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Anomalous behaviour of the Curie temperature of Au-Ni-Au sandwiches at ultra-low Ni thickness

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Résumé. — Nous avons réalisé et soigneusement caractérisé des sandwichs Au-Ni-Au avec une épaisseur d'Au d'environ 200 Å, diverses épaisseurs de Ni entre 4 Å et 18,6 Å, et une orientation (111) des interfaces. Nous avons étudié les propriétés magnétiques de ces sandwichs entre 2 K et 300 K et en champ magnétique appliqué inférieur à 10 Œ. Nous pouvons en déduire la variation de la température de transition ferromagnétique T_c du film de Ni, en fonction de son épaisseur : une décroissance brutale de T_c est observée autour de 12 Å, qui pourrait être reliée à une longueur caractéristique du magnétisme itinérant de Ni.

Abstract. — We have studied, between 2 K and 300 K and in fields up to 10 Œ, the magnetic behaviour of Au-Ni-Au sandwiches of Au thickness 200 Å and Ni thickness ranging from 4 Å to 18.6 Å. The crystalline structure of our samples has also been carefully investigated. From the observed magnetic behaviour we can estimate the ferromagnetic transition temperature T_c : it shows an abrupt decrease around a Ni thickness of 12 Å, which could be related to a characteristic length of itinerant electron magnetism in Ni.

1. Introduction.

The behaviour of ultra-thin films of ferromagnetic transition metals has received a lot of attention in the past thirty years. As pointed out by Gradmann [1] there are mainly two problems : (1) The influence on the magnetism of the drastic reduction of one spatial dimension, becoming of the order of a few atomic layers. (2) The effect of either the break of symmetry at the surface or the interaction with the substrate at the interface, related to the itinerant character of transition metal magnetism.

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While the first calculations [2] based on localized magnetic moments were devoted to point (1), some experiments [3] seemed to detect new effects such as *dead layers* that could rather be due to point (2) : that induced, in turn, a lot of experimental and theoretical work. The difficulty comes from the fact that theorists can build a perfect crystalline film on any substrate, while this is not so simple experimentally. Fortunately, the last ten years have seen tremendous progress both in the preparation and the characterization of the films, and also in magnetic measurements. In addition, new computational methods giving the polarized band structure at 0 K have made possible precise predictions on point (2) (see, for instance, the recent reviews by G. Bayreuther [4] on experiments and A. J. Freeman *et al.* [5] on band calculations).

Ni being held as a good example of an itinerant ferromagnet, its behaviour on different substrates has been widely studied. In agreement with band calculations at 0 K [5, 6] such different experiments as polarized photoemitted electron spectroscopy [7], electron capture spectroscopy [8], anomalous Hall effect [9] and electron spin polarized tunnelling measurements [10] find a reduced but non-zero magnetization of the first layer of Ni deposited on noble metals such as Cu or Au. But these experiments have all been made in high applied fields ($H > 1$ kOe) and at one fixed temperature. So we think there is a great challenge for precise measurements in low fields, around T_c, on films whose crystalline structure, though certainly non-perfect, would at least be well known and controlled.

Despite the large misfit between the lattice parameters of Au : $a_{Au} = 4.08$ Å and Ni : $a_{Ni} = 3.52$ Å, we can grow Au-Ni-Au sandwiches of good crystalline quality, with a (111) orientation of the film. We have also built a SQUID magnetometer specially designed for high precision low field magnetization measurements on thin films.

We report here on first results on the thickness dependence of T_c and the low field behaviour around T_c of samples with Ni thickness ranging from 4 Å to 18.6 Å : a very sharp and puzzling increase of T_c is found around a Ni thickness of 12 Å.

2. Samples and experimental techniques.

2.1 THE SAMPLES : Au-Ni-Au SANDWICHES. — The Au-Ni-Au sandwiches are made in an ultra-high vacuum deposition unit by evaporation. The residual pressure before the process is 10^{-10} torr. The thickness of the film is monitored by a quartz crystal gauge and its resistivity is measured during the Ni deposition.

First an Au film of 200 Å is grown at a rate of 0.5 Å/s on a clean polished glass platelet, and then annealed at 170 °C for 2 hours. As shown in previous studies [12, 13] the resulting Au film is continuous, monocrystalline through the total thickness and atomically flat, with a (111) orientation of the surface. The mean lateral size of the crystals is about 2 000 Å. The main defects at the surface are monoatomic steps, separated by about 100 Å.

The Ni is then slowly evaporated at a rate of 0.25 Å/min, and a second Au film of same thickness as the first one is deposited as a coverage.

During Ni evaporation the resistivity of the Au substrate first increases rapidly, then saturates above a deposited Ni thickness of less than 4 Å (about 2 atomic layers). This behaviour provides valuable information on the type of growth [12] : (i) there is no diffusion of Ni into the Au substrate. (ii) the Ni film does not grow layer by layer, but the Au substrate is nearly fully covered after deposition of less than two atomic layers of Ni on the average.

Out of the deposition unit we can perform X-ray diffraction (X.R.D.) and transmission electron microscopy (T.E.M.). The X.R.D. experiment [13] first allows us to calibrate the quartz crystal gauge for each film, then confirms that we surely have no diffusion of Ni into Au, even after several months. From the existence of fringe patterns of same appearance for all Ni thicknesses and all diffraction angles we can conclude than the roughness of the second interface Ni-Au is about 2 or 3 atomic layers, in agreement with point (ii), and does not depend on Ni thickness.

The samples are then peeled off from the glass platelet with a special varnish, mounted in copper grids and studied by T.E.M. On all our samples, up to a Ni thickness of 18.6 Å, we measure the same distribution of crystals lateral sizes as for a 200 Å annealed Au film alone, with as sharp grain boundaries; only few Moiré fringe patterns appear in some places, indicative of local slight misorientations between crystallographic axes of corresponding Au crystals in the substrate and the coverage. Moreover, we get, through all our sandwiches, diffraction patterns of single crystals. Clearly, the Au coverage has same crystalline structure as the substrate, and thus also, to a large extent, the Ni film.

From these characterization experiments we can conclude that we have a continuous, polycrystalline Ni film, with a (111) orientation of the surface, and a rather good bidimensional character, as the lower interface is atomically flat and the upper one spreads on no more than 3 atomic layers. We cannot determine the lattice parameter of Ni in the film, but we certainly have an average pseudomorphism of the first layers with the Au substrate, together with misfit dislocations : similar structure have been theoretically predicted [15] and experimentally observed for couples of metals with lattice misfits near ours [11, 13, 14].

2.2 THE SQUID MAGNETOMETER. — We have built a SQUID magnetometer which allows us to make absolute magnetic measurements between 2 K and 300 K, in fields up to 10 Oe, with a residual field lower than 0.4 mOe. The precision of the thermometry is better than 10^{-3} in the range 2 K-100 K. The lowest detectable magnetic moment is as low as 2×10^{-10} cgs emu in fields below 10^{-2} Oe and above increases to be 4×10^{-8} cgs emu at 10 Oe. All runs at constant temperature are fully automatized.

3. Magnetic behaviour of the Au-Ni-Au sandwiches.

In bulk Ni the distance between two adjacent (111) planes is about 2.03 Å, and the saturation magnetization of a (111) plane is 1.03×10^{-5} cgs emu cm^{-2}.

We have measured between 300 K and 2 K the magnetic moment of 15 samples of thickness ranging from 4 Å to 18.6 Å. Experiments were performed in constant field applied either parallel or perpendicular to the film.

The magnetization of all our samples in a perpendicular field was always found to be very weak, and undistinguishable from the effect of a possible slight misalignment of the samples. Indeed a simple calculation on a Ni (111) monolayer gives a parallel anisotropy field of 6 kOe, stronger than the perpendicular field expected from magnetocrystalline anisotropy with bulk parameters [17]. Recent experiments [16] have also shown the importance of surface anisotropy in such films.

In a parallel field the common behaviour of all our samples between 4 Å and 10 Å is displayed in figure 1. The field cooled magnetization (FCM) shows a reversible behaviour at all fields below 10 Oe. The zero field cooled magnetization (ZFCM) is fully irreversible : each step increase of the temperature is followed by a slow drift of the magnetization, until a temperature T_c^* where FCM and ZFCM join together. The remanent magnetization at 5 K, after applying 5 kOe, decreases when the temperature increases, with an irreversible behaviour very similar to that of the ZFCM. A rather high inverse field of about 600 Oe is necessary to reverse this magnetization at 5 K.

The field cooled magnetization M is proportional to H for $T \gg T_c^*$. When T decreases, an evident saturation of M *versus* H begins to occur. In field as low as 0.1 Oe the linearity is already broken at a temperature still a few degrees higher than T_c^*. The values we obtain at 4.2 K with our low field or remanent magnetization measurements are always smaller, although of the order of the saturation values that can be estimated from the bulk data.

Let us concentrate on what happens around T_c^*. Figure 2 displays the behaviour *versus* temperature of the relative FCM : $M(T)/M(0)$, of a 6 Å sample, at two different fields of 0.04 Oe and 1 Oe. The two curves join below T_c^*, which also corresponds to a slight break of slope on the 0.04 Oe curve.

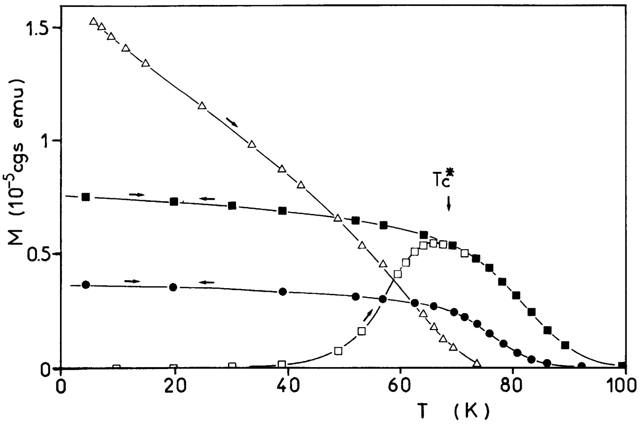

Fig. 1. — Magnetic behaviour of a Au-Ni-Au sandwich of Ni thickness 8.83 Å (●) : reversible field cooled magnetization (FCM) in applied field $H = 0.1$ Oe ; (■) : FCM with $H = 1$ Oe ; (□) : irreversible zero field cooled magnetization (ZFCM) with $H = 1$ Oe ; (△) : irreversible decrease with temperature of the remanent magnetization (RM) in zero field, after applying 5 kOe at $T = 5$ K. The ZFCM and RM values have been measured more than one hour after each change in temperature, and are rather near equilibrium values.

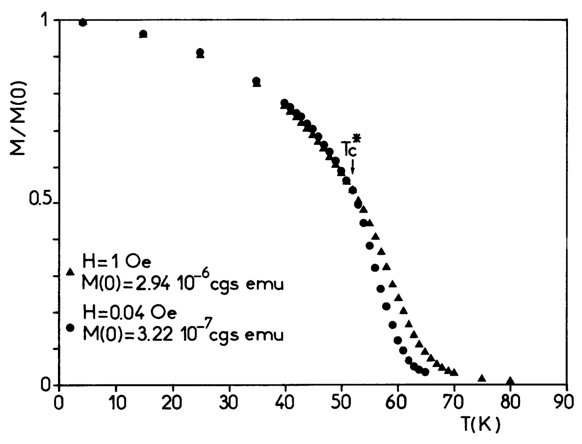

Fig. 2. — Relative field cooled magnetization $M(T)/M(0)$ *versus* temperature for a Au-Ni-Au sandwich of Ni thickness 6 Å in two different applied fields H.

4. Interpretation.

A similar magnetic behaviour has already been observed by Hitzfeld *et al.* [18], on a 3D ferromagnetic sample which had been first severely deformed to produce enough dislocations for domain wall pinning. Our samples can be understood by a simple model of an assembly of magnetic domains, related to the known polycrystalline structure of the films.

Let T_c be the Curie temperature of an infinite monocrystalline Au-Ni-Au sandwich with the same interface structure as ours. In our films, we know that the crystal orientation in the plane changes from one crystal to another. So, due to magnetocrystalline or magnetoelastic anisotropy, for instance, there must exist in the plane a weak anisotropy axis, particular to each crystal. In bulk Ni magnetocrystalline anisotropy creates 3 easy axes for the magnetization in (111) plane, with associated anisotropy fields around 100 Oe at low temperature [17].

Let us now consider the F.C.M. of our sandwiches, in applied field H low compared to the anisotropy fields. We first suppose that all crystals have the same lateral size $D \simeq 2\,000$ Å. Above T_c and as long as the magnetic correlation length ξ of Ni remains small, in-plane anisotropy has a negligible effect. Very near T_c, ξ diverges and reaches D at a temperature T_c^* : we can imagine that magnetic domains will set up and freeze, following the polycrystalline structure of the film, and with a configuration of moment orientations on the anisotropy axis depending on H. T_c^* is thus a better approximation of T_c as H is smaller and D greater. It should appear on the FCM as a break of slope, and the distribution of size in the real film will then result in some rounding of the curve. This effect can be seen in figure 2. Moreover, we can expect below T_c that both the magnetic moments of each domain will remain frozen in their initial orientations, and the domain walls will remain pinned on the important crystalline defects in the Ni film corresponding to the grain boundaries of the Au substrate. Thus, we measure a weighted sum of the spontaneous magnetization of all grains. Indeed we observe in figure 2 that the relative FCM : $M(T)/M(0)$ does not depend on the applied field below T_c^*.

As long as ξ remains below the size of the crystals, we should be able to observe the critical behaviour of our samples. Figure 3 displays the logarithm of M/H *versus* the logarithm of the reduced temperature $t = (T - T_c^*)/T_c^*$, for our 6 Å sample. In the range $0.15 < t < 0.6$ we measure an effective exponent $\gamma = 3.1 \pm 0.3$, consistent with the rapid divergence expected for a 2 D XY compound [19, 20]. Clearly we cannot discriminate between the displayed power law and the otherwise predicted exponential divergence on such a limited range of temperature. The rounding observed below $t = 0.15$ and highly dependent on the applied field may be explained either by an effect of limited grain size, or of the above mentioned in plane anisotropy.

We have carefully measured T_c^* for all samples between 4 Å and 13 Å. Above 13 Å, the magnetic moment changes very little between 300 K and 4.2 K, which means that the T_c is very high, near the bulk one. Figure 4 displays the variation of T_c^* *versus* the thickness e of the film : there is a very sharp decrease of T_c^* between 13 Å and 10 Å. To our knowledge such a behaviour has never

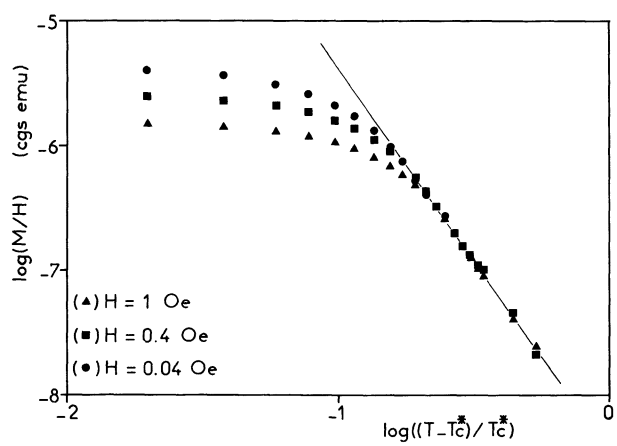

Fig. 3. — Log-log plot of M/H *versus* the reduced temperature $t = \dfrac{T - T_c^*}{T_c^*}$, at several applied fields H, for a Au-Ni-Au sandwich of Ni thickness 6 Å. M is the field cooled magnetization. For this sample $T_c^* = 52$ K. The straight line represents the law $M/H = C.t^{-\gamma}$ with $\gamma = 3.1$ and $C = 3.2 \times 10^{-8}$ cgs emu.

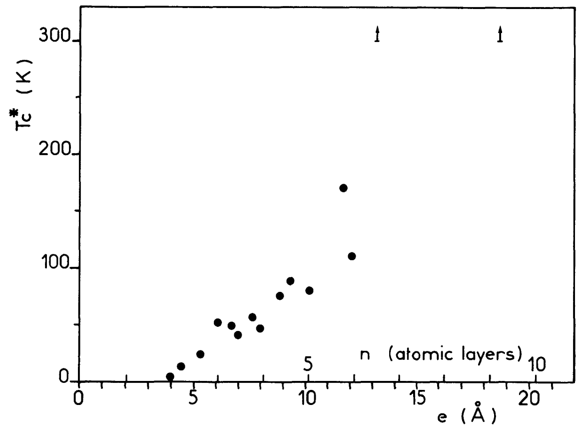

Fig. 4. — Dependence of the transition temperature T_c^* of our Au-Ni-Au sandwiches on the average Ni thickness e ; M is the average number of atomic layers calculated from e with the bulk spacing. The arrows correspond to T_c values above 300 K which could not be measured by the present apparatus. The bulk transition temperature of Ni is $T_c = 627$ K.

been observed. A second interesting point is the very low value of T_c^* (6 K) for our 4 Å sample, coupled with a vanishingly small FCM (6×10^{-7} cgs emu/cm^2 at $T = 2.3$ K in field 10 Oe), which could mean a disappearance of ferromagnetism in thinner films.

5. Discussion.

Two important effects are observed in our experiments :

1) The magnetic moment at $T \to 0$ together with the Curie temperature T_c seems to vanish below 4 Å.

2) T_c drops down drastically below 13 Å.

Band calculations on Ni thin films at 0 K [5, 6] do not take into account pseudomorphism and dislocations that certainly exist in our samples. It is nevertheless interesting to observe that the vanishing of ferromagnetism below 4 Å is consistent with their prediction of a strong reduction of the magnetization at Cu-Ni interface for a (111) film orientation. It should be noticed that these calculations also predict only a weak reduction at the interface for a (100) orientation [6] and an enhancement of the surface magnetization [5], which could explain the apparent discrepancy between our results and previous experiments [7-11] made on thin films with one surface layer, and for some of them in (100) orientation.

It is more difficult to explain the sharp variation of T_c around 13 Å. Due to the large lattice misfit between Au and Ni (13.6 % following Gradmann's definition [11]), a giant expansion of the Ni lattice in its pseudomorphic growth on Au and a correlative strong decrease of T_c for low Ni thickness could be expected. This mechanism has been previously proposed to explain the drastic change of magnetic properties of Pd on Au [21]. The sharp increase of T_c around 13 Å observed here would, however, imply a corresponding abrupt change in the lattice parameter of Ni. For very low values of the lattice misfit, such a critical thickness may exist [22]. This behaviour seems to us very unlikely to occur here with the large value of the lattice misfit between Au and Ni.

Another hypothesis would be to relate this magnetic behaviour to a more fundamental reason. We are indeed dealing here with band ferromagnetism, where the magnetism carriers are itinerant electrons. When reducing the thickness of the films, we break the 3D translational symmetry of the Ni crystal. There might thus exist a given thickness, related to a characteristic length of itinerant magnetism in Ni, where the system undergoes an abrupt transition from 3D to 2D band ferromagnetism : that would be the origin of the step in the curve. The slow subsequent decrease of T_c^* between 10 Å and 4 Å would then be due to secondary causes such as the one described above in this discussion.

The previous calculations of T_c for thin films [2], based on localized magnetic moments, could certainly not predict such an effect. It is more difficult to analyse why it would not yet have been detected by previous experiments on transition metal films. It is well known that Ni has a slightly different itinerant magnetism than Co and Fe, on which most of the experiments [1, 4] have been performed. These hypotheses will be checked by further similar studies on Au-Co-Au and Cu-Ni-Cu sandwiches now in progress.

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