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Spin correlations and Kondo effect in a strong ferromagnet

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(Received 28 April 2011; published 29 July 2011)

The spin structure and electron-transport behavior of Pt-substituted MnBi thin films have been investigated. The electrical resistivity of these ferromagnetic films shows an unusual low-temperature resistance minimum or Kondo effect accompanied by positive magnetoresistance. First-principles calculations show that Mn atoms displaced to the bipyramidal interstitial sites are antiferromagnetically coupled to the Mn atoms on their regular lattice sites. We explain the observed Kondo effect and the positive magnetoresistance as the consequences of local spin correlations involving Mn atoms displaced to interstitial sites by Pt doping.

DOI: 10.1103/PhysRevB.84.014431 PACS number(s): 75.20.Hr, 72.10.Fk, 72.15.Qm, 73.50.–h

I. INTRODUCTION

The Kondo effect is one of the most widely studied phenomena in condensed-matter physics. Its most famous manifestation is a resistance minimum as a function of temperature, but the effect has recently received renewed attention due to developments in nanoscience. In the classical Kondo effect, the resistance minimum is caused by spin-flip scattering of conduction electrons by dilute magnetic impurities. In magnetically ordered Kondo lattices (heavy-fermion compounds), relatively weak interatomic exchange and Kondo spin-flip scattering can operate simultaneously. However, in strong ferromagnets with large exchange interaction and ordering temperatures above room temperature, the Kondo effect is suppressed, because it fixes the local spin directions. Here, we present our investigation of how unusual spin correlations can create a resistance minimum consistent with the Kondo effect in such a material, Pt-substituted MnBi.

MnBi is an intriguing ferromagnetic material, both magnetically and structurally. Manganese alloys tend to exhibit antiferromagnetic (AFM) order, because they have nearly half-filled 3d bands, but MnBi is one of the few ferromagnetic (FM) manganese compounds discovered so far, and it can be used as a permanent-magnet material. Other interesting magnetic properties are an extraordinarily large Kerr rotation, a Curie temperature well above room temperature, a large perpendicular room-temperature anisotropy in thin films, and a high coercivity that increases with temperature. The situation is further complicated by the involvement of ordered and disordered phases. The low-temperature phase (LTP) of MnBi is ferromagnetic and has the hexagonal NiAs structure shown in Fig. 1(a). It consists of alternating Mn and Bi layers with ABAC stacking (as contrasted to the ABC and AB stackings of the fcc and hcp structures) and exhibits large trigonal-bipyramidal interstitial sites, which may be occupied by dopant or Mn atoms. With increasing temperature, the material remains ferromagnetic up to 628 K and then undergoes a coupled structural and magnetic phase transition to a paramagnetic high-temperature phase (HTP). The high-temperature phase is a disordered NiAs phase where 10–15% of the large bipyramidal interstitial sites are occupied by Mn atoms. Rapid cooling of HTP MnBi yields a quenched high-temperature phase (QHTP), which is ferromagnetic with a Curie temperature of about 440 K.

II. MATERIALS AND METHODS

Our Pt-doped MnBi thin films were prepared using an e-beam evaporation system by sequential evaporation of Bi, Mn, and Pt onto a glass substrate. To form the alloys, Bi/Mn bilayer and Bi/Mn/Pt trilayer samples were deposited at a substrate temperature of 125°C and then annealed in situ at 375°C for 1 h. Data were collected on samples having stoichiometries of Mn_{55-x}Pt_{x}Bi_{45} (x = 0, 1.5, 3, 4, 4.5) and a thickness of about 32 nm. Figure 1(b) shows the x-ray diffraction patterns for the Mn_{55-x}Pt_{x}Bi_{45} thin films with x = 0 and x = 4.5. The polycrystalline films have a hexagonal NiAs crystal structure and are highly textured. The strong diffraction peaks from (002) and (004) planes indicate that the films have a preferred c-axis orientation. Since room-temperature MnBi exhibits an easy magnetization direction along the c axis, this corresponds to a magnetocrystalline easy axis perpendicular to the film plane. Therefore, there is no evidence for alloy secondary-phase formation and Mn clustering, although reflections from unreacted Bi have been detected.

III. RESULTS AND DISCUSSION

The magnetic hysteresis loops were recorded in the out-of-plane geometry where the magnetic field was applied perpendicular to the film plane. Figure 2(a) compares the out-of-plane room-temperature hysteresis loop of the film with the highest Pt content (x = 4.5) with that of Pt-free Mn_{55}Bi_{45}. All Mn_{55-x}Pt_{x}Bi_{45} thin films exhibit nearly rectangular hysteresis loops, but the saturation magnetization M_{S} and coercivity H_{c} change significantly as a function of Pt concentration. The magnetization decreases from 506 emu/cm\(^3\) (x = 0) to 311 emu/cm\(^3\) (x = 4.5) and coercivity increases from 5.7 kOe (x = 0) to 17.7 kOe (x = 4.5). It is interesting to note that the magnetization decreases much faster than predicted by simple dilution from the fraction of Pt atoms; that is, a 40% drop in magnetization is caused by only 4.5% Pt. The disproportional magnetization decrease suggests that the Pt enhances the interstitial occupancy of the Mn atoms, which are coupled...
antiferromagnetically to the original Mn sublattice. In fact, this is consistent with neutron diffraction data that indicate interstitial manganese tends to couple antiferromagnetically to its Mn neighbors on the regular lattice sites. This is a natural consequence of the predominantly antiferromagnetic exchange of Mn atoms, which need specific requirements, such as the regular lattice occupancy in MnBi, to become ferromagnetic.

Support for the interstitial mechanism of magnetization reduction due to Pt addition is provided by first-principles calculations that we performed using the projector augmented-wave method and its implementation in the Vienna *ab initio* simulation package (VASP) code within the Perdew-Burke-Ernzerhof generalized gradient approximation. We have implemented full atomic relaxation with total forces of less than 0.005 eV/Å after relaxation and have examined both the FM and AFM couplings between interstitial and regular Mn spins. Four types of supercells are considered, each containing 32 atoms: (i) ordered MnBi (Mn16Bi16), corresponding to the LTP; (ii) disordered MnBi (Mn16Bi16), roughly corresponding to the QHTP; (iii) solid solution of Pt in ordered MnBi, where one Mn atom in each cell is replaced by Pt (Mn15PtBi16); and (iv) Pt in disordered MnBi, where the Pt displaces one Mn atom per supercell from the regular site to the interstitial site (Mn15PtBi16).

The calculations predict AFM couplings between the interstitial and regular Mn atoms in both (ii) disordered MnBi and (iv) disordered MnBi-Pt. However, the magnitude of the magnetic moment reduction due to Pt addition is provided by first-principles calculations that we performed using the projector augmented-wave method within the Perdew-Burke-Ernzerhof generalized gradient approximation.21 We have implemented full atomic relaxation with total forces of less than 0.005 eV/Å after relaxation and have examined both the FM and AFM couplings between interstitial and regular Mn spins. Four types of supercells are considered, each containing 32 atoms: (i) ordered MnBi (Mn16Bi16), corresponding to the LTP; (ii) disordered MnBi (Mn16Bi16), roughly corresponding to the QHTP; (iii) solid solution of Pt in ordered MnBi, where one Mn atom in each cell is replaced by Pt (Mn15PtBi16); and (iv) Pt in disordered MnBi, where the Pt displaces one Mn atom per supercell from the regular site to the interstitial site (Mn15PtBi16).
FIG. 3. (Color online) (a) Low-temperature resistivities of Pt-doped MnBi thin films with Pt concentrations of 0%, 1.5%, 3%, 4%, and 4.5%. The temperature is on a logarithmic scale and the baselines of the plots for 1.5%, 3%, 4%, and 4.5% Pt concentrations are shifted for clarity (see tic marks on the left). The curves are merely guides to the eye. (b) Comparison of the resistivity of Mn50Pt5Bi45 film in zero magnetic field (open circles) and in a field of 7 T (solid circles). The straight-line fit to the resistivity below T_{min} shows that the temperature dependence of the resistivity is logarithmic. The dashed black line fits the empirical form of the numerical renormalization group (NRG) results, \( \rho(T) = \rho_0 [1 + (2^{1/\xi_s} - 1)(T/T_k)^{\alpha_s}]^{-\alpha_s} \) to the low-temperature resistivity data.

FIG. 4. (Color online) (a) Temperature of resistivity minima \( T_{min} \) as a function of Pt concentration \( c_p \) in a linear scale. (b) Extrapolation of the data in \( T_{min} \) vs \( c_p^2 \) plot to estimate the value of \( T_{min} \) for 1.5% Pt. The open circle corresponds to the estimated value of 1.5 K for 1.5% Pt concentration.

NRG results for \( \xi_s = 2 \) and Kondo temperature \( T_K = 5.1 \) K, where the experimental data fall above the NRG results at low temperature. This suggests that the magnetic moments responsible for Kondo scattering are not fully screened at our lowest available temperature. This is consistent with the fact that the experimental \( \rho(T) \) curve shows a slow approach to saturation with decreasing temperature. We also have found that the temperature \( T_{min} \) of the resistivity minimum increases according to \( T_{min} \propto c_p^2 \) from 6 K for \( c_p = 3 \% \) to 14 K for \( c_p = 4.5 \% \), as shown in Figs. 4(a) and 4(b). The value of \( T_{min} \) for 1.5% Pt estimated from the extrapolation of the \( T_{min} \) versus \( c_p^2 \) plot is 1.5 K, which is consistent with the fact that the sample with 1.5% Pt doping does not show a resistivity minimum down to our lowest available temperature of 2 K [see Fig. 4(b)]. We note that \( T_{min} \) does not follow the standard scaling law with Pt concentration. This is natural because the Kondo scattering is not realized by the added Pt atoms but by the concentration of loosely exchange-coupled interstitial Mn atoms. The Pt changes this concentration as a regular but nonlinear function of the Pt content.

Figure 3(b) compares the resistivity of Mn50Pt5Bi45 in zero magnetic field and in a perpendicular magnetic field of 7 T. The measured magnetoresistance is positive, as contrasted to the usual suppression of the Kondo effect by an external magnetic field, which corresponds to a negative magnetoresistance. Although a positive magnetoresistance is observed in simple metals\(^{37}\) and also in some ferromagnets due to a quantum interference effect,\(^{38}\) we propose a different model to explain the resistance minimum and the unexpected positive magnetoresistance in our system. We assume as discussed above that Pt displaces some of the Mn atoms from their regular positions in the NiAs structure to interstitial sites. This displacement and the presence of the Pt atoms weaken the ferromagnetic exchange between the Mn atoms and eventually create a certain fraction of interstitial Mn spins that are only weakly exchange-coupled to the remainder of the crystal.

The above first-principles calculations yield the exchange constants \( J' = |E_{AFM} - E_{FM}|/2 \) for a Mn atom displaced to an interstitial site, namely \( J'/k_B = -1770 \) K for the Mn16Bi16 supercell and \( J'/k_B = -320 \) K for the Mn53PtBi16 supercell. This must be contrasted to the ferromagnetic exchange of the Mn atoms on their regular lattice sites \( (J_0 > 0) \). In fact, there are many ways to coordinate an interstitial Mn atom by Mn, Bi, and Pt nearest and more distant neighbors, and...
large supercells would be necessary to accurately describe the exchange interaction of the individual Mn atoms. However, we have calculated the effect of the larger Pt concentration. This allows us to explore the effect of two Pt atoms in the neighborhood of an interstitial Mn. We find that the presence of a second Pt as the nearest neighbor alters the exchange interactions and, depending on the relative position of the second Pt atom with respect to the first, the onsite exchange parameter may be either FM (0.022 eV = 260 K) or AFM (−0.034 eV = −396 K) with a reduced magnitude of the exchange.

Figure 5 illustrates this mechanism by showing a schematic distribution $P(J)$ of the Mn exchange interactions. The Kondo effect is realized by Mn atoms with weak interatomic exchange (gray area). These spins are able to undergo Kondo spin-flip scattering and to yield a resistance minimum. To understand the positive magnetoresistance, it is necessary to consider a distribution function of the Mn exchange interaction. The FM coupling of the Mn on the regular sites ($J_0 > 0$) and the AFM coupling of Mn of the lattice sites considered above ($J' < 0$) indicate broad exchange distributions with two or more smoothed FM and AFM peaks. As a consequence, $P(J)$ is nonzero over a fairly broad range of exchange constants $J$. If some of these $J$ values are zero or very small, then they can undergo Kondo flipping and enhance the resistivity. The challenge is now to estimate the fraction $W$ of such spins as a function of the magnetic field $H$.

The Kondo effect persists down to very low concentrations of localized moments, and it is safe to assume that $W \ll 1$. In fact, most Mn spins are subject to strong AFM or FM interactions, and neither the external magnetic field nor the Kondo interactions are able to switch these spins. This means that most Mn spins are frozen (Fig. 5) and that the remaining fraction $W$ of loosely coupled spins $\hat{\delta}$ interact with the remaining frozen spins $\hat{\delta}'$ via a mean-field interaction of the type

$$\hat{H} = -\sum_j J_{ij} \hat{\delta}_i \cdot \langle \hat{\delta}'_j \rangle - \mu_0 \mu H \cdot \sum \hat{\delta}_i.$$  

This equation, which neglects the interactions between loose spins, provides a definition for the effective exchange of the $i$th spin, $J(i) = \sum_j J_{ij} \langle \hat{\delta}_j \rangle$. The fraction $W$ of loose spins is then described by the distribution $P(J)$. We note that $W$ is a largely unknown function of the Pt concentration. In fact, the smearing of the main peaks of the distribution function in Fig. 5 requires a certain degree of disorder, and virtually no Kondo scattering is expected for small Pt concentrations. This is consistent with the aforementioned $c_{pt}^2$ dependence of $T_{\text{min}}$.

Equation (1) means that the magnetic field adds to the exchange and effectively shifts the distribution $P(J)$. A trivial example is that a strong positive field fixes all spins in the $\uparrow$ direction and completely suppresses the Kondo effect. However, our fields are rather weak, of the order of 5 K in temperature units, compared to the FM or AFM exchange interaction of the order of 500 K. The probability $W$ therefore corresponds to a thin slice of the distribution, as indicated in Fig. 5. Assuming that Kondo flipping occurs for some range $|J| \ll \delta J$, we find

$$W = \int_{-\delta J}^{\delta J} P(J - \mu_0 \mu H) dJ.$$  

With increasing field $H$, the fraction $W$ of loose spins increases or decreases, depending on $P(J)$, and the corresponding change is described by $W = -2\delta J P - 2\delta J \mu_0 \mu H dP/dJ$. Here both $P$ and $dP/dJ$ refer to $H = 0$. Since the magnetoresistance increases with $W$, negative and positive slopes $dP/dJ$ correspond to a positive or negative magnetoresistance, respectively. For the schematic exchange distribution of Fig. 5, the magnetoresistance is positive (dark gray area), which provides a qualitative explanation of positive magnetoresistance. In particular, our first-principles calculations indicate that the addition of Pt reduces the magnitude of the negative exchange of the interstitial Mn. This means that the AFM peak of the distribution $P(J)$ moves toward $J = 0$, thereby enhancing $P$ and $dP/dJ$ compared to the undoped material.

IV. CONCLUSION

In summary, our MnBi-Pt system shows three unusual features. First, it exhibits a low-temperature Kondo resistance minimum in a strong ferromagnetic material with a Curie temperature well above room temperature. Second, we have shown that the nonmagnetic Pt content controls the Mn spin correlations and the Kondo effect. Third, the system exhibits a positive magnetoresistance, which is unusual for Kondo systems. Both the Kondo effect and the positive magnetoresistance are explained as a materials-specific exchange effect, caused by the disorder in the MnBi lattice due to the Pt-induced displacement of Mn atoms onto interstitial sites.

ACKNOWLEDGMENTS

We would like to thank R. D. Kirby and E. Tsymbal for helpful comments. This work was supported by the NSF-MRSEC, DOE (P. K. and D. J. S.) and NCMN. The computational part was performed utilizing the Blackforest Cluster Computing Facility at UNO.
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