Magnetocrystalline anisotropy and orbital moments in transition-metal compounds

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The magnetocrystalline anisotropy energy and anisotropy of the orbital angular momentum have been calculated from first principles for Co and for a variety of intermetallic compounds including YCo_5. For all compounds the predicted easy axes are in agreement with experiment. A strong correlation between the anisotropy of the orbital angular momentum and the energy is found for the compounds that do not contain Pt. For those that do contain Pt, Pt is shown to contribute significantly to the anisotropy energy.

Much of the interest in the transition-metal compounds YCo_5,[1] $FePd$,[2] $FePt$,[3] and $CoPt$,[4] is related to their large magnetocrystalline anisotropy energies (MAE), which are of the order of 0.5 meV per magnetic $3d$ atom. In general the anisotropy energies found in transition-metal compounds are much smaller. Why these compounds exhibit such a large anisotropy energy and why the easy axis is oriented along the c axis is not known. Since the work of Brooks[5] more than 50 years ago, there has been little progress towards a quantitative theory of the magnetocrystalline anisotropy for transition-metal compounds with itinerant d electrons. In this paper we shall demonstrate that the calculation from *first principles* of the MAE of such compounds is now possible.

Within the framework of the local-spin-density approximation[6] we have previously shown that, although the correct magnitude of the anisotropy energy of bcc Fe, hcp Co, and fcc Ni was calculated, the wrong easy axis was predicted for Co and Ni.[7] Predictions for [111] Co/Pd, Co/Cu, and Cu/Ag multilayers,[8] and [001] Co/Pd multilayers,[9] for which the anisotropy energy is as much as a factor of 10 larger than that for bulk hcp Co, were in good agreement with experiment. For the multilayers, however, the structures are not well characterized experimentally and the influence on the MAE of the interface roughness and of the strain resulting from the lattice mismatch of the component materials are not known. Calculations of the MAE for the compounds mentioned above, for which the crystal structure is well known, will enable a better comparison between theory and experiment.

In this article results are presented for the calculated anisotropy energy, ΔE, and the anisotropy of the orbital angular momentum, ΔL, for Co, YCo_5, FePd, FePt, CoPt, and the hypothetical compounds CoPd, FeIr, and CoIr. We have investigated the influence of a recently proposed orbital polarization correction, introduced by Brooks[10] to account for the magnetic moments in nearly localized $5f$ electron compounds.[10,11] This correction yielded larger orbital moments in Fe, Co, and Ni and thus a better agreement of the calculated g factors for Fe and Co with experiment.[12] The easy axis is predicted correctly for all compounds. When the orbital polarization correction is included, the magnitude of the MAE is in quite good agreement with experiment. By calculating ΔE and ΔL as a function of the bandfilling we demonstrate that a simple correspondence exists between them, with the exception of the compounds containing Pt. An easy c axis orientation is found for a wide range of fillings around the actual Fermi energy, indicating that this result does not depend strongly (on a scale of 0.1 electron per $3d$ atom) on the location of the Fermi energy with respect to specific energy bands. However, because ΔE assumes both negative and positive values for variations with the bandfilling on a scale of 1 electron per $3d$ atom, the large value and sign of the MAE of the compounds must be regarded as being due to a favorable (but accidental) position of the Fermi energy.

The MAE as a function of the bandfilling q, $\Delta E^n(q)$, is obtained by first solving the Kohn-Sham equations[6] self-consistently for the scalar-relativistic spin-polarized[13] Hamiltonian for the material with n valence electrons. This is done using the linear muffin-tin orbital method in the atomic sphere approximation including s, p, d, and f partial waves in the basis.[14] The spin-orbit coupling term, $\xi l \cdot \sigma$, is then added and the full Hamiltonian is diagonalized for two directions of the magnetization, $\hat{n}$. The force theorem[15] is employed to yield the anisotropy energy as the difference in sums of Kohn-Sham eigenvalues for bandfilling q. The convergence of the Brillouin-zone integrals is as good as that reported in Refs. 7 and 8. The magnetostatic anisotropy energy, calculated by performing a dipole-dipole sum,[7] is smaller than the MAE by more than an order of magnitude. It will be omitted in the following.

The orbital polarization term[10-12] in the Hamiltonian has the form $-BLl \cdot \hat{n}$, where the Racah B parameter is calculated using the radial d wave functions. The orbital angular momentum, L, is obtained by iterating the relativistic Hamiltonian (including both spin-orbit coupling and orbital polarization) to self-consistency with $\hat{n} \parallel c$. The MAE then calculated using the force theorem is correct to first order in the changes in the charge, spin and orbital angular-momentum densities upon a rotation of the magnetization direction.[7,15]

YCo_5 forms in the $CaCu_5$ structure, in which the Cu atoms occupy sites of two different symmetries, denoted $2c$ and $3g$. FePt, FePd, and CoPt are ordered solid solutions with the AuCu structure, but for CoPd such an

TABLE I. Calculated spin and orbital contributions to the magnetic moment (in μ_B per unit cell) together with data for the c/a ratios and atomic sphere radii, S (in a.u.). The orbital moment is calculated without (M_{L_0}) and with (M_L) orbital polarization. Including orbital polarization self-consistently, the spin magnetic moment changes by a few 0.01 μ_B at most. This result has not been listed separately in the table, but is included in the total calculated magnetic moment M (OP). The two spin moments for Co in YCo$_5$ refer to the $2c$ and $3g$ sites, respectively. The orbital angular moments for these sites are equal.

	c/a	$S_{Co,Fe}$	S_{oth}	$M_S^{Co,Fe}$	$M_{L_0}^{Co,Fe}$	$M_L^{Co,Fe}$	M_S^{oth}	$M_{L,0}^{oth}$	M (OP)	M (expt.)
Co	1.633	2.621		1.57	0.08	0.13			1.70	1.75
YCo$_5$	0.810	2.645	3.497	1.32–1.49	0.12	0.23	-0.31	0.02	8.0	8.3
FePd	0.960	2.701	2.915	2.92	0.09	0.15	0.33	0.03	3.4	3.3
FePt	0.960	2.701	2.915	2.91	0.08	0.13	0.34	0.07	3.4	3.4
CoPd	0.979	2.624	2.901	1.87	0.14	0.29	0.32	0.03	2.5	
CoPt	0.979	2.624	2.901	1.86	0.12	0.25	0.32	0.06	2.5	2.4
FeIr	0.960	2.701	2.915	2.06	0.11	0.24	-0.01	-0.07	2.3	
CoIr	0.979	2.624	2.901	0.88	0.10	0.18	0.08	-0.03	1.1	

ordering is not known. For CoPd and FePt calculations have been carried out using the experimental lattice constants of CoPt and FePd, respectively. Atomic sphere radii are listed in Table I together with the c/a ratios used.

The results for the anisotropy energy versus the bandfilling for Co, YCo$_5$, FePd, CoPd, FePt, and CoPt, obtained including spin-orbit coupling together with orbital polarization are shown in Fig. 1 by the solid lines; dotted lines indicate results obtained including spin-orbit coupling only. The corresponding anisotropy energies, $\Delta E \equiv \Delta E^n(n)$, are indicated by the solid and open circles. It is seen that for all compounds the correct easy axis is predicted, both with and without orbital polarization, and only fair agreement between the experimental and theoretical energies is obtained with spin-orbit coupling only. The experimental values in the figure are the most recently reported ones.[1–4] Except for FePt, they are low-temperature values. Upon including orbital polarization the functional form of $\Delta E^n(q)$ does not change, but the MAE is enhanced and the agreement with experiment is improved (except for the Pt compounds; the reason for this will be discussed below). For Co, inclusion of the orbital polarization term leads to the correct sign of the
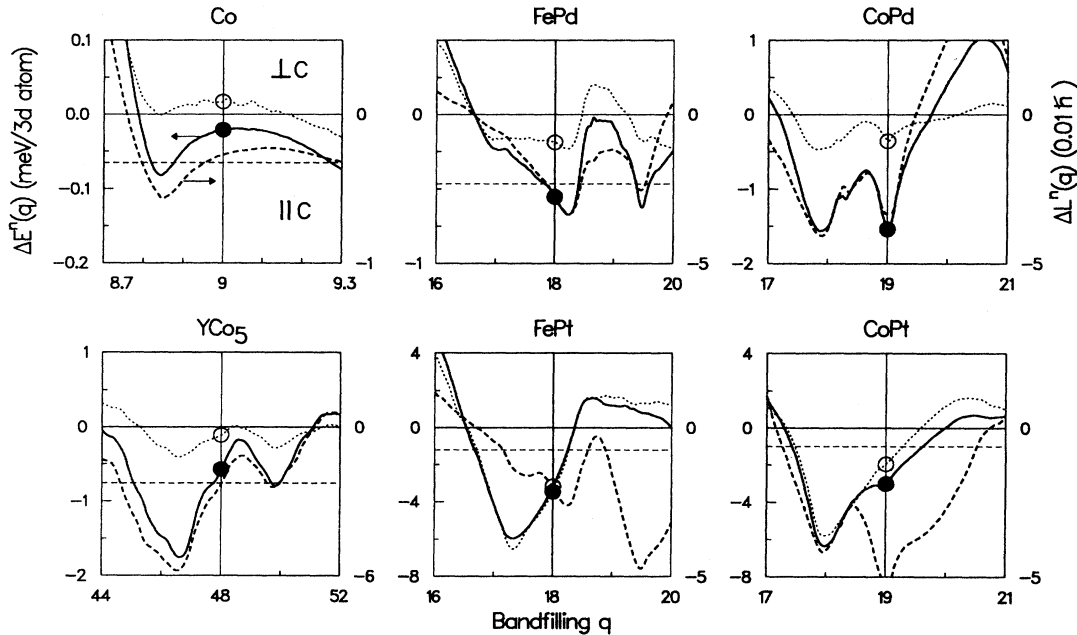

FIG. 1. The magnetocrystalline anisotropy energy per $3d$ atom, $\Delta E^n(q)$, vs bandfilling q for Co, FePd, CoPd, YCo$_5$, FePt, and CoPt. The solid curves were calculated with spin-orbit coupling and orbital polarization terms. The dotted curves were calculated without the orbital polarization correction. The anisotropy in the $3d$ orbital angular momentum per $3d$ atom (calculated including spin-orbit coupling and orbital polarization), $\Delta L^n(q)$, is shown by the dashed curves referring to the right-hand vertical axis. The actual number of valence electrons, n, is denoted by the vertical line. The calculated anisotropy energies, $\Delta E \equiv \Delta E^n(n)$, are denoted by the solid and open circles, and the experimental value is indicated by the horizontal dashed line.

MAE.

There is a clear correlation between the anisotropy in the orbital angular momentum per $3d$ element (shown as the dashed curves in Fig. 1) and the anisotropy energy, but again not for the Pt compounds. Resolving the anisotropy in the orbital angular momentum into contributions from the $2c$ and $3g$ types of atoms in YCo_5 (Fig. 2), it can be seen that the peaked structure in $\Delta L^n(q)$ is mainly determined by the Co($2c$) atoms. Although there were experimental indications that the anisotropy is associated with these atoms,[1] we find that at the actual Fermi energy ($q = n$) ΔL_{3g} exceeds ΔL_{2c}.

In Table I the results for the spin and orbital contributions to the magnetic moment are listed, obtained with and without orbital polarization. The effect of including orbital polarization is to double the orbital moments. For YCo_5 the orbital moments contribute 15% to the magnetization, about twice as much as in hcp Co. This confirms expectations based upon experimental observations.[1] The discrepancy between the total calculated magnetic moment and the experimental value is about 0.05 μ_B per Co atom, which is similar to that for hcp Co.

Within the minority spin subband, orbital polarization represents an enlarged effective spin-orbit coupling parameter $\bar{\xi} = \xi + BL$. Within perturbation theory[16] the orbital angular momentum is proportional to ξ. Under the additional assumption that mixing due to the spin-orbit coupling between the majority and minority spin subbands is negligible (i.e., in the large exchange limit), one expects, upon including orbital polarization, a new orbital angular momentum of $L = L_0/(1-L_0B/\xi)$, where L_0 is the orbital angular momentum obtained without orbital polarization. This relation is well obeyed by the orbital moments given in Table I if we use the values for the spin-orbit coupling parameter ξ and the Racah parameter B evaluated at the center of gravity of the occupied minority spin energy bands. For Fe and Co, respectively, these parameters are $\xi=24$ and 33 meV and $B/\xi=4.7$ and 3.9. With the same approximations, the energy gain upon including spin-orbit coupling and orbital polarization is given by $E^n(q,\hat{n}) - E^n_{\xi=0}(q) = \frac{1}{2}\xi L^n(q,\hat{n})$. The proportionality factor between $\Delta E^n(q)$ and $\Delta L^n(q)$ in Fig. 1 is described quite well by this simple expression, except for the Pt compounds.

The total spin magnetic moment of 3.3 μ_B per formula unit FePd and FePt (Table I) is much larger than the 2.2 μ_B found for bcc Fe. We will only outline the origin of the enhanced moment for FePd in the following, but a similar explanation holds for the enhancement of the moments in the other AuCu structure compounds. In the AuCu structure, both Fe and Pd have only four nearest neighbors of the same type. If we switch off the hybridization between the Fe-d and the Pd-d states as well as the hybridization between both types of d-states and the free-electron-like sp and f states, then the bandwidths of the resulting unhybridized Fe and Pd d bands are about a factor of 2 smaller than if Fe or Pd were surrounded by 12 nearest neighbors of the same type.[17] These bandwidths are 2.7 eV for the minority-spin and 2.0 eV for the majority-spin Fe d bands and 2.7 eV for
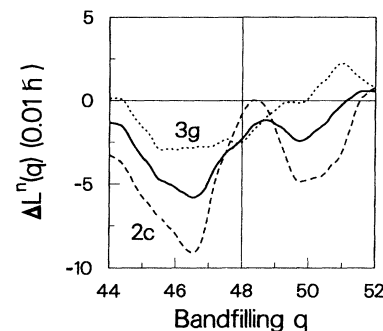

FIG. 2. The anisotropy in the orbital angular momentum per Co atom at the $2c$ site (dashed) and $3g$ site (dotted) in YCo_5, and the average anisotropy per Co atom (solid).

both majority- and minority-spin Pd d bands. The exchange splitting of the Fe d bands is 2.6 eV, so that the top of the Fe majority spin d bands and the bottom of the Fe minority spin d bands are separated by a small energy gap. Because the center of gravity of the Pd d bands is about 3.0 eV below that of the minority Fe d bands, the majority Fe d bands as well as the majority and minority Pd d bands are completely filled. If Fe and Pd are assumed to have one s electron each, then only Fe will have a magnetic moment of 4 μ_B.

When hybridization between the d states and the free-electron-like states is included, strong ferromagnets typically have $n_{maj} = 5.30$ occupied majority spin states per atom,[18] leading to a total magnetic moment of $(2pn_{maj} - n)$ μ_B, where p is the number of atoms per unit cell. This gives a total spin magnetic moment of 3.2 μ_B for FePd, in good agreement with the self-consistent value of 3.3 μ_B.

The hybridization between the Fe d and the Pd d states causes a significant broadening of the Fe and Pd majority-spin bands because they coincide in energy. Because of their separation in energy, the hybridization between the Pd and Fe minority d bands is weak, the minority-spin d bandwidth remains small, and the hybridization introduces 0.4 Pd d holes. The oppositely magnetized free-electron-like states reduce this spin moment to the slightly smaller value of 0.33 μ_B found for Pd in the full calculation (Table I).

A large orbital moment of 0.07 μ_B is calculated for Pt, compared to only 0.03 μ_B for Pd. In Fig. 1 we see that the amplitudes of $\Delta E^n(q)$ for the compounds that contain Pt is about a factor of 5 larger than for compounds containing Pd. We repeated the calculation of $\Delta E^n(q)$ for CoPt and FePt but replaced ξ_{Pt} with ξ_{Pd}. The resulting $\Delta E^n(q)$ curves were essentially the same as those found for FePd and CoPd. This demonstrates that the large spin-orbit coupling interaction of the Pt d electrons ($\xi_{Pt} = 0.32$ eV at the center of the occupied d bands), together with the small exchange splitting of the Pt d bands, strongly influences the magnetic anisotropy. The situation is thus reversed with repect to the $3d$ elements, where the spin-orbit coupling parameter is small, but the exchange splitting is large.

The dependence of $\Delta E^n(q)$ on q for FePt and CoPt suggests that if $q = n - 1$, i.e., if the number of valence

electrons in FePt ($n = 18$) or CoPt ($n = 19$) could be reduced by one, a large anisotropy energy with a preferred c axis orientation of the magnetization would occur. Calculations for FeIr and CoIr in the AuCu structure showed, however, that the easy axis is oriented *perpendicular* to the c axis. The reason why $\Delta E^n(q)$ does not predict the anisotropy energy correctly for $q \neq n$ is related to the contribution of the Pt d states, whose exchange splitting is small, to the anisotropy energy. The rigid band model may only be applied to the anisotropy energy, i.e., $\Delta E^n(q) \approx \Delta E^q(q)$ when the exchange splitting is large.[7]

In conclusion, the easy axis and MAE of several compounds with an anisotropy energy of about 0.5 meV/$3d$ atom has been succesfully predicted using *ab initio* calculations. A simple correspondence between the anisotropy in the orbital angular momentum and the energy was shown to exist for a wide range of band fillings. The magnetic polarization and large spin-orbit coupling parameter of Pt has a particularly large influence on the anisotropy energy curve. Large anisotropy energies can, at least in principle, be obtained in compounds containing $5d$ elements, where only a small induced magnetic moment on the $5d$ element is needed due to the large spin-orbit coupling interaction on the $5d$ electrons.

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