Observation of the Exchange Interaction at the Surface of a Ferromagnet

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The temperature dependence of the surface magnetization $M_S(T)$ in the spin-wave regime is obtained from measurement of the spin polarization of the low-energy cascade electrons. With the $T^{3/2}$ law, the ratio k of the mean spin deviation in surface and bulk is determined, where k reflects the perpendicular exchange interaction $J_\perp$. In the ferromagnetic glass $FeNiB_{0.5}$, $J_\perp$ depends critically on the chemistry of the first layer and is weakened even with a bulklike surface composition.

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Magnetism at transition-metal surfaces is an extremely active field, yet despite recent advances, many important issues have not been resolved.[1] A classical law of surface magnetism which is valid at low temperatures was first stated by Rado,[2] and later developed in more detail by Mills and Maradudin.[3] The magnetization at the surface, $M_S(T)$, should follow the $T^{3/2}$ law according to

$$M_S(T)/M_S(0) = 1 - kCT^{3/2}, \quad (1)$$

where C is the constant describing the decrease of the bulk magnetization due to spin waves, and $k=2$. The factor 2 arises because the spin waves become standing waves at the surface, and the last layer is always an antinode because the surface represents a free end. Therefore, for spin waves of any wavelength, the spin deviation at the surface is twice as large as the average in the bulk. One might expect that the surface induces new spin-wave states below the bulk band and that these states reduce $M_S(T)$ even further than the classical law predicts. This is not the case because the total number of spin waves in the bulk and at the surface is fixed. Therefore, each surface spin wave leaves a hole in the bullk band. Since the surface and bulk modes are approximately degenerate in energy, both effects cancel and the density of spin waves at the surface remains unchanged, leading to the simple classical law under all circumstances.

This classical law is contradicted by several experiments. Elastic scattering of spin-polarized electrons from the surface of the amorphous ferromagnet $FeNiB_{0.5}$ showed that $M_S(T)/M_S(0)$ decreased with increasing T according to Eq. (1) but with $k \simeq 3$.[4] Later, Mössbauer spectroscopy yielded a similar result with the Fe(110) surface.[5,6] Mathon and Ahmad[7] proposed a solution to this paradox. They found that Eq. (1) with $k=2$ holds only for $T/T_C \leq 0.01$ under all circumstances, even when the magnetic moment changes at the surface and even when the exchange coupling on a path perpendicular to the surface becomes arbitrarily weak. However, for weak perpendicular exchange $J_\perp$, and at higher temperatures, a law of the form of Eq. (1) is still valid approximately, yet the effective k can now be larger than 2 depending on the value of $J_\perp/J$, where J is the exchange interaction in the bulk. If this prediction holds, the measurement of $M_S(T)$ offers unique possibilities to study the exchange interaction at surfaces as we shall show here.

The amorphous ferromagnet $FeNiB_{0.5}$ with a Curie point $T_C \simeq 700$ K is particularly suited to test the predictions of Mathon and Ahmad.[1,7] The main prerequisite of the theory is that the bulk magnetization $M_B(T)$ follows Eq. (1) with $k=1$. By measurement of $M_B(T)$ in a Josephson magnetometer, this was found to apply at $T \leq 300$ K, and $C = 17.8 \times 10^{-6}$ deg$^{-3/2}$ was obtained in close agreement with earlier results.[4] Furthermore, one basic prediction of the general approach,[2,3,7] namely, that $M_S(T)$ also follows Eq. (1) but with $k > 1$, has already been convincingly demonstrated by the electron-scattering experiments.[4,8]

We have chosen to measure the spin polarization $P(T)$ of the low-energy cascade electrons excited with an unpolarized beam of primary electrons. $P(T)$ is believed to reflect the average magnetization over a probing depth of $l \simeq 5$ Å from the surface.[9] P is, however, not equal to M_S; we shall show below that $P \rightarrow 21\%$ for the cleanest surface we could prepare as $T \rightarrow 0$ K. From the Bohr magneton number $n_B = 2.40\mu_B$ per $NiFeB_{0.5}$ molecule at $T=0$ and the average number n of valence electrons, one would expect $P = n_B/n \simeq 13\%$. Enhancement of P over M_B is a common observation in most magnetic materials, yet its origin is at present still under discussion. Therefore, we shall only assume here that $P(T) \propto M_S(T)$ which means that the enhancement factor is independent of T. To prove the validity of this assumption it is sufficient to show that $P(T)/P(0)$ follows the $T^{3/2}$ law as it is already known that the law is valid for $M_S(T)/M_S(0)$ with the same material.[4,8] To specifically test the predictions of Mathon and Ahmad,[1,7] one has to demonstrate further that k in Eq. (1) increases as $J_\perp$ weakens while the $T^{3/2}$law is still preserved.

The sample, a ribbon 3 mm wide and 0.025 mm thick, was glued with silver paint across the 2.0-mm gap of a

horseshoe electromagnet. The primary beam with an energy of 3 keV was focused onto a spot of 0.1 mm in the middle of the sample. The low-energy secondary electrons emerging from the sample were imaged with an extraction lens system onto the entrance diaphragm of a medium-energy (40 keV) Mott polarization analyzer as described by Gray *et al.*[10] To permit the observation of the small changes of $M_S(T)$, the relative accuracy in the measurement of P has to be very high. This accuracy can be measured by our employing the fact that $NiFeB_{0.5}$ exhibits square magnetization loops with magnetic saturation occurring in external magnetic fields $H \geq 1$ Oe. It follows that $P(H)$ must be constant at $H \geq 1$ Oe which provides an internal relative standard against which the precision of the apparatus can be verified for every hysteresis loop. On the basis of this test, the systematic errors are estimated to be of the order of $\Delta P = \pm 0.1\%$. Hysteresis loops were recorded at each T and the data taken in magnetic saturation yet at different values of H were averaged. A typical hysteresis loop is shown in the inset of Fig. 1.

The sample was bombarded with Xe ions at an energy of 500 eV with a dose equivalent to the removal of $\simeq 25$ Å. After each treatment, and before and after each temperature cycle, an Auger spectrum was taken. The spectra showed that within the accuracy of a few percent, the surface had the bulk composition. C and O could be removed with a few of the above Xe treatments to less than 5% of a monolayer each. We shall name the surface obtained after a large number of cycles a "clean" surface. We observed that $P(T)$ depends critically on spurious contamination caused by adsorption of residual gas molecules. Only under excellent UHV conditions was it possible to return to the starting polarization after completion of a cooling and warming cycle in $\simeq 1$ h.

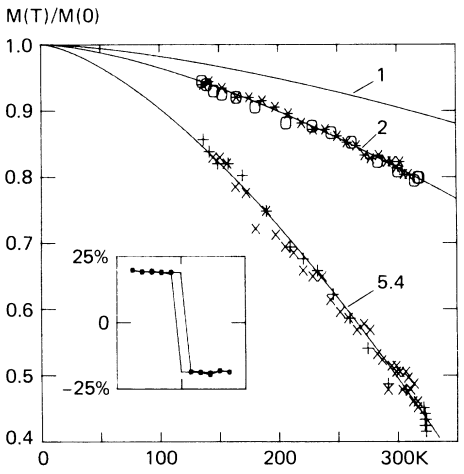

FIG. 1. Temperature dependence of the low-energy cascade relative spin polarization $P(T)/P(0)$, for a clean surface of $FeNiB_{0.5}$ (cooling, circles; warming, asterisks) divided by $P(0) = 21\%$, and for same surface covered with $\simeq \frac{1}{2}$ monolayer of Ta (cooling, plusses; warming, crosses) divided by $P(0) = 12\%$. Solid lines, temperature dependences of $M(T)/M(0)$ calculated from Eq. (1) with $k = 1$, 2, and 5.4. Inset: Hysteresis loop measured with the clean surface at $T = 170$ K. The magnetic field was swept from +6 to −6 Oe and back. The five points in saturation were averaged, and the difference between the average in positive and negative saturation yielded one datum point of $P(T)$.

Figure 1 shows $P(T)/P(0)$ versus temperature for $T/T_C \leq 0.4$ for a clean surface of $FeNiB_{0.5}$, and for a surface with $\simeq \frac{1}{2}$ monolayer of Ta. $P(0)$ and k were chosen to provide the best fit of the data by Eq. (1). It is apparent that the relative surface polarization $P(T)/P(0)$ follows the $T^{3/2}$ law very well, for both the clean and the chemically modified surface, if the two parameters k and $P(0)$ are chosen appropriately. This proves, first, that the spin polarization $P(T)$ of the cascade electrons is proportional to the surface magnetization, and second, that the theoretical findings of Mathon and Ahmad[1,7] apply, leading to a surprisingly large increase of the T dependence of M_s with as little as $\simeq \frac{1}{2}$ monolayer of Ta.

To examine more closely the dependence of the surface magnetization on the concentration of Ta, $P(T)$ was measured for nine different surfaces. In each case, the data were well described by the $T^{3/2}$ law. Figure 2 shows the values of the parameters $P(0)$ and k obtained from the fit of the data by Eq. (1), plotted against the number of sputter-cleaning treatments with the Xe beam, starting at point 1 with a surface covered with $\simeq 1$ monolayer of Ta. Each subsequent treatment was found to reduce the Auger signal from the Ta atoms by $\simeq 50\%$. With repeated treatments, $P(0)$ rises monotonically to 21% for the clean surface, whereas k shows a maximum value of 5.4 at $\simeq \frac{1}{2}$ monolayer of Ta, and then decreases to 2.

To interpret the observations in more detail, one has to know the actual value of the magnetic probing depth l. Of particular interest is the question of whether $k = 2$ as observed with the clean surface indicates that $NiFeB_{0.5}$ will obey the classical law[2,3] if the surface is properly

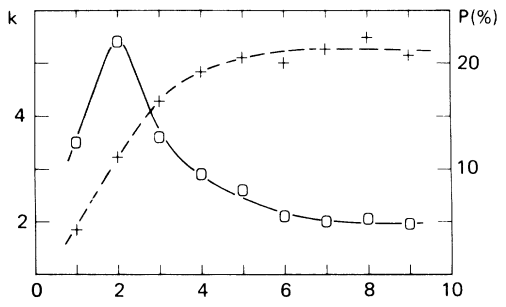

FIG. 2. k (full line) and $P(0)$ (dashed line) vs the number of cleaning steps. At point 1, there is $\simeq 1$ monolayer of Ta at the surface. Each step removes $\simeq 50\%$ of the Ta atoms.

prepared. It will be shown below that this is not the case. Even when we assume the lowest possible value of l, the clean surface must have a weakened exchange too. Abraham and Hopster[9] found that $l=3$–4 atomic layers at the Ni(110) surface. Taborelli[11] determined $l=3$ layers for Fe(100) grown epitaxially on Au(100). From the work of Taborelli,[11] it is estimated that $l \gtrsim 4$ Å in the present experiment with a 3-keV primary electron beam. This l must be compared to the magnetization profile generated by the spin waves reflected at the surface.

For the "ideal" surface with Heisenberg exchange and bulk values of the exchange constant right up to the last layer, the probability of finding a reversed spin at a distance x from the surface is given by

$$p(x,T) \propto \int_0^\infty dq \frac{q^2 \cos^2(qx)}{e^{E/k_B T}-1},$$

where q is the magnon wave number, k_B the Boltzmann constant, and $E=Dq^2$. The spin-wave stiffness $D \simeq 150$ meV·Å^2 is known from neutron scattering in the bulk,[4,12] or from Brillouin scattering,[13] or may be estimated from C in Eq. (1).[13] The inset of Fig. 3 shows $p(x,T)/p(\infty,T)$ for $T=150$ and 300 K. It is apparent that $k=2$ can only be observed with a probing depth of $l=0$. The actual spin polarization expected with $l>0$ is calculated for the ideal surface from

$$\frac{P(T)}{P(0)} = 1 - CT^{3/2} \frac{1}{l} \int_0^\infty p(x,T) e^{-x/l} dx.$$

Figure 3 shows the result of this calculation. It appears that within the accuracy of the experiment one would still be able to fit data with the $T^{3/2}$ law, but one would obtain an effective $k_{\text{eff}}=1.3$ with $l=4$ Å. We observed $k=2$ on the clean surface of $FeNiB_{0.5}$. It follows that even with the clean material, the exchange interaction $J_\perp$ on a path perpendicular to the surface is reduced.

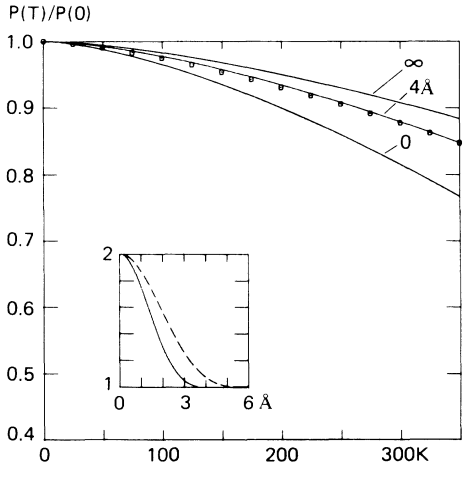

FIG. 3. The temperature dependence of the relative spin polarization calculated for a probing depth of $l=\infty$, 4 Å, and 0. It is assumed that $J_\perp = J$(ideal surface). The fit of the points calculated for $l=4$ Å by the $T^{3/2}$ law yields $k_{\text{eff}}=1.3$. Inset: Probability $p(x,T)$ to find a reversed spin at a distance x (angstroms) from the surface, for $T=300$ K (full line) and $T=150$ K (dashed line). $p(\infty,T)$ was normalized to 1.

Pierce *et al.*[4] observed $k=3$ by elastic electron scattering on $NiFeB_{0.5}$. However, the Auger spectra showed a surface concentration of C comparable to that of B which means that $\simeq 20\%$ of the surface could have been covered with C. With approximately the same relative Auger signal from C, we found $k=3$ as well, but from the spin polarization of the cascade. Therefore, it appears that the probing depth for elastic electron scattering at an energy of 100 eV is not much different from the probing depth of the low-energy cascade, and/or that the recovery of the magnetization with distance from the surface is slow compared to l. Both possibilities are in sharp contrast to earlier beliefs yet consistent with Refs. 10 and 11. It would of course be very desirable to compare M_s obtained with different techniques on the same surface to obtain more information on the magnetization profile created by the spin waves on a *real* surface.

Finally, we can consider a qualitative interpretation of the dependence of k and $P(0)$ on the amount of Ta at the surface as displayed in Fig. 2. The Ta atom has no magnetic moment of its own and therefore contributes unpolarized electrons to the cascade. This explains part of the increase of $P(0)$ upon the removal of Ta. Ta presumably also donates electrons to Fe and Ni which each have higher electronegativities, thereby changing the occupancy and shape of the $3d$ wave functions. This obviously must have a dramatic effect on the exchange interaction; it is even possible that the Ta atoms generate a magnetically dead region in their neighborhood. In any case, it can be assumed that the effect of Ta is stronger when it is buried in the subsurface than when it sits on top of the surface. Because of the small sputtering cross section of Ta, some of the Ta atoms will be buried in the subsurface by the recoil from the backscattered Xe beam. This could explain why the weakening of the perpendicular exchange $J_\perp$ is strongest after the first treatment with the Xe beam, although less Ta is actually detected in the Auger spectrum. According to Mathon,[14] the maximum value of $k=5.4$ reached at nominally $\simeq \frac{1}{2}$ monolayer of Ta corresponds to $J_\perp/J=0.1$.

In conclusion, we note that the experiments fully confirm the work of Mathon[1,14] and Mathon and Ahmad.[7] The surface magnetization follows the $T^{3/2}$ law stated in Eq. (1) at $T/T_C \leq 0.4$. The prefactor k is a measure of the exchange coupling on a path perpendicular to the surface. The perpendicular exchange depends critically on the chemical state of the surface. Even for a clean surface, it is markedly reduced compared to the spherically averaged value in the bulk. Different techniques to measure the surface magnetization in the spin-wave regime with different probing depths should be compared to study the magnetization profile generated

by the spin waves near a real surface, which turns out to be quite different from the ideal surface assumed in most theoretical studies. Experiments with low-energy cascade electrons are comparatively simple and generally applicable also to crystalline materials, and therefore will be extremely valuable for gaining a microscopic understanding of the exchange interaction at surfaces and interfaces.

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