irreversible hysteresis loop for $T < 40$ K.
The $M(H)$ loops for $T \geq 40\,\text{K}$ are reversible in both the quadrants, also the virgin curve coincides with the corresponding part of the hysteresis loop. The critical field of the metamagnetic transition decreases significantly upon increasing temperature. The feature of the metamagnetic transition completely vanishes at 160 K, where we find soft FM behavior and finally a paramagnetic transition completely vanishes at 160 K, where we find corresponding part of the hysteresis loop. The critical field of $M(H)$ loop taken at different $T$.

![FIG. 3. (Color online) ZFC $M(H)$ loops taken at different $T$.](image)

![FIG. 4. (Color online) Total energies for various magnetic configurations in case of inverse (black) and regular (red line) Heusler structures. The energy of the inverse Heusler structure in the nonmagnetic state is taken as reference. The chemical composition of each configuration is schematically depicted by the 4x4-atom diagrams drawn closer to the corresponding energy points. Light green, yellow and hollow spheres mark Pt, Ga and Mn atoms, respectively. Arrows on Mn spheres indicate the directions of the local magnetic moments.](image)

The disorder influenced first-order magnetic to magnetic transition in Mn$_2$PtGa is found for the first time in any Heusler compound. The observation of different magnitudes of field-induced irreversibility is a direct consequence of the competition between the potential and thermal energy. Though the AFM phase possesses a lower energy at $H = 0$ for $T \leq 15\,\text{K}$, the field induced FI phase forms a pinning potential, where disorder provides the pinning centers. When the field is reduced to zero the thermal energy cannot overcome this potential and the AFM phase is not restored resulting in the observed irreversibilities. At higher temperatures the thermal energy becomes large enough to allow for a partial recovery of the AFM phase by field cycling. Only above 40 K the thermal energy becomes larger than the pinning potential and a reversible hysteresis loop is observed. Similar phenomena have been reported in systems undergoing a first-order magnetic to magnetic transition. Although some of the Heusler systems with martensitic transition show a similar type of field induced irreversibility, the underlying physics for such a behavior categorically differs from the case of Mn$_2$PtGa. In the former materials the field induced structural change plays a major role in inducing the irreversibilities, which become stronger on approaching the martensitic transition upon increasing temperature. This is in contrast to Mn$_2$PtGa which does not show any structural transition.

To map out the exact magnetic configuration in Mn$_2$PtGa, we have performed calculations using the fully-relativistic linearized muffin-tin orbitals band-structure method within the PYA-LMTO program package. The unit cell parameters were taken from experiment. The exchange-correlation potential was treated using the Vosko-Wilk-Nusair form of the local density approximation. The comparison of the total energy calculated for the different configurations (see Fig. 4) indicates that the nonmagnetic configurations are energetically the most unfavorable (regular and inverse variants). The energy is substantially reduced by switching on the magnetism on the Mn atoms. For a ferromagnetic configuration this results into a large magnetic moment: 7.2 $\mu_B$/f.u. in case of the regular and 7.12 $\mu_B$/f.u. for the inverse Heusler structure. In this fully ferromagnetic
setup both regular and inverse structures possess rather similar total energies of about -15 meV/atom compared with the nonmagnetic inverse structure. For the regular Heusler variant the ferromagnetic state is the most stable. Enforcing any type of antiparallel alignment of Mn moments within the regular structure always leads to a locally nonmagnetic state. On the other hand, by varying the magnetic configurations further within the inverse structure, the total energy still can be lowered. By reverting the directions of the magnetic moments in each second pair of layers, we arrive in the fully compensated antiferromagnetic state, with an energy lowered by about 4 meV/atom compared with the ferromagnetic state. The lowest energy configuration is achieved when the Mn moment is reverted within each layer (FI state). Since the positions of the Mn atoms in the adjacent layers within the inverted Heusler structure are nonequivalent by symmetry, the total magnetic moment is not completely compensated: a small total moment of about 0.55 μB/f.u., which is the result of 3.65 μB/f.u. [Mn(I)] - 3.1 μB/f.u. [Mn(II)], remains. Our results emphasize that the formation of the magnetic state is driven by two mechanisms – ferromagnetic exchange between Mn atoms at long and antiferromagnetic at short distances. The observation of a magnetization of 0.8 μB/f.u. at 7 T is slightly larger than the calculated value (0.55 μB/f.u.). This can be explained by ferromagnetic clusters embedded in the strongly-compensated ferrimagnetic host. The ferromagnetic ordering inside the clusters is due to the regular Heusler structure, i.e. the interchange between Mn and Pt atoms (the so-called antisite disorder, which often takes place in Heusler materials). Samples prepared under different annealing and/or quenching conditions exhibit a slightly changed magnetization. This is most likely connected to an atomic rearrangement toward the more stable, inverse Heusler structure. The latter phase forms an almost compensated host, which surrounds the ferromagnetic clusters.

Based on the first-principle calculations and experimental results we propose a simple model for the ZFC EB in Mn2PtGa. We assume an exchange interaction between two dissimilar magnetically anisotropic phases. The irreversibility between ZFC and FC M(T) curves in low fields (≤ 0.1 T), the frequency dependence of χ′′(T) below TC, and the theoretical calculations indicate the presence of magnetically inhomogeneous states originating from local FM clusters in a FI background. Upon applying field the virgin magnetization process will try to align the moments in the FI and FM phases along the field direction, which implies that the interface spins of the FI and FM phases will align in the same direction to minimize the energy. This sets up the exchange interaction between the magnetically soft FM phase and the magnetically hard FI phase. Further, this implies an increase of the coercive field in a perfectly ordered material, because the ferrimagnetically ordered moments collectively change their direction 27. However, one would expect a rough interface with disorder and uncompensated moments in the FI phase and additional defects in the bulk 27 29. All of these factors collectively contribute to the ZFC EB behavior. The fact that HEB obtained from the FC M(H) loops measured after field cooling in 7 T, where the sample is only in the FI phase below TC, and the HEB derived from the ZFC loops almost match rule out any significance of the first-order FI to AFM transition in the formation of the ZFC EB. This is furthermore supported by the observation of a small EB at 160 K, which is above the FI to AFM transition. The pulsed field experiments up to 60 T find only a very small change in HEB. This shows that once the exchange interaction is set up the field does not change the FI phase significantly to observe a change in HEB. These findings distinguish Mn2PtGa from the off-stoichiometric Ni-Mn-In Heusler alloys where recently a ZFC EB has been reported 8. Mn2PtGa exhibits a too weak frequency dependence of the peak in χ′′(T) to indicate super spin-glass behavior resulting in super FM clusters during the initial magnetization process as in Ni-Mn-In 8. One common factor, however, is the existence of FI ordering in both systems. Therefore, we argue that the presence of FI ordering with embedded FM clusters is an important ingredient for the appearance of a ZFC EB.

In conclusion, we have synthesized and studied the new Heusler compound Mn2PtGa. Though, Mn2PtGa orders ferrimagnetically at Tc = 230 K, it undergoes an unusual first order FI to AFM phase transition below TC. We demonstrated, to our knowledge for the first time, the presence of a ZFC EB effect in a stoichiometric bulk Heusler compound. We further show that the appearance of this ZFC EB effect is related to the presence of FI ordering with embedded FM clusters. We ruled out any role of the first-order transition in the observation of the ZFC EB.

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