Continuous and Reversible Change of the Magnetic Coupling in an Fe/Nb Multilayer Induced by Hydrogen Charging

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We show in this Letter that the magnetic coupling of a [26 Å Fe/15 Å Nb] × 18 multilayer is changed in a continuous and reversible way by introducing hydrogen into the sample. The magnetic structure and its change during hydrogen charging (and the following decharging) is measured *in situ* by neutron reflectivity. The alteration of the magnetic coupling upon hydrogenation is confirmed by SQUID magnetization measurements. We attribute the change of the coupling to a change of the effective Fermi wave vector in Nb due to hydrogen uptake.   [S0031-9007(97)02308-9]

In the ten years since the discovery of antiferromagnetic (AFM) exchange coupling in magnetic thin film structures [1] a large amount of experimental and theoretical work has appeared on this subject [2]. This research field receives its impetus not only from the challenging possibility to study magnetic properties on a length scale of atomic layers but also from the fact that technical applications of these AFM coupled layered structures are in sight. The technical applications make use of the "giant" magnetoresistance (GMR) effect [3] to construct miniaturized magnetic field sensors.

After the experimental discovery that the exchange coupling is oscillating in sign, i.e. that with increasing spacer layer thickness alternately ferro/antiferromagnetic coupling is observed, several theories were developed to describe the phenomenon. In Ruderman-Kittel-Kasuya-Yoshida-like models [4] as well as in the quantum interference model [5] the coupling energy J oscillates in crude approximation as

$$J \propto \frac{1}{(2k_F t_S)^2} \sin(2k_F t_S), \qquad (1)$$

where k_F and t_S are the Fermi wave vector and the thickness of the nonmagnetic layer, respectively. Up to now, the dependence of the exchange energy on the spacer layer thickness has been extensively studied in many systems. But, surprisingly, only very few papers exist in the literature dealing with a manipulation of the Fermi wave vector [6]. An example for the change of the Fermi vector is the $Fe/V_x Cr_{1-x}$ system in which V and Cr form a solid solution over the entire composition range. It has been shown experimentally and theoretically that by changing the electron concentration of the spacer layer by alloying, the period as well as the amplitude of the coupling energy can be altered.

In this Letter, we present evidence for a *continuous* and *reversible* change of the magnetic coupling *in one and the same* multilayer sample. In the present case the sample is charged with hydrogen from the gas phase at 473 K. At this temperature hydrogen enters or leaves the sample according to the concentration in equilibrium with the applied external hydrogen atmosphere [7]. As argued above, one expects a manipulation of the exchange coupling by hydrogen charging [8] via the change of the electronic structure in the spacer layer. Fe/Nb multilayers were chosen for these experiments since oscillating FM/AFM coupling had been positively identified in recent experiments [9,10] and Nb, as the spacer layer, has a high solubility for hydrogen [8].

The samples consisted of stacks of Fe/Nb double layers on Si wafers with a 50 Å Cr buffer layer between Si and the stack and a 50 Å Pd cap on the top of the multilayer to facilitate hydrogen uptake (for details, see [10]).

We have already shown in Ref. [10] by means of neutron reflectivity measurements that the magnetic coupling of our Fe/Nb multilayers oscillates between AFM and FM coupling as a function of increasing Nb spacer layer thickness. Antiferromagnetic coupling of adjacent Fe layers is evidenced in neutron reflectivity by the appearance of magnetic half-order superlattice reflections [11]. Ferromagnetic coupling yields a small magnetic contribution to the chemical Bragg reflection but no extra feature and therefore is less sensitively detected than antiferromagnetic ordering. The uncharged multilayers (a full set of reflectivity spectra will be presented in [12]) have maxima of the antiferromagnetic coupling at Nb thicknesses of 15.1, 24.0, and 36.8 Å and regions of ferromagnetic coupling at 8.0 and 19.0 Å (this is in reasonable agreement with an earlier examination of this system where an oscillation length of 9 Å was reported [9]). These and the present measurements were performed with unpolarized neutrons ($\Theta/2\Theta$ geometry, $\lambda = 4.7$ Å) since they are sufficient for the present problem, they permit higher counting statistics and most important, they do not require an external field. Avoiding external fields is particularly important for the samples with layer thicknesses larger than 20 Å Nb since after application of an external field the samples did not return to the antiferromagnetic state [10].

The multilayers were charged with hydrogen from the gas phase in a vacuum chamber around the sample position of the neutron reflectometer. This allowed an *in situ* observation of changes of the magnetic coupling

during the hydrogenation. The samples were first annealed for 30 min at 473 K in a vacuum of $<1 \times 10^{-5}$ mbar, and then charged at this temperature. At 473 K the diffusion of hydrogen into the films is relatively fast as was seen from the on-line monitored resistivity increase which saturated a few minutes after the hydrogen inlet. In earlier experiments we have shown by means of nuclear reaction analysis that in Fe/Nb multilayers hydrogen is accumulated in the Nb layers while the Fe layers remain essentially hydrogen-free [8]. Hydrogen charging does not destroy the crystalline structure of the multilayer since the superlattice reflections in large angle x-ray diffraction remain observable.

Figure 1 shows neutron reflectivity data for two multilayer systems with Nb thicknesses of 15 Å (first AFM maximum) and 23 Å (second AFM maximum), respectively. The half order reflections at 1.7° and 1.3° are due to the AFM coupling of adjacent Fe layers.

We find for $t_{Nb} = 15$ Å that the antiferromagnetic coherence in the direction normal to the layers covers 90% to 95% of the total multilayer thickness. However, the
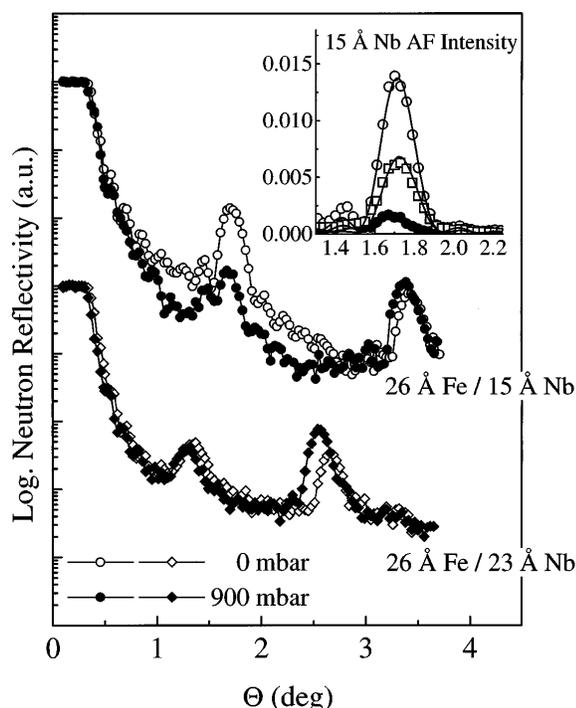

FIG. 1. Small angle neutron reflectivity spectra of multilayers with [26 Å Fe/15 Å Nb] × 18 and [26 Å Fe/23 Å Nb] × 14 before (open symbols) and after (filled symbols) hydrogen charging at 900 mbar, respectively. No external field was applied during the measurements. The inset shows on a linear scale the reflectivity curves in the angular range around the antiferromagnetic peak of the 15 Å Nb multilayer (open dots: for the sample in the as-prepared state; filled dots: after hydriding at 900 mbar; and open squares: after removing the hydrogen atmosphere). The continuous lines in the inset represent fits to the data with theoretical functions based on optical theories [13].

values of the Fe moments used in the fits are reduced to 60% of the values measured with SQUID magnetometry, where all Fe moments are aligned to the external field. The reduced moments can be explained by formation of magnetic domains. Specular neutron reflectivity measurements average over in-plane domains of width smaller than the coherence length of the neutron (approximately 100 μm). The picture of domain formation is further supported by the observation [12] of off-specular scattering in the region of the AFM peaks (the rocking curves of both the 15 and 23 Å samples are significantly broader than the resolution of the spectrometer). A similar observation of domain formation has also been found in earlier measurements on Fe/Nb multilayers [14].

In case of the 15 Å system hydrogen charging at 900 mbar strongly diminishes the intensity of the AFM peak, indicating a drastic loss of AFM coupling. This becomes even more clear on the linear plot of the data in the inset of Fig. 1. It also reveals that the AFM intensity can be recovered (although not completely) after removing the hydrogen from the charging chamber.

The lower part of Fig. 1 shows that hydrogen charging has practically no effect on the AFM intensity (at $\Theta \approx 1.3°$) for the 23 Å Nb film. The reason is that for this larger Nb layer thickness the coupling energy is weaker and does not surmount the pinning energy. The large change in the intensity and the shift of the position of the chemical Bragg reflection (at $\Theta \approx 2.6°$) shows that a large amount of hydrogen has been introduced into the Nb layer: $[H]/[Nb] \approx 90$ at. % (for details see Ref. [10]). In contrast, the hydrogen concentration of the 15 Å Nb sample is only ≈ 25 at. %, due to an interface effect, which will be discussed in a forthcoming paper.

Figure 2 shows the effect of hydrogen charging (and the following decharging) on the AFM coupling for the 15 Å Nb sample as a function of hydrogen pressure in the second charging cycle. It can be seen that, starting at a H_2 pressure of ≈ 30 mbar, the intensity of the AFM reflection drastically decreases as the H_2 pressure increases. At 900 mbar the reflectivity is reduced to only ≈ 20% of its maximum value.

The hysteresis in Fig. 2 between the charging and decharging branch is due to a remanence of the magnetic ordering and not to a nonequilibrium hydrogen concentration since the hydrogen uptake (as monitored by the resistivity increase) is fast and shows no hysteresis. In this second charging cycle the data are fully reversible. A possible explanation of the loss of the AFM intensity after the first hydrogen charging cycle is that, generally speaking, the reestablished antiferromagnetic ordering (after removal of the hydrogen) is less perfect than in the as-grown sample, or more specifically, that, e.g., smaller domain sizes are formed which give rise to a reduction of the AFM peak intensity (see below).

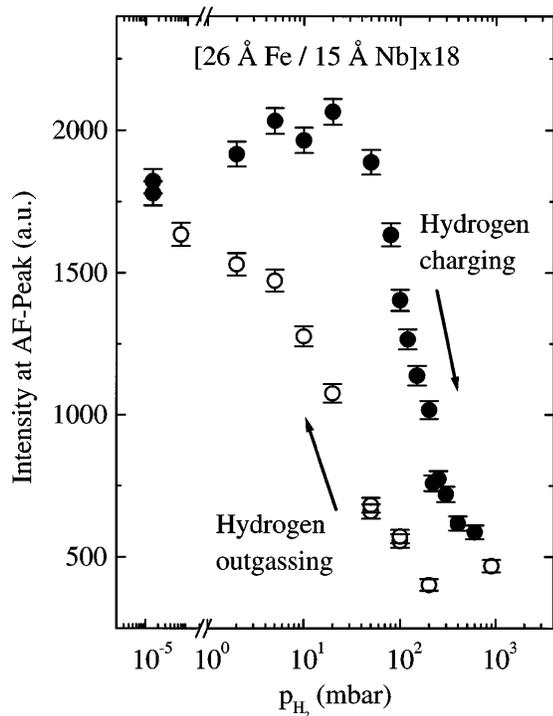The reduction of the AFM reflection when hydrogen is introduced in the Nb spacer layers shows that the

FIG. 2. Intensity of the antiferromagnetic Bragg peak of the multiplayer [26 Å Fe/15 Å Nb] × 18 as a function of the external hydrogen pressure for the second charging cycle. Filled symbols correspond to increasing, open symbols to decreasing hydrogen pressure. Note the break in the scale of the abscissa.

a small number of domains remain AFM coupled due to local inhomogeneities in the coupling or pinning strength.

Since the increase of the spacer layer thickness (estimated from the shift of the chemical Bragg reflection of the 15 Å Nb sample) is only approximately 0.5 Å at 900 mbar, i.e., much less than half an oscillation (4.5 Å) of the coupling energy, the expansion of the spacer layer cannot be the cause of the sign reversal of the coupling. Therefore, according to formula (1) the Fermi wave vector must have been changed. In view of the persistence of the AFM coupling of the 23 Å Nb sample despite massive hydrogen uptake (in this case the Nb layers are expanded by $\approx 8\%$ in the growth direction) also other possible explanations for the change of the coupling in the 15 Å sample as inhomogeneous strain or nonuniform concentration of hydrogen within the Nb layers seem to be unlikely.

The hydrogen charging experiment has been repeated in SQUID magnetization measurements on the same sample. Because of technical difficulties, it was not possible to charge the sample inside the magnetometer. Therefore the sample was charged externally at 473 K, cooled down to room temperature in H_2 atmosphere, and transferred to the SQUID cryostat. At room temperature, the diffusion rate is too low to allow hydrogen to leave the sample during the time of the transfer. Figure 3 shows a comparison of the magnetization measurements of the uncharged (a), hydrogen charged (b), and outgassed (c) [26 Å Fe/15 Å Nb] × 18 multilayer at room

antiferromagnetic ordering has been removed but does not necessarily mean that the sign of the coupling has been changed to ferromagnetic. Unfortunately, the uptake of hydrogen and the change of the coupling from AFM to FM have the same consequence to the chemical Bragg reflection, namely an enhancement of the intensity. Thus a conclusive experimental proof cannot be given here. However, we have an indirect argument that the coupling has switched to ferromagnetic: A mere weakening of the coupling without a reversal of the sign would not change the magnetic structure. The reason is the pinning of the magnetic domains which is most likely caused by defects due to the large lattice mismatch of the Fe and Nb layers. Generally, a magnetic structure persists until a force surmounting the pinning strength reverses the ordering. The remanence in Fig. 2, the persistence of the magnetic structure upon hydrogen charging of the 23 Å Nb sample, and the irreversible field dependence found in AFM coupled multilayers with $t_{Nb} > 20$ Å [10] are clear manifestations of this pinning effect. Because of these considerations, another possible interpretation of the data shown in Fig. 2, namely that the reduction of the AFM intensity upon hydrogen charging is solely a signature of noncollinear spin alignment, is much less probable. Most likely, the small resulting AFM intensity of the charged sample can be put down to the fact that
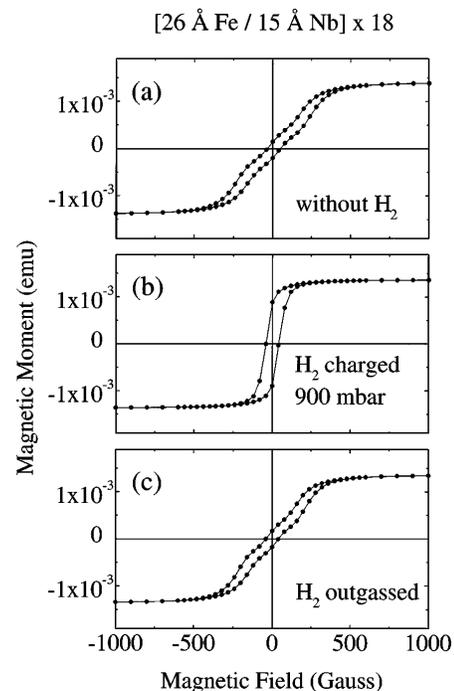

FIG. 3. SQUID magnetization measurements at RT on the multilayer [26 Å Fe/15 Å Nb] × 18 (a) in the as-prepared state, (b) after hydrogen charging at 900 mbar, and (c) after the hydrogen has been removed from the sample.

temperature. The outgassing was done in the SQUID magnetometer by raising the temperature. The change of the hysteresis loop from the form of Fig. 3(b) to that of 3(c) occurs around 360 K.

The almost linear slope of the hysteresis curves and the small remanence (at $H = 0$ G) in Figs. 3(a) and 3(c) are characteristic for an antiferromagnetic system, whereas the nearly squared hysteresis loop in Fig. 3(b) is typical for a ferromagnetic system with remanence. The magnetization results shown in Fig. 3 confirm our conclusions from the neutron measurements that the magnetic coupling changes the sign upon hydrogen charging. It should be noted that the sample's magnetic moment at saturation is not influenced by hydrogen.

As shown above, the magnetic coupling of the $t_{Nb} = 15.1$ Å multilayer system becomes ferromagnetic upon hydrogen charging. Attributing this change to a shift of the Fermi wave vector, k_F must have become either larger or smaller. In order to decide between these two possibilities we performed hydrogen charging experiments at the SQUID magnetometer on two AFM coupled multilayers with t_{Nb} slightly higher and smaller than 15 Å. We found that the $t_{Nb} = 12.6$ Å system changes sign (indicated by a behavior as shown in Fig. 3) but the $t_{Nb} = 16.8$ Å system does not. This behavior can be reproduced by assuming that k_F in formula (1) has decreased upon hydrogen charging by approximately 15%.

The reported switching of the magnetic coupling can be observed only in a small window of Nb thicknesses around 15 Å, since for larger thicknesses the coupling is too weak to overcome magnetic pinning effects, and for smaller thicknesses not enough hydrogen can be loaded into the Nb interlayers to affect the coupling. We have found experimentally that the maximum achievable concentration is strongly thickness-dependent and is practically zero below 10 Å.

In conclusion, we have shown that the magnetic coupling in Fe/Nb multilayers can be changed by hydrogen charging. This change is performed on one and the same sample, it is continuous and reversible. We attribute the effect to a change of the effective Fermi wavevector k_F.

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