Prediction and Confirmation of Perpendicular Magnetic Anisotropy in Co/Ni Multilayers

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(Received 30 September 1991)

On the basis of first-principles (local-spin-density-approximation) calculations of the magnetocrystalline anisotropy energy we have predicted a perpendicular orientation of the magnetization in a $[111]_{fcc}$ Co_1/Ni_2 multilayer. This multilayer was then grown by vapor deposition and found to have the predicted properties. The saturation magnetization of 1 T is much larger than that of known magnetic multilayers with perpendicular anisotropy.

PACS numbers: 75.70.−i, 71.25.Pi, 75.10.Lp, 75.30.Gw

One of the most pressing issues relating to magnetism at interfaces is to understand what factors determine the preferred orientation of the magnetic moment relative to the crystal axes [1]. Although it was pointed out long ago [2] that the lowered symmetry at a surface (or interface) might result in anisotropy energies larger than those found in bulk materials, little theoretical progress was made until the pioneering investigations by Gay and Richter into the magnetocrystalline anisotropy energy (MAE) of free-standing monolayers [3] renewed interest in this important problem. There is particular interest in finding materials whose MAE is such that the magnetization is perpendicular to the plane of a thin film of the material. $[111]_{fcc}$-oriented Co/X multilayers (ML), where the Co layer is only a few atomic layers thick and X=Pd [4], Pt [5], Au [6], and Ir [7], have this property. Because the mechanisms responsible for this are so poorly understood, the search for new materials proceeds empirically.

In this Letter we report the prediction, from *ab initio* calculations, of a perpendicularly oriented magnetization in a novel multilayer comprising *two* magnetic elements, Co and Ni, together with its subsequent experimental verification. From an analysis made possible by the calculation we find that there are two factors which contribute to this result: (i) The presence of an interface between ultrathin close-packed layers of the magnetic elements Co and Ni, which differ by only one valence electron, is sufficient to give rise to a large magnetic anisotropy energy, and (ii) the total number of valence electrons in Co_1/Ni_2 positions the Fermi energy close to bands with x^2-y^2 and xy character (the z axis is chosen to be normal to the interface) whose spin-orbit interaction favors a perpendicular orientation of the magnetization.

The present work was motivated by our recent calculations of the MAE of [001] Co/Pd and [111] Co/Pd, Co/Cu, and Co/Ag ML's [8]. There we showed that parameter-free calculations of the MAE within the framework of the local-spin-density approximation (LSDA) [9] yield remarkably good agreement with experimental results. Whereas the MAE was found to be independent of the thickness of the Cu and Ag layers, a slight Pd thickness dependence appeared which we interpreted as being due to the magnetic polarization of a number of Pd layers close to the interface. This led naturally to the question as to whether a multilayer with Pd replaced by ferromagnetic Ni, which has the same number of valence electrons, would also have a perpendicularly oriented magnetization. The MAE would have to be sufficiently large to overcome the demagnetization energy favoring an in-plane magnetization, which is increased compared to the case where only one type of layer is magnetic. For this reason only ML's consisting of one of the magnetic elements Fe or Co together with a *nonmagnetic* late $3d$, $4d$, or $5d$ transition-metal element have been studied extensively, and the possibility of finding a perpendicular orientation of the ML magnetization in which *both* elements are magnetic has been neglected or dismissed [10].

The ML structure used in the calculations was chosen to consist of close-packed Co and Ni planes stacked in an *ABCABC* . . . sequence, i.e., [111] planes of an fcc lattice. The unit cell then consists of multiples of three atoms. Because of the small lattice mismatch (0.8%) between bulk Co (in its fcc form) and Ni the same lattice constants were used for the Co and Ni layers. We have verified that our predictions are not sensitive to changes in the lattice parameters of a few percent. The magnetocrystalline anisotropy energy (which is the difference in the ground-state energies for two different orientations of the magnetization) is a consequence of the simultaneous occurrence of exchange splitting and spin-orbit coupling in the Hamiltonian. By taking advantage of the variational expression for the ground-state energy, the change in energy due to the inclusion of spin-orbit coupling may be written as the change in the sum of single-particle eigenvalues [11,12]. The ground-state energy is obtained by first solving the scalar-relativistic spin-polarized Kohn-Sham equations self-consistently and then adding the spin-orbit coupling in a final step. This is done using the linear muffin-tin orbital method in the atomic spheres approximation including s, p, d, and f partial waves in the basis [13]. The von Barth–Hedin parametrization of the LSDA is used [14]. Account must be taken of magnetostatic contributions to the total energy which are not included in local-spin-density approximations of the exchange-correlation energy. The demagnetization energy ΔE_D, whose origin has been discussed in detail by Jan-

sen [15], is calculated by summing the magnetostatic interaction energies between magnetic dipoles on lattice sites in the multilayer [16]. The integration over the Brillouin zone (BZ), determining the numerical accuracy of the calculated MAE, is performed using the improved tetrahedron method [17].

The results of our calculations of the anisotropy energy (including ΔE_D) for Co_1/Ni_2, Co_1/Ni_5, and Co_2/Ni_1 ML's (where the subscripts denote the number of atomic layers per unit cell) are shown in Fig. 1. The anisotropy energy is plotted as a function of the volume element v used to evaluate the three-dimensional BZ integral. An infinitely dense integration mesh corresponds to $v \to 0$. The calculations are seen to be well converged. A perpendicular orientation of the magnetization is predicted for Co_1/Ni_2, whereas an in-plane orientation is found for Co_2/Ni_1. For Co_1/Ni_5 we find an anisotropy energy of $+0.01 \pm 0.03$ meV, where the error bar is derived from the convergence of the integral, shown in Fig. 1. Thus a definite prediction cannot be made for Co_1/Ni_5. The differences in the calculated anisotropy energies either between Co_1/Ni_2 and Co_1/Ni_5 or between Co_1/Ni_2 and Co_2/Ni_1 can not be attributed to the demagnetization energy which is about -0.08 meV per Co atom and -0.01 meV per Ni atom. Thus *both* a Co *and* a Ni thickness dependence of the magnetocrystalline anisotropy energy is predicted. The calculated magnetization of Co_1/Ni_2 is 1.1 T.

These predictions have been investigated experimentally. Polycrystalline Co/Ni ML's were prepared by *e*-beam evaporation onto oxidized Si and glass substrates at room temperature. Deposition rates were controlled at 0.1–1.0 Å/s for Co and 0.2–2.0 Å/s for Ni using oscillating quartz sensors. Chemical analysis proved the nominal thicknesses to be correct within about 15%. Prior to multilayer fabrication a polycrystalline Au base layer with [111] texture was deposited on the substrates to induce the same texture for the multilayer, as was verified by x-ray diffraction (XRD). The periodic structure was confirmed by small-angle XRD. Transmission electron microscopy showed an *ABC* stacking sequence of the atoms as in an fcc lattice [18]. The magnetic properties of the samples were investigated by means of vibrating-sample magnetometry and by torque magnetometry in fields up to $H = 1300$ kA/m at room temperature.

For Co/Ni ML's where the Co thickness t_{Co} is 6 Å or more, the preferred orientation of the magnetization is in the plane of the film for all Ni thicknesses t_{Ni}. For $t_{Co} = 4$ Å the easy axis is out of the plane for $t_{Ni} = 6$–8 Å, and for $t_{Co} = 2$ Å the easy axis is out of the plane for t_{Ni} between 2 and ~12 Å. The in-plane and out-of-plane hysteresis loops of 20×(2-Å Co+4-Å Ni) or 20×Co_1/Ni_2 are shown in Fig. 2. The perpendicular loop shows a remanence of 100% of the saturation magnetization value of ~1.0 T. The anisotropy energy constant K, calculated from the area between the two magnetization curves, is in this case 0.57 MJ/m^3. The maximum value of KD (where D is the bilayer period) which we found was about 0.40 mJ/m^2, in fair agreement with the theoretical prediction of 0.65 ± 0.1 mJ/m^2 (Fig. 1).

The occurrence and the magnitude of the perpendicular anisotropy were found to depend critically on various deposition parameters. This is subject to current investigations and will be reported on later. That the perpendicular anisotropy is undoubtedly due to the layered structure is demonstrated by the magnetic torque curves

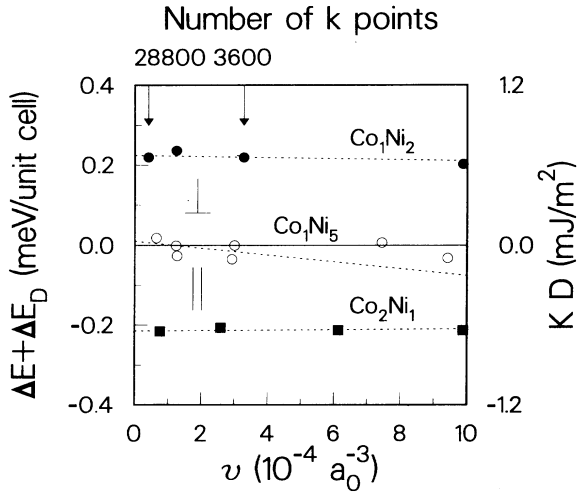

FIG. 1. The anisotropy energy per unit cell, $\Delta E + \Delta E_D$, of Co_1/Ni_2 (●), Co_1/Ni_5 (○), and Co_2/Ni_1 (■) multilayers as a function of the volume element v used to perform the Brillouin zone integration. The right-hand vertical axis denotes KD, the anisotropy energy constant K times the layer period D. The sign of KD is such that $KD > 0$ favors an out-of-plane orientation of the magnetization. Extrapolation of the anisotropy energy to an infinitely dense mesh $v \to 0$ is indicated by straight lines.

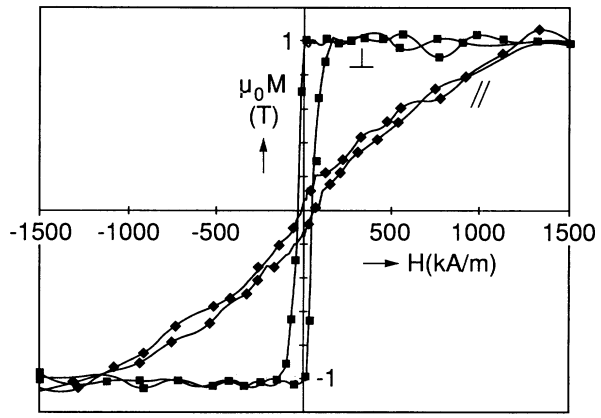

FIG. 2. Hysteresis loops of a 20×(Co_1/Ni_2) multilayer with applied field H oriented parallel and perpendicular to the film plane. The remanent magnetization in the out-of-plane direction is 100%, with $\mu_0 M_s \sim 1.0$ T.

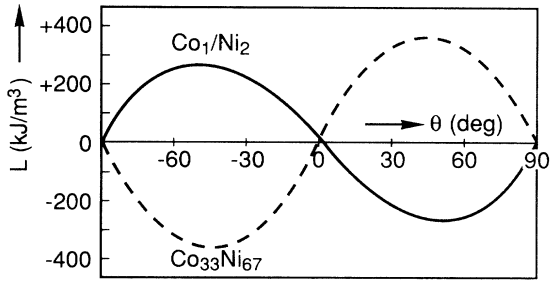

FIG. 3. Magnetic torque curves of a $100\times(Co_1/Ni_2)$ ML yielding $K=+0.27$ MJ/m^3, and of a 600-Å-thick $Co_{33}Ni_{67}$ alloy thin film with $K=-0.36$ MJ/m^3.

shown in Fig. 3 for a 100×(2-Å Co+4-Å Ni) ML and for a 600-Å-thick $Co_{33}Ni_{67}$ alloy, both deposited on glass with a 1000-Å Au underlayer. In contrast to the ML, the alloy film has a (normal) in-plane magnetization. Additional evidence is obtained from measurements summarized in Fig. 4, where it is shown that the anisotropy energy constant determined by torque measurements is inversely proportional to the bilayer period of Co/Ni ML's with constant ratio $t_{Ni}/t_{Co}=2.2$; i.e., $KD=K_VD+2K_S$. The perpendicular magnetic anisotropy of ML's with $D\leq 16$ Å is caused by the positive value of 0.31 mJ/m^2 of the interface anisotropy energy constant K_S.

As a result of the small lattice mismatch between Co and Ni the ML's are likely to be coherent up to large layer thicknesses. In this case magnetoelastic anisotropy due to coherency strains contributes to K_V rather than to K_S [7]. Using bulk magnetostriction constants for Co and Ni we calculated that for a ratio $t_{Ni}/t_{Co}=2$ this contribution favors an in-plane orientation, mainly because the Co layers are compressed, but is very small.

Our calculations indicate that Co_1/Pd_2 and Co_1/Ni_2 ML's are particularly favorable for obtaining perpendicular anisotropy. To understand why, we use the band structures calculated self-consistently with n valence electrons to calculate the anisotropy energy as a function of the band-filling q [12]. The resulting function, $\Delta E^n(q)$, is shown in Fig. 5 for Co_1/Ni_2 ($n=29$), Co_2/Ni_1 ($n=28$), and Co_1/Pd_2 ($n=29$). We also calculated $\Delta E^n(q)$ within the virtual crystal approximation for a number of different values of n and the same atomic positions. The maximum value of the MAE found attainable with this model of a random alloy is much smaller than when there is an interface, even when this is as "weak" as the interface between Co and Ni.

The similarity of $\Delta E^n(q)$ for Co_1/Ni_2 and Co_2/Ni_1 indicates that the in-plane magnetization of Co_2/Ni_1 is essentially due to the different position of the Fermi level in the d band structure. This similarity is a consequence [12] of the fact that Ni and Co are strong ferromagnets differing by only one valence electron so that the electronic structure may in a first approximation be described by a rigid band model. A number of valence electrons of less

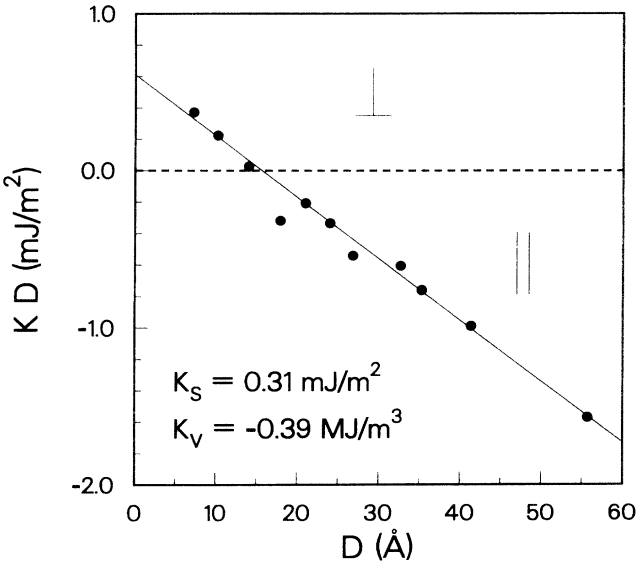

FIG. 4. KD from torque measurements vs bilayer thickness D for Co/Ni ML with constant thickness ratio $t_{Ni}:t_{Co}=2.2:1$. The number of repetitions was $N=20$ up to $D=24$ Å and decreased to $N=10$ for $D=60$ Å.

than ~28 or more than ~30 is unfavorable for obtaining large positive anisotropy energies. Therefore, the MAE of ML's is not solely due to the reduced symmetry of atoms at the interfaces, as in Néel's model of surface anisotropy [2], but also depends on the interface electronic structure [19]. An analysis of the various contributions to the MAE allows us to attribute the out-of-plane mag-

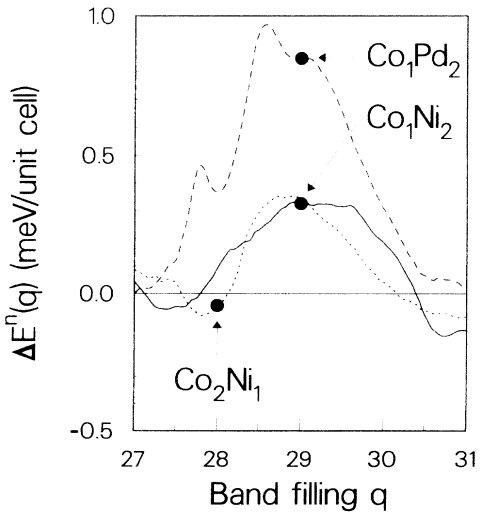

FIG. 5. $\Delta E^n(q)$ as a function of the band filling, calculated using the self-consistent band structure of Co_1/Ni_2 (solid, $n=29$), Co_1/Pd_2 (dashed, $n=29$), and Co_2/Ni_1 (dotted, $n=28$). The magnetocrystalline anisotropy energy of each of these multilayers, $\Delta E\equiv\Delta E^n(n)$, is denoted by a solid circle. The demagnetization energy is not included.

netization of Co_1/Ni_2 to the presence of states with x^2-y^2 and xy character close to the Fermi level. The spin-orbit interaction of these states, which are extended in the plane of the multilayer, favors a perpendicular orientation of the magnetization. The (lengthy) details of this analysis will be given in a separate publication [19].

The q (band-filling) dependence of ΔE^n is qualitatively very similar for Co_1/Ni_2 and Co_1/Pd_2. However, for Co_1/Pd_2 the amplitude of the variation is larger. This is mainly a consequence of the strong hybridization of the Co and Pd d bands in combination with the large spin-orbit coupling constant ξ_d^{Pd} of Pd. If we set ξ_d^{Pd} to zero, then the MAE is approximately halved.

In conclusion, our theoretical and experimental results indicate that a large interface anisotropy may occur not only if magnetic and nonmagnetic elements are combined in a ML, but also if magnetic elements *only* are used. This leads to the prospect of new multilayered films combining a perpendicular magnetization with a high saturation magnetization, both attractive properties in magnetic recording technology.

The authors would like to thank J. Kerkhof, H. J. Donkersloot, J. aan de Stegge, K. Jager, and W. Hoving for sample preparations and E. Janssen for the magnetic measurements. Also, discussions with M. F. H. Schuurmans, S. T. Purcell, and W. B. Zeper were very stimulating.

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