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First-principles prediction of high Curie temperature for ferromagnetic bcc-Co and bcc-FeCo alloys and its relevance to tunneling magnetoresistance

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The authors determine from first principles the Curie temperature T_C for bulk Co in the hcp, fcc, bcc, and body-centered-tetragonal (bct) phases, for FeCo alloys, and for bcc and bct Fe. For bcc Co, $T_C = 1420$ K is predicted. This would be the highest Curie temperature among the Co phases, suggesting that bcc-Co/MgO/bcc-Co tunnel junctions offer high magnetoresistance ratios even at room temperature. The Curie temperatures are calculated by mapping *ab initio* results to a Heisenberg model, which is solved by a Monte Carlo method. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2710181]

In the past few years we are witnessing a compelling race of different research groups[1–4] hunting the maximum tunneling magnetoresistance ratio (TMR) of magnetic tunnel junctions[5] (MTJs) at room temperature (RT). MTJs, made of two ferromagnetic electrodes separated by an insulating barrier, open vistas to a wide field of technological applications, in particular, in nonvolatile magnetic random access memory or recording heads for ultrahigh-density hard-disk drives.

After the initially reported observations of TMR at room temperature[6] in Al_2O_3-based junctions, reaching 30% at 4.2 K and 18% at 300 K, giant values of over 150% at RT have been experimentally achieved for fully epitaxial MgO-based MTJs.[1–4,7] Theory predicts (at temperature $T=0$) extremely high TMR of over 1000% for Fe/MgO/Fe (Ref. 8) and even higher for epitaxial bcc-Co/MgO/bcc-Co junctions.[9] bcc Co is a metastable phase and cannot be grown as a single crystal. Recently, however, it has been possible to grow bcc Co in contact with MgO,[7,10,11] and epitaxial bcc-Co/MgO/bcc-Co(100) MTJs have shown a high TMR, unusually stable[11] with T.

In most MTJs there is a large difference of the TMR between cryogenic and room temperatures. The TMR (relative change of resistance when the magnetic leads are coupled either ferromagnetically or antiferromagnetically) depends on the details of the electronic structure, such as the spin polarization of the ferromagnet at the Fermi level E_F (Ref. 12) and the spin-dependent symmetry of the states at E_F.[7,13] At $T>0$, magnetic excitations mix the two spin channels, decreasing the TMR.[14] One can infer that a high T_C and spin stiffness entail a temperature stability of the magnetic structure and of the TMR. In this letter we investigate the Curie temperature of bcc-Co and $Fe_{1-x}Co_x$ alloys and relate it to fcc Co, hcp Co, and bcc Fe, concluding that a high (calculated) (Ref. 20)T_C of bcc Co is responsible for the temperature stability[11] of TMR in Fe/bcc-Co/MgO/bcc-Co/Fe junctions.

We calculate the Curie temperature using a standard recipe: the adiabatic approximation for the calculation of magnon spectra.[15,16] *Ab initio* total-energy results are mapped to the classical Heisenberg model,

$$H = -\sum_{i,j;i\neq j} J_{ij}\mathbf{e}_i \cdot \mathbf{e}_j. \tag{1}$$

Here, J_{ij} are the exchange constants between the magnetic moments at sites i and j, and $\mathbf{e}_i$ is a unit vector along the moment of atom i. T_C was calculated within this model by a Monte Carlo method (using 1728 atoms in the supercell) by locating the susceptibility peak.

The *ab initio* results are calculated within the generalized gradient approximation[17] to density-functional theory. We employ the full-potential Korringa-Kohn-Rostoker (KKR) Green function method,[18] using the coherent potential approximation for the electronic structure of the $Fe_{1-x}Co_x$ random alloys. The exchange constants J_{ij} are related to the Green function[16] assuming an infinitesimal direction change of the moments at sites i and j. For Fe and Co we also compare to a complementary method, where finite-angle static magnon dispersion relations, $J(\mathbf{q})$, are calculated on a dense mesh of $\mathbf{q}$ points in the Brillouin zone within the full-potential linearized augmented plane-wave method (FLAPW).[19] From $J(\mathbf{q})$, the real-space constants J_{ij} are found via a Fourier transform.[15] The two methods give the same trends. We stress that the trends are important for our conclusions and not the absolute values of T_C, which are off the experimental value (bcc Fe: $T_C=1043$ K; fcc Co: $T_C=1403$ K)[20,21] by ~10%.

Our calculations include bcc Fe and Co, body-centered-tetragonal (bct) Fe and Co [considering growth on MgO(001)], the disordered alloys $Fe_{0.75}Co_{0.25}$, $Fe_{0.50}Co_{0.50}$, and $Fe_{0.75}Co_{0.25}$, and the ordered alloy FeCo (in the CsCl structure). In order to see the effect of compression on the magnetic properties, we calculated the results at two lattice parameters: $a=2.30$ a.u.$=2.804$ Å, corresponding to the calculated equilibrium lattice parameter of bcc Co, and $a=2.40$ a.u.$=2.857$ Å. We find for hcp Co an equilibrium lattice parameter $a=2.488$ Å, with $c/a=1.623$ (experimental values are $a=2.51$ Å, $c/a=1.623$), for fcc Co $a=3.52$ Å (experimental value is $a=3.54$ Å), for bcc Co $a=2.804$ Å (extrapolated experimental value is $a=2.819$ Å),[22] and for bcc Fe $a=2.825$ Å (experimental value is $a=2.867$ Å). For Co and Fe on MgO(001) we find a mismatch of 5% in the surface lattice parameter (compared to $a_{MgO}/\sqrt{2}=2.978$ Å), resulting in a ratio $c/a=0.857$ for bct Co and $c/a=0.909$ for

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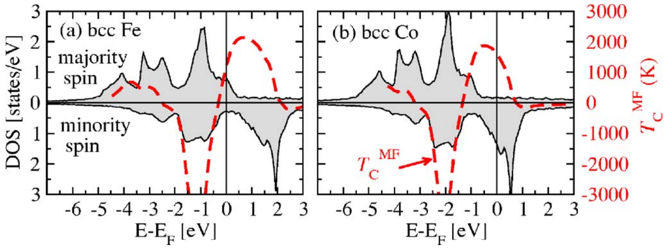

FIG. 1. (Color online) Density of states (solid line) and mean-field ordering temperature (dashed line) for (a) bcc Fe and (b) bcc Co.

bct Fe. The ground state spin moments per Co atom, $M^{\mathrm{hcp}}=1.6$, $M^{\mathrm{fcc}}=1.65$, and $M^{\mathrm{bcc}}=1.75\mu_B$, change with the crystal structure by less than 10%. The density of states (DOS) of bcc Co, shown in Fig. 1, exhibits the typical bimodal behavior of the bcc lattice with bonding and antibonding states. The spin polarization at E_F, $P=-82\%$, is negative and has a larger (absolute) value than for bcc Fe ($P=52\%$). Our calculated band structure agrees with the one of Ref. 23.

Our results on the magnetic properties are summarized in Table I. A striking effect is that the first-neighbor exchange constants and the T_C increase with the Co concentration in $\mathrm{Fe}_{1-x}\mathrm{Co}_x$ alloys, with a maximum of about $T_C=1670$ K for the ordered FeCo alloy and a $T_C\approx 1400$ K for bcc and bct Co. In contrast, bct Fe suffers a 20% decrease of T_C compared to bcc Fe. We also find interesting trends in the magnetic moments and in the lattice-parameter dependence of the exchange constants. As the Co concentration increases, the local moment of Fe becomes larger, climbing from $M_{\mathrm{Fe}}\approx 2.2\mu_B$ in pure Fe to about $2.6\mu_B$ in $\mathrm{Fe}_{0.25}\mathrm{Co}_{0.75}$. The Co moment is comparatively independent of concentration, about $1.73-1.80\mu_B$. Moreover, the Fe–Fe first-neighbor exchange constants $J_1(\mathrm{Fe-Fe})$ are strongly dependent on the lattice parameter for low Co concentrations x but much less so for high x; the Co–Co and Fe–Co exchange constants, $J_1(\mathrm{Co-Co})$ and $J_1(\mathrm{Fe-Co})$, are much less affected by the lattice parameter at any x. The same behavior is found for the longer-distance exchange constants (not shown here). This leads to a strong dependence of T_C on the lattice parameter for Fe-rich alloys and a weak dependence for Co-rich alloys.

The change of the Fe properties upon increasing the Co concentration can be explained by observing that Fe progressively changes character from a weak ferromagnet (i.e., both majority- and minority-spin d states, $d^{\uparrow}$ and $d^{\downarrow}$, are only partly occupied for pure Fe) to a strong ferromagnet ($d^{\uparrow}$ states become fully occupied); Co itself is a strong ferromagnet. The progressive change occurs because the d(Fe)-d(Co) hybridization is weaker than the d(Fe)-d(Fe) hybridization, as the Co d states are more localized (they are deeper in the atomic potential well) than the Fe d states. As a result, an increased coordination with Co results in an increase of the Fe moment and exchange splitting, driving the Fe $d^{\uparrow}$ states lower and the Fe $d^{\downarrow}$ states higher in energy. The Co moment, on the other hand, is rather stable (around $1.8\mu_B$), since the Co $d^{\uparrow}$ states are always fully occupied.[24] The average moment per unit cell, $\bar{M}$, first rises upon alloying with Co, due to the rapid increase of the Fe local moment, then peaks and drops for higher Co content (because of the comparatively lower Co moment). This peak of $\bar{M}$ in Fe–Co alloys is long known,[25–28] and is related to the triangular shape of the Slater-Pauling curve at the center of the 3d series;[27] density-functional calculations reproduce this behavior, although they underestimate the local Fe moment by about 10% in these alloys.[28]

In a weak ferromagnet the magnetic properties can be easily affected by structural perturbations (compression or tetragonalization) because an extended part of the Fermi surface has $d^{\uparrow}$ and $d^{\downarrow}$ characters, allowing for $d^{\uparrow}$-$d^{\downarrow}$ charge transfer upon the structural perturbation. Such $d^{\uparrow}$-$d^{\downarrow}$ transfer can affect the local moment, but even more the spin suscep-

TABLE I. Calculated (within KKR) magnetic moments (in μ_B), first-neighbor exchange constants J_1 (in meV), and T_C (in K) of bcc FeCo alloys, bcc Fe and Co, bct Fe and Co, and fcc and hcp Co. The bcc structures are considered at two lattice constants to show the effect of compression. For the bct structures, the in-plane lattice constant was adapted to MgO and c/a was relaxed. T_C is calculated by a Monte Carlo method with exchange constants derived from the KKR or FLAPW methods.

Alloy	a (Å) (c/a)	M_{Fe}	M_{Co}	$\bar{M}$	$\bar{M}_{\mathrm{exp}}$ [a]	$J_1^{\mathrm{Fe-Fe}}$	$J_1^{\mathrm{Co-Co}}$	$J_1^{\mathrm{Fe-Co}}$	T_C^{KKR}	T_C^{FLAPW}
Fe bcc	2.804	2.107	⋯	2.107	2.22	17.45	⋯	⋯	970	1120
	2.857	2.197	⋯	2.197		15.25	⋯	⋯	900	
Fe bct	2.978 (0.909)	2.321	⋯	2.321	⋯	12.71	⋯	⋯	750	
$\mathrm{Fe}_{0.75}\mathrm{Co}_{0.25}$	2.804	2.421	1.785	2.263	2.45	25.80	24.54	31.78	1390	
(Disordered bcc)	2.857	2.512	1.803	2.335		26.93	24.61	31.67	1490	
$\mathrm{Fe}_{0.50}\mathrm{Co}_{0.50}$	2.804	2.523	1.778	2.151	2.35	28.55	22.05	30.76	1600	
(Disordered bcc)	2.857	2.588	1.801	2.194		27.99	22.13	30.27	1600	
FeCo	2.804	2.729	1.727	2.228	2.42	⋯	⋯	28.84	1660	
(Ordered CsCl struct.)	2.857	2.803	1.743	2.273		⋯	⋯	28.50	1670	
$\mathrm{Fe}_{0.25}\mathrm{Co}_{0.75}$	2.804	2.560	1.759	1.959	⋯	26.64	20.01	28.33	1520	
(Disordered bcc)	2.857	2.633	1.791	2.002		26.42	20.06	28.01	1540	
Co bcc	2.804	⋯	1.751	1.751	⋯	⋯	18.48	⋯	1420	1670
	2.857	⋯	1.790	1.790		⋯	18.71	⋯	1370	
Co bct	2.978 (0.857)	⋯	1.740	1.740	⋯	⋯	16.76	⋯	1380	
Co fcc	3.519	⋯	1.646	1.646	⋯	⋯	13.82	⋯	1280	1200
Co hcp	2.487 (1.623)	⋯	1.602	1.602	1.71	⋯	14.66	⋯	1300	1350

[a] References 21 and 25.

tibility (and exchange constants J_{ij}) which is sensitive to $d^{\uparrow}$-$d^{\downarrow}$ Fermi-surface crossing or nesting[29] because of virtual $d^{\uparrow}$-$d^{\downarrow}$ spin-flip excitations. In the case of strong ferromagnetism (Co or FeCo alloys), small structural perturbations cannot cause a $d^{\uparrow}$-$d^{\downarrow}$ charge transfer, because the $d^{\uparrow}$ band is fully occupied and well under E_F. Thus the exchange interactions are more stable in Co and FeCo alloys.

We proceed to the discussion of the exchange interactions and T_C by introducing[16] the coefficient $J_0=\Sigma_{i\neq 0}J_{0i}$, corresponding to the band-energy cost for flipping the magnetic moment of a single atom, reflecting a "single-site spin stiffness." It is related to the mean-field Curie temperature via $k_B T_C^{\mathrm{MF}}=2J_0/3$ (k_B is Boltzmann's constant). (It is well known that mean-field theory overestimates T_C, but it is a useful tool for trends analysis.) By treating E_F as a parameter, we calculate $T_C^{\mathrm{MF}}(E)$ as a function of band filling; in this way we are able to see the individual contribution of the states at each energy to the exchange interactions. In Fig. 1 we show $T_C^{\mathrm{MF}}(E)$, together with the DOS, for bcc Fe and Co. Evidently, $T_C^{\mathrm{MF}}(E)$ has a very similar form for Fe and Co, up to the approximately rigid band shift (it also has slightly higher values for Fe because of the stronger *d*-*d* hybridization); thus, Fe and Co can be compared in a unified picture. The negative values of $T_C^{\mathrm{MF}}(E)$, peaking around −2 eV for Co and −1 eV for Fe, indicate an antiferromagnetic coupling, known from δ-Mn.[27] At higher energies the double-exchange mechanism sets in and $T_C^{\mathrm{MF}}(E)$ obtains strong positive contributions as E crosses the final part of the $d^{\uparrow}$ states and the antibonding $d^{\downarrow}$ states. Finally it drops to zero once the $d^{\downarrow}$ states are filled and the exchange mechanism is not present anymore.

In Fe, E_F is located at a steep, ascending point of $T_C^{\mathrm{MF}}(E)$, before the maximum. Therefore, small structural perturbations resulting in band shifts have a strong influence on the T_C of Fe, as seen in Table I. For Co, $T_C^{\mathrm{MF}}(E)$ is already descending at E_F but is not as steep as for Fe. From this argument, Co is expected to have a higher and more robust T_C than Fe. In an FeCo alloy E_F is in-between, at the maximum of $T_c^{\mathrm{MF}}(E)$; then one expects the highest and most robust T_C, as is found by the Monte Carlo calculations.

In conclusion, ferromagnetism is found to be more robust in bcc Co than in bcc Fe. The T_C of bcc Co is calculated to be the highest among all Co phases and stable with respect to structural changes even in the tetragonalized (bct) structures. This is advantageous in the temperature-dependent TMR of Co/MgO/Co MTJs compared to Fe/MgO/Fe, as observed in recent experiments.[11] Studies have shown[30] that the TMR depends on the detailed interface properties, including the interface magnetization $M_I(T)$. Supported by the comparatively thick ferromagnetic back lead (>100 ML), the interface shows the same T_C as the lead, which approaches quickly the bulk value.[31]

We suggest FeCo/bcc Co/MgO/bcc Co/FeCo(100) as an ideal junction for high TMR at room temperature. The reasons for this are as follows: (i) FeCo has the highest T_C and is thus an ideal back lead. (ii) The T_C of bcc Co is also very high (higher than Fe), promising lower magnetic fluctuations at the interface. (iii) Epitaxial bcc-Co/MgO(100) interfaces present excellent coherent spin-dependent transport properties,[9,32] unlike a possibly disordered FeCo/MgO interface. We therefore conclude that, at RT, the suggested junction has a higher TMR than Fe/MgO/Fe(100) or even Fe/bcc Co/MgO/bcc Co/Fe(100).

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