Magnetism of Ni polylayers on different metallic substrates

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(Received 24 January 1983)

Thin Ni films on top of different nonmagnetic metals have been studied by means of the anomalous Hall effect. Ni on the surface of Mg, In, and Sn does not possess magnetic moments when its thickness is less than about 2.5 atomic layers, whereas on noble-metal substrates even a monolayer of Ni is magnetic.

I. INTRODUCTION

Studies of inhomogeneous magnetic systems have considerably improved our understanding of magnetism. Such inhomogeneities exist in dilute and concentrated magnetic alloys where the formation of magnetic moments depends on the local density of states.[1] Other classes of inhomogeneities are surfaces of magnetic materials and interfaces between a ferromagnetic and a nonmagnetic metal. In a way these are one-dimensional inhomogeneities of magnetic systems. The experimental results gained on these systems can progressively be compared to theory. During the last ten years calculations of the magnetic ground state have improved remarkably (although fundamental difficulties in understanding the behavior at finite temperatures remain). Therefore, at present the theoretical concepts which hold for the ground state of the homogeneous periodic ferromagnet are applied to the inhomogeneous systems.

Much interest has been focused on the properties of magnetic surfaces. A particularly interesting question is whether the surface atoms lose their magnetic moments and form magnetically "dead layers." Experimentally no "dead layers" have been found in surfaces of magnetic transition metals.[2–5] Band-structure calculations for a few layers of Ni (Refs. 6–8) show clear changes but no suppression of the magnetic moment at the surface (although some of the results are still controversial).

Contrary to the results on surfaces of pure transition metals one might expect a suppression of magnetic moments for ferromagnetic atoms in an interface to a nonmagnetic metal. The first experiment including such an interface was reported by Liebermann *et al.*[9] who investigated thin Ni films electroplated onto Cu and Au. (This technique of film preparation is burdened with hydrogen adsorption which could reduce the nickel's magnetic moment, e.g., Ref. 10.) By extrapolating their data of ferromagnetic flux taken as a function of Ni thickness to $T=0$ K Liebermann *et al.* found two magnetically "dead" Ni layers. This result stimulated many other experiments on various systems with Ni as the preferred ferromagnetic component. Ni on Cu was again examined by Pierce and Siegmann[11] who determined the spin polarization of photoemitted electrons (measured at 80 K). The data did not allow a clear statement about the behavior of a monolayer of Ni but ferromagnetism was certainly present for more than two layers of Ni. Wang *et al.*[12] calculated self-consistently the magnetic moment of a five-layer Cu(100) slab with a single Ni layer on each surface. Though the magnetic moment was decreased in the Ni overlayer with respect to the bulk value the layer was *not* magnetically "dead." Tersoff and Falicov,[13] on the other hand, considered one or two Cu layers on top of the (100) face of a semi-infinite ferromagnetic Ni crystal in tight-binding approximation. They also calculated a reduced Ni moment at the interface, but the value was not zero.

One of the authors measured the magnetic properties of Ni on amorphous $Pb_{75}Bi_{25}$ (Ref. 14) by means of the anomalous Hall effect (see Sec. II). Only Ni coverages of more than 2.5 atomic layers showed magnetic moments. Below that thickness the sandwich had a temperature-independent Pauli susceptibility. Its value was enhanced and became very large when the Ni coverage was about 2.5 atomic layers, indicating the ferromagnetic instability.

Meservey *et al.*[15] determined the spin polarization of electrons tunneling through junctions consisting of Al(sc)-Al_2O_3-Ni-Al. The Ni film was not ferromagnetic as long as its thickness was below 3 atomic layers.

The disparate results for Ni on different substrates suggest a need for a systematic investigation. In this paper we examine the magnetic properties of Ni on top of the following nonmagnetic metals: Mg, In, Sn, Cu, Ag, and Au. Particular interest is directed to the question of whether the substrate's valence has a decisive influence on the magnetic moment of Ni.

II. EXPERIMENTAL PROCEDURE

The cryostat used to perform the experiments has been described elsewhere (e.g., Refs. 16 and 17). In an ultrahigh vacuum of about 10^{-11} Torr the metals of interest were condensed onto a crystalline quartz plate held at about liquid-helium temperature (4.2–10 K). The nonmagnetic substrates, evaporated from annealed tantalum or tungsten foils heated by an alternating current, were chosen to be about 50 atomic layers thick. Before the measurement was performed at 7 K, these films were "annealed" at about 35 K for a few minutes, so the coarsest lattice defects could heal and no changes in structure could occur at the lower measuring temperatures. Nevertheless, the degree of disorder remained high (indicated by the large resistivities of the films). On top of these metals the ferromagnetic substance Ni was condensed (from the wire) at about 10 K. Its thickness was measured by a quartz balance and increased either by half of an atomic layer or by one atomic layer[18] per evaporation step. The corresponding frequency change was directly monitored by a frequency time recorder and so the accuracy was within about $\frac{1}{30}$ of an atomic layer. The Ni atoms were statistically distributed on the substrate's surface. Their diffusion was very small because the measuring temperature was not raised above 7 K. All metals had a nominal purity of 99.999% (except Mg which was specified to be 99.998% pure).

After each condensation the Hall resistance was determined in fields from -7 to $+7$ T by means of two opposite electrodes. For the films investigated the absolute error of about $\pm 2\times 10^{-5}$ Ω corresponds to a relative accuracy of about 10^{-3}. This suffices to detect magnetism in the thinnest Ni "film" of about 0.5 atomic layers. (Even the paramagnetic behavior of $\frac{1}{50}$ monolayer of a magnetic transition metal could be detected.[19,20]) The measurement unavoidably includes Ohmic contributions. They are eliminated by analyzing only that part of the Hall voltage which is an odd function of the field B. Data registration and all processes of regulation as, for example, the adjustment of desired magnetic field strength, were controlled by means of a computer.

The sandwiches were heated by a metal film resistor glued to the bottom of the quartz substrate just as the Au–Fe-chromel thermocouple for measuring the films' temperature. The Hall resistance $R_{xy} = U_H / I$ (U_H is the Hall voltage; I is the current) allows us to study the magnetic properties of the condensed metal films. In all magnetic fields (up to 7 T) the low-field condition ($\omega_c^* \tau \ll 1$; ω_c^* is the cyclotron frequency; τ is the mean lifetime between two collisions) is fulfilled and so those sandwiches without magnetic moments only show the normal Hall effect with no deviations from linearity: $R_{xy} \sim B$. Magnetic atoms, e.g., condensed onto the surface of a nonmagnetic substrate alter this behavior if they do not lose their moments. They exhibit an additional so-called "anomalous" contribution which does not linearly change with magnetic field. It saturates in high fields and can thus be separated from the normal Hall effect. The origin of this anomalous Hall effect, which is rather complicated, has been discussed intensively.[21–25]

III. RESULTS

A. Polyvalent substrates: Mg, In, Sn

The experimental results for Ni on top of Mg, In, and Sn are qualitatively the same. First we discuss the properties of the InNi sandwich in some detail. The thickness of the In substrate was about 11 nm. After "annealing" its resistivity was about 0.4×10^{-6} Ω m. The measurement of the Hall resistance revealed a linear dependence on magnetic field B. Condensation of as much as 3.1 atomic layers of Ni on top of the In does not change the linearity of the Hall curves. Only their slopes alter with increasing Ni coverage. Figure 1(a) shows the deviation from linearity for two different Ni coverages. The values belonging to the InNi(3.1 atomic layers) sandwich merely scatter randomly about the abscissa indicating the absence of magnetic moments. 3.6 atomic layers of Ni produce an anomalous contribution (with a saturation value of about 1% of the total measured value at 7 T). This sandwich contains magnetic moments. Figure 1(b) shows the anomalous Hall resistance ΔR_{xy} for 7.4 atomic layers of Ni on the same In substrate as a function of magnetic field B. ΔR_{xy} is proportional to the magnetization of the Ni layers. Its shape is typical of a thin ferromagnetic film in a perpendicular magnetic field (see, e.g., Ref. 26). In what follows we call the saturation of the anomalous Hall effect $R_{xy}(0)$ (because it is identical to the linear extrapolation of the high-field Hall resistance toward zero field).

Figure 2 is a plot of $R_{xy}(0)$ against the Ni film thickness on top of In. The absolute value of $R_{xy}(0)$ increases quickly with Ni coverage after the onset of magnetism at a Ni film thickness of 3.6 atomic layers.

On the surface of Sn or Mg, Ni shows nearly the same behavior as on In. There are also "dead layers" where no magnetic moments are detectable (Fig. 3). For Ni on top of Sn one could not observe magnetic moments by means of the anomalous Hall effect up to thicknesses of 3.4 atomic layers. Ni on the surface of Mg showed 2.6 "dead layers." Sum-

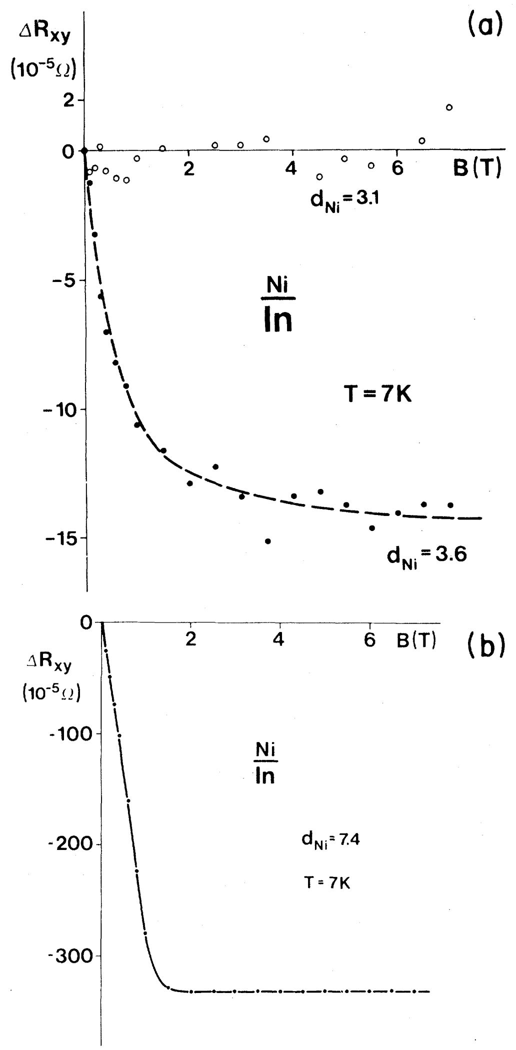

FIG. 1. (a) Nonlinear portion of the Hall resistance ΔR_{xy} plotted as a function of magnetic field B for two different Ni coverages (○ are for 3.1 atomic layers; ● are for 3.6 atomic layers) on In (measured at 7 K). (b) Anomalous Hall resistance ΔR_{xy} plotted as a function of magnetic field B for 7.4 atomic layers of Ni on top of In (measured at 7 K).

marizing, all three polyvalent substrates depress the magnetic moment in thin Ni films on top over a thickness range of about 3 atomic layers. This region nearly does not depend on the substrate's valence.

B. Noble metal substrates: Cu, Ag, Au

Because the maximum thickness for which a Ni film is nonmagnetic is nearly independent of the valence of the polyvalent substrate, one might expect similar behavior of the Ni if Cu is chosen as the sub-

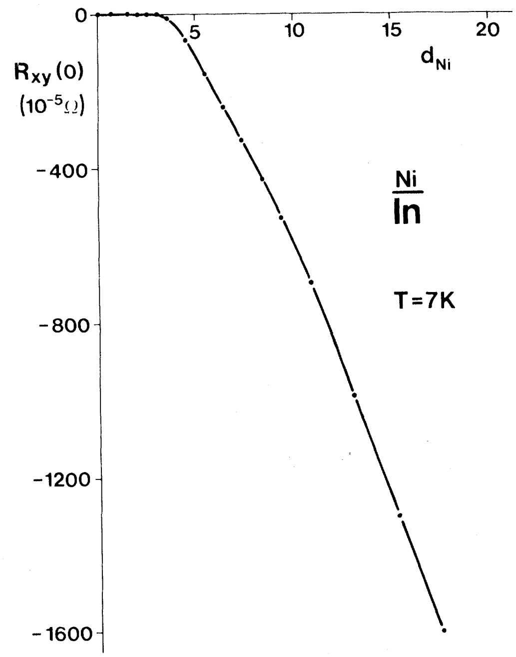

FIG. 2. $R_{xy}(0)$ plotted as a function of Ni film thickness—given in atomic layers—on the surface of In (measured at 7 K).

strate instead of Mg. Figure 4 shows the anomalous Hall curves (ΔR_{xy} against B) for Cu and Ag covered by a monolayer of Ni. The nonlinear runs prove the existence of magnetic moments. On the surface of Au the same behavior is found so that none of the noble metals suppresses the Ni magnetism. This is

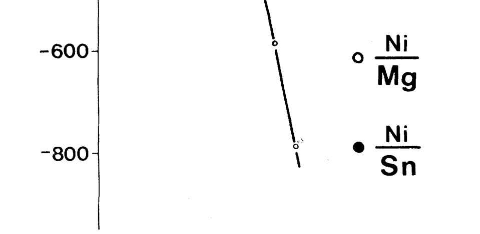

FIG. 3. $R_{xy}(0)$ as function of Ni film thickness—given in atomic layers—on top of Mg (○) and Sn (●) (measured at 7 K).

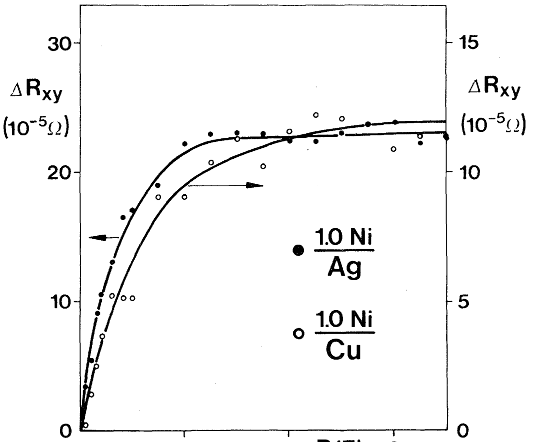

FIG. 4. Anomalous Hall curves ($\Delta R_{xy}/B$) for a monolayer of Ni on top of Cu (○) and Ag (●) (measured at 7 K).

additionally obvious in Fig. 5 where $R_{xy}(0)$ is plotted as function of Ni coverage for all noble metals. It is also striking that $R_{xy}(0)$ changes sign with increasing Ni thickness. Only when the coverage exceeds about 4 atomic layers does $R_{xy}(0)$ become negative, as is typical of bulk Ni. This change of sign is discussed in more detail in the Appendix. The measurements, therefore, show that noble metals and polyvalent substrates have a different influence on the magnetism of thin Ni coverages.

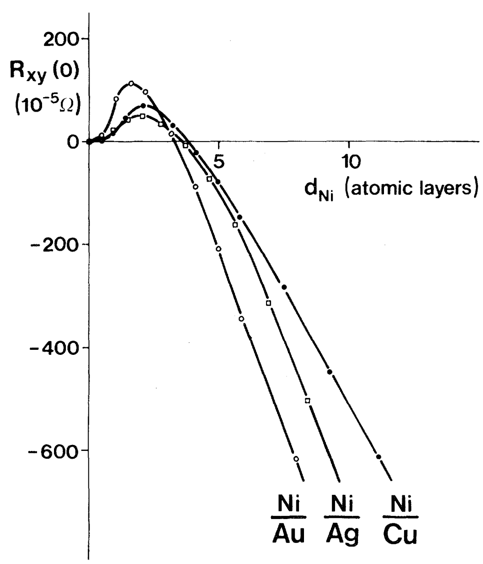

FIG. 5. $R_{xy}(0)$ plotted as a function of Ni film thickness on the surface of Au (○), Ag (□), and Cu (●).

IV. DISCUSSION

The measurements show that the magnetism of thin Ni films strongly depends on the choice of substrate. Nearly all existing calculations are confined to the CuNi system consisting of perfect planes packed along certain directions. In contrast, the experiments under discussion were done on polycrystalline films. The results, therefore, are an average over all possible orientations. A second effect is that particularly extremely thin Ni films interact more strongly with the substrate because of the surface roughness than is expected on ideal surfaces.

The electronic structure of ultrathin Cu(100) films covered with Ni was calculated by Wang *et al.*[12] using the self-consistent linearized augmented-plane-wave method. The result was a reduced magnetic moment per Ni atom with respect to its bulk value. Qualitatively the same was found by Tersoff and Falicov[13] in a different calculation in tight-binding approximation. Recently, Tersoff and Falicov extended their calculations.[8] Because it had been stated[13,27] that hybridization effects cause a reduction of the Ni moment these authors[8] investigated the role of coupling between the Ni *d* band and the substrate conduction band. They multiplied each matrix element in their Hamiltonian which couples the Ni *d* orbitals to the Cu *s* and *p* orbitals by a factor *t*. The Ni film magnetization proved to be strikingly sensitive to the degree of coupling. By increasing the coupling strength *t* the Ni formed first one and after that two "dead layers." Then their number stayed constant with further increased coupling strength. If one assumes that the coupling of the Ni *d*-wave functions to the *s*-*p*—electron wave functions of the polyvalent metals is much stronger than their coupling to the *s*-electron wave functions of the noble metals, then these calculations reproduce the experimental result, i.e., the number of "dead" Ni layers on top of Mg, In, and Sn is almost substrate independent. A theoretical calculation of the coupling between the Ni and the different substrates would be very desirable. The real situation is more complicated; in addition to the interface there is always a free Ni surface which exhibits an enhanced magnetization compared to the bulk.[8] Consequently, "dead" Ni layers only appear when the coupling in the interface layers is strong enough to overcompensate the enhancement resulting from the missing neighbors in the surface. The suppression of the magnetic moment exists as long as the Stoner criterion $U \times N_0 > 1$ (U is the Coulomb interaction; N_0 is the local *d* density of states at the Fermi energy) is not fulfilled. This takes place for Ni on top of the investigated polyvalent substrates giving nearly a constant, valence-independent number of "dead" Ni layers. On the other hand, the noble metals do not suppress the moments of a Ni monolayer on top. The Hall measurements, especially with Cu, complete the experiments done by Pierce and Siegmann[11] who could not give a clear statement about the magnetism of a Ni monolayer on top of Cu.

Whereas Ni on top of Mg, In, and Sn proved to be nonmagnetic within about 3 atomic layers other magnetic transition metals behave quite differently. One of the authors reported on the magnetic moments for Fe on the same substrates even with coverages of only 2% of an atomic layer.[19] Such drastic differences in the magnetic behavior of transition metals have only been qualitatively discussed by theory.[28] Nevertheless, it suggested the dependence of the magnetism of thin transition-metal films on both the nonmagnetic substrate and the magnetic material itself.

V. SUMMARY

The anomalous Hall effect is a sensitive method for detecting magnetic moments in thin metal films. Ni on the surface of different nonmagnetic metals was investigated to study their influence upon its magnetism. Two groups can be distinguished with respect to their effect: the polyvalent and the noble-metal substrates. On top of Mg, In, and Sn, Ni films of less than about 2.5–3 atomic layers are nonmagnetic. In these cases the substrate's valence is of nearly no importance. On the contrary, the substances Cu, Ag, and Au do not suppress the Ni moments. A recent model calculation performed by Tersoff and Falicov[8] agrees with these results if one assumes that the coupling of the Ni d band to the conduction band of the polyvalent substrate is much stronger than that to the s band of the noble metals. It is an interesting task for the theory to calculate the actual coupling in the interface of two different metals.

APPENDIX

As is presented in Fig. 5 the anomalous Hall resistance of Ni on top of the noble metals displays two signs: Only for more than about 4 atomic layers does the sign become negative, as in the bulk metal.[29] For small coverages the anomalous Hall effect is positive, i.e., has the "wrong" sign. The question arises whether this change of sign is a peculiarity of Ni on noble-metal surfaces. Obviously, it does not exist when Ni is condensed upon the surface of polyvalent sp metals (Mg, In, Sn). For the purpose of comparison Co and Fe were also investigated on the surface of Cu (Fig. 6). The results are similar to those for Ni on Cu: For small thicknesses $R_{xy}(0)$ shows the "wrong" sign. Thus this effect is no special feature of Ni. But also the noble-metal substrates are not decisive by themselves. One of the authors found the same effect for Fe on Pb, In, and Sn.[19] The range of "inverted" sign, however, was restricted to very small coverages (up to 0.1 atomic layers). All results obtained so far can be summarized in the following way: If there are magnetic moments within the first atomic layer of a ferromagnetic material condensed on top of a nonmagnetic substrate, $R_{xy}(0)$ starts with the "wrong" sign for small ferromagnetic film thickness. The physical reason for this effect is not yet clear. Especially it is not understood why the range of "wrong" sign in $R_{xy}(0)$ varies so strongly for different ferromagnetic materials and various substrates. The hybridization of the d-wave function of the transition-metal atoms with the conduction band of the substrate at the interface might be of importance. Anyhow, the wave function's spatial symmetry is strongly distorted for the ferromagnetic atoms in the interface layers.

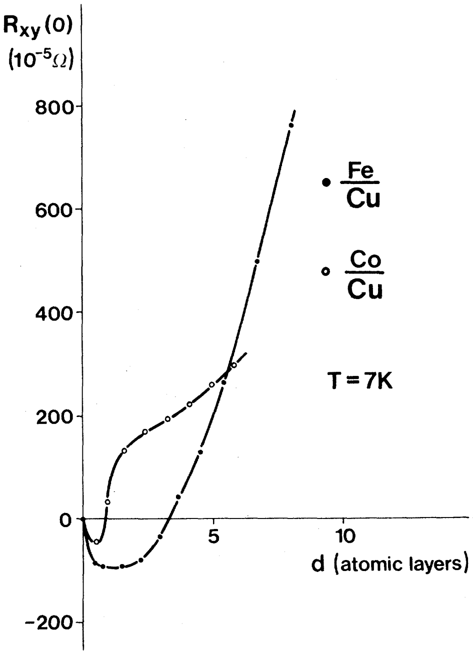

FIG. 6. $R_{xy}(0)$ plotted as a function of Fe (●) and Co (○) film thicknesses on top of Cu (measured at 7 K).

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