Layered antiferromagnetism with high Neel temperature in the intermetallic compound Mn₂Au

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On the basis of earlier experimental studies the intermetallic compound Mn₂Au has been characterized as a nonmagnetically ordered material. Here we report the results of first-principles calculations based on local spin-density approximation that describes Mn₂Au to have a narrow ground state with rigid local moments on the Mn sites. Calculations of the interatomic exchange constants based on the magnetic force theorem and a Monte Carlo modeling of the resulting Heisenberg-like Hamiltonian predict a high Neel temperature of ~1600 K. This temperature is considerably higher than for the other known high-temperature antiferromagnetic $L1_0$-type Mn based binary alloys used in magnetic storage applications. © 2008 American Institute of Physics. [DOI: 10.1063/1.3003878]

Antiferromagnetic (AF) order is more common in nature than collinear ferromagnetism. Up to very recently, AF materials had only rather limited importance for technological applications. This situation has largely changed after the discovery and wide utilization for practical uses in giant magnetoresistance (GMR) (Ref. 1) and tunneling magnetoresistance (TMR) (Ref. 2) devices where AF materials are used as pinning layers. This situation has triggered intense studies and a search for new antiferromagnets with advanced properties as required by high performance applications. One particular property is the temperature stability of the AF ordered state, which requires a high value of the Neel temperature. During recent years a considerable attention was given to the AF transition metal oxides (e.g., NiO) and ordered Mn-based transition metal alloys with high Neel temperatures $T_N$. In particular, MnPt has been often used as an AF layer in practical devices because of high temperature stability of its ordered AF state ($T_N \approx 970$ K). Recently, it has been reported that the ordered alloy MnIr has the highest $T_N$ (at about 1145 K) among Mn-based binary alloys.

Due to their rather low $T_N$, AF Mn–Au systems have attracted much less interest from the point of view of their applications as AF pinning materials. The ordered alloy MnAu has a $T_N \approx 513$ K and even lower for MnAu₃ and MnAu₅ with 140 and 354 K, respectively. The alloy MnAu₄ is ferromagnetic (FM) (Ref. 8) with $T_C \approx 373$ K. The most famous representative of these series is the compound MnAu₂, in which, for the first time ever, helical spin ordering ($T_N \approx 365$ K) has been observed in neutron diffraction experiments. Experimental estimates led to rather large magnetic moments, order of 3–4 $\mu_B$, at the Mn sites. These values, as well as the type of magnetic ground state, were very well described by first-principles calculations within the framework of the local spin density approximation (LSDA) including also MnAu and MnAu₂.⁴¹

Because of the limited solubility of Au in Mn, the binary alloy Mn–Au phase diagram contains only a single stable Mn-rich compound—Mn₂Au. Mn₂Au crystallizes in the MoSi₂-type structure (see Fig. 1), which is exactly the same as the structure of the helimagnetic MnAu₂ but with opposite “coloring” of the lattice sites. It is quite surprising that MnAu₂ has been reported to be nonmagnetic (nonmagnetically ordered). This conclusion was derived from the analysis of ¹⁹⁷Au Mössbauer spectra as well as from magnetization measurements. The temperature dependence of the magnetic susceptibility has a maximum at low temperature (~5 K) and low constant value at higher temperatures without any anomalies pointing to a magnetic order-disorder phase transition. At low temperatures Mn₂Au also shows a metamagneticlike behavior in applied external magnetic

FIG. 1. Crystal structure of Mn₂Au. Gold atoms are showed as dark and Mn atoms as light symbols. The arrows show Mn magnetic moment directions in respective (001) layers in AF ground state (note: only relative orientations of the moments are relevant since the magnetic anisotropy is not known).
field. It thus has been concluded that Mn$_2$Au is paramagnetic and close to the onset itinerant electron magnetism.\textsuperscript{15} Weakly itinerant magnetism in Mn-based compounds is not a common phenomenon, in particular, in pure transition metal alloys. However, weakly magnetic materials such as the famous MnSi (Ref. 16) have attracted a considerable and long standing interest.

In attempts to identify an origin of the weak magnetic behavior of Mn$_2$Au and to understand its different character from other Mn--Au systems, we perform first principles calculations based on local spin-density approximation\textsuperscript{17} and bulk Korringa–Kohn–Rostoker (KKR) method in atomic sphere approximation (ASA).\textsuperscript{18,19} The derived results suggest a quite different picture of magnetism in this material. The ground state is found to be AF with large and well-localized moments on Mn sites, which is in strong contrast to earlier interpretations of experimental results. Moreover a large energy difference between AF and FM states suggests a high stability of AF state. The Neel temperature was estimated from direct calculations of exchange constants of Heisenberg-like Hamiltonian using the first-principles magnetic force theorem (MFT),\textsuperscript{20} followed by a Monte Carlo simulation. The calculated Neel temperature $T_N \approx 1600$ K has been found to be much larger than peritectoid melting temperature of $\approx 950$ K.\textsuperscript{13} This may explain the absence of any sign of magnetic phase transition in the available experiment—Mn$_2$Au is magnetically ordered in whole temperature region of its structural stability. Even more, the symmetry of the AF ground state explains also the absence of magnetic features in the Mössbauer spectra of Mn$_2$Au.

The electronic structure calculations were performed for the experimental\textsuperscript{12} Mn$_2$Au geometry with lattice parameters of body-centered-tetragonal (bct) structure (Fig. 1) $a = 3.328$ Å and $c = 8.539$ Å, which are taken from the Wells and Smith\textsuperscript{12} paper. The partial waves in the KKR-ASA (Refs. 18 and 19) calculations have been expanded up to $l_{\text{max}} = 3$ inside the atomic spheres, which were set equal on Mn and Au sites. The total energy was calculated using multipole screening electrostatic corrections (up to $l=6$) to the electrostatic potential and energy as described in Ref. 21. All calculations were performed within the scalar relativistic approximation, which contains all relativistic effects with the exception of spin-orbit coupling. The calculations were converged with 14 827 nonequivalent $k$-points distributed in the irreducible wedge of Brillouin zone (IBZ). A single-site coherent potential approximation (CPA) has been applied to calculate the electronic structure and magnetic state of Mn antisite impurity atoms on the Au sublattice and for calculations in the disordered local moment (DLM) approach as described by Györffy et al.\textsuperscript{22}

The calculated total energies and magnetic moments of Mn are shown in Table I for three different magnetic states: FM, DLM state, and AF ground state. The latter AF state is shown in Fig. 1 by respective arrows, which indicate the atomic spin directions on the Mn sites. This state is composed of ferromagnetically ordered basal Mn layers with alternating stacking along the $c$-axis of the MoS$_2$ structure and its energy is much lower than the energy of FM state. We note that calculated atomic Mn moments are about the same in both the AF and FM states and have values similar to those found in other Au richer Mn--Au alloys.\textsuperscript{3–7} The energy differences between the magnetically ordered states and the nonspin polarized one are a few orders of magnitude larger than the typical L SDA overestimation of the magnetic stability in nearly FM and weak FM materials such as YCo$_2$ (Ref. 23) and Ni$_3$Al.\textsuperscript{24} In the paramagnetic DLM state (fully disordered), the Mn moments also remain almost unchanged. These latter two observations rule out any weak itinerant scenario of magnetism in Mn$_2$Au. The local moment character of Mn can be also seen from the calculated density of states (DOS). In Fig. 2 we show the calculated DOS for the nonspin-polarized and the AF ground state. It can be seen that the spin splitting of the majority and minority spin bands of Mn ($\approx 0.3$ Ry) is larger than the bandwidth ($\approx 0.2$ Ry) of the rather narrow Mn $d$-bands. The DOS presented in Fig. 2 shows signs of a pseudogap in the AF state, which is typical for high-temperature AF Mn-based alloys like MnPt (Ref. 4) and MnIr.\textsuperscript{6}

A large energy difference between AF ground state and paramagnetic DLM state suggests a high value of the Neel temperature. In a simple molecular field approximation, this energy difference provides an estimate of the total effective exchange coupling constant, $J_0$, and thus allows a rough estimate for $T_N$: $T_N^\text{AF} = -\frac{3}{2}k_B(E_{\text{DLM}} - E^\text{AF})$, where the energy is

<table>
<thead>
<tr>
<th>$E$, mRy/atom</th>
<th>FM</th>
<th>DLM</th>
<th>AFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m (\text{Mn}), \mu_B$</td>
<td>3.56</td>
<td>3.58</td>
<td>3.64</td>
</tr>
</tbody>
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taken per magnetic atom.\textsuperscript{25} This gives the value $T_{N}^{\text{MF}} \approx 2033$ K, which is much higher than the mean-field estimate made for MnIr (1490 K) also from earlier first-principles calculations.\textsuperscript{6} It is known, however, that the mean-field approximation yields overshooting values of the ordering temperature. In order to calculate it more precisely, we applied a Green’s function technique based on first principles, namely, the MFT (Ref. 20), to calculate the pair magnetic exchange constants $J_{ij}$ of a classical Heisenberg-type spin Hamiltonian: $H = -\sum_{i,j} J_{ij} \vec{e}_i \cdot \vec{e}_j$, where $\vec{e}_i$ are unit direction vectors of the magnetic moment on $i$th Mn site. The implementation of the MFT in the bulk KKR-ASA method used here was done and described by Ruban et al.\textsuperscript{26} For an estimation of the Neel temperature of Mn$_2$Au, we have considered the pair exchange interactions calculated in the paramagnetic DLM state with more than 10$^8$ k-points distributed in IBZ, since the exchange in the paramagnetic DLM state is more relevant to physical situation\textsuperscript{27} at $T_{N}$. However, their values are found to be not too much different from those calculated for the AF ground state due to the pronounced localization of the Mn moments in Mn$_2$Au. We also want to acknowledge that recently the energy of the spin-spiral formation in the “twinn” gold-rich Mn$_{1-x}$Au$_x$ compound and related alloys was successfully described with similar MFT based calculations.\textsuperscript{11}

Thick bonds in Fig. 1 denote three strongest magnetic interactions in Mn$_2$Au, which completely determine the type of magnetic order. The first one, $J_1 = -2.51$ mRy, is between a given Mn site and its four nearest neighbors (NN) in neighboring Mn (001) layer. The second, $J_2 = -3.37$ mRy, is between Mn moments in neighboring Mn layers separated by a layer of gold. Both interactions are strong and negative (AF) thus defining the AF stacking of Mn layers along the $c$-direction of bct lattice. Since the neighboring Mn sites in the same (001) plane have one common Mn neighbor in the adjacent layer (see Fig. 1), the strong AF $J_1$ interaction leads to the necessarily FM ordering within the Mn(001) planes. In addition, the calculated direct interaction between Mn NN in the basal plane $J_3 = +0.73$ mRy is FM. The high value of $T_N$ is thus also a consequence of the fact that the strongest interatomic exchange interactions do not compete with each other but all enhance the stability of the most stable AF configuration. The Monte Carlo simulations with the classical Heisenberg Hamiltonian including the interactions calculated for the first nine NN shells were done on a cluster of 9192 Mn atoms ($16 \times 16 \times 16$ primitive cells of the MoSi$_2$ structure) employing periodical boundary conditions and using the conventional Metropolis algorithm. The estimated values of the ordering temperature are $T_{N} = 1610 \pm 10$ K being far above of the temperature at which Mn$_2$Au becomes structurally unstable ($\sim 950$ K).\textsuperscript{13}

We can thus predict Mn$_2$Au as an AF material with high magnetic ordering temperature. The magnetic order-disorder phase transition cannot be observed since its temperature is higher than peritectoid temperature. Due to the symmetry of the lattice in the AF ground state, the Au positions have an equal number of Mn neighbors with spin up and spin down in each of neighboring shells. In the calculations this leads to a zero moment on Au in the AF state, whereas in FM state the induced moments on Au atoms have values of about 0.14 $\mu_B$. This compensation may explain the absence\textsuperscript{14} of magnetic features in Mössbauer spectra of $^{197}$Au. Low temperature anomalies observed in temperature behavior of the susceptibility and metamagneticlike magnetization curve in the field can be related to small amounts of antisite Mn atoms on Au positions. Our CPA calculations of Mn impurity on Au site in a Mn$_2$Au host yield a local moment of 3.79 $\mu_B$ per impurity. Since at these Au positions the molecular field of the neighboring Mn atoms vanishes by mutual compensation, the Mn antisite moments may be easily aligned in an external field and cause the observed low temperature anomaly in the susceptibility.

We believe that the high temperature antiferromagnetism of Mn$_2$Au may have quite an impact in technology. In particular, it can be considered as a candidate for the application as a “pinning” layer in GMR devices. Note: Provisional U.S. patent Ser. No. 61/1066,413 application filed.\textsuperscript{28}