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Transition from Pauli Paramagnetism to Band Ferromagnetism in Very Thin Ni Films

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Ni, Co, and Fe films of a few atomic layers are condensed in UHV at 10 K on metallic substrates. Anomalous–Hall-effect measurements are used to determine the magnetization and the susceptibility of the films. Ni films with a thickness smaller than two atomic layers possess no magnetic moment but show an enhanced susceptibility. Between two and three atomic layers of Ni the susceptibility diverges and thicker films possess a magnetic moment. For Co and Fe, the first monolayers already shows a magnetic moment.

Thin magnetic films or surfaces of magnetic materials are modified in their magnetic properties. Of particular interest is the existence of so called "dead layers" in which the ferromagnetism and even the magnetic moments are suppressed. A discussion of "dead layers" has to distinguish two completely different situations and problems: (i) dead layers at the surface of a bulk magnetic material; (ii) dead layers in a thin film of a magnetic metal on top of a nonmagnetic one.

The existence of dead layers in the surface of Fe, Co, and Ni has been experimentally disproved. Mössbauer measurements of ferromagnetic Co[1] demonstrated that the surface atoms possess an unchanged magnetic moment. Spin-polarized electrons[2,3] did not find dead surface layers for Fe, Co, and Ni.

The history of magnetism of thin films is rather eventful[4-12] (see Gradmann[13]) and demonstrates in particular the important role played by sample preparation conditions. For the most promising candidate, Ni, Liebermann *et al.*[9] extrapolated from their data the existence of two magnetically passive monolayers at liquid He temperature. These films were formed by electroplating from an aqueous solution of Ni salts. Their results have been contradicted by Pierce and Siegmann[10] who condensed thin Ni films onto Cu and measured the spin polarization of photoemitted electrons. They concluded from their results that ferromagnetism already occurs in Ni films with one to two atomic layers.

In the present work we examine experimentally the basic question: At which film thickness do Ni, Co, and Fe *atoms* begin to possess a magnetic moment? How does the occurrence of the magnetic moment happen, i.e., with a divergence of the susceptibility as the theory of band magnetism suggests or by formation of magnetic clusters?

In the investigation of the magnetic properties of thin films of a few atomic layers one has to overcome a number of technical difficulties: (i) avoiding oxidation and impurities, (ii) diffusion into the metallic substrate, (iii) the formation of islands, (iv) the exact determination of the thickness of the films, and (v) the sensitivity of the equipment.

I detect the magnetic moments of the Ni (Co, Fe) and their ordering by a rather unconventional but extremely sensitive method, the anomalous Hall effect. Atoms with a magnetic moment scatter the conduction electrons asymmetrically. This asymmetric scattering yields a voltage perpendicular to the current, like the Hall effect, and is called the "anomalous Hall effect." The anomalous Hall resistivity is proportional to the magnetization of the sample[14] so that

$$\rho_{xy}{}^{an} = R_s J_z,$$

where R_s is the anomalous Hall constant and J_z is the z component of the magnetization; the magnetic field is in the z direction. It is additive to the normal Hall resistivity $R_0 B_z$.

In recent investigations[15] I demonstrated that in amorphous ferromagnets this anomalous Hall effect is a factor of 100–1000 larger than the normal Hall effect of simple metals. It is therefore well suited to investigate the magnetic behavior of these metals. The method is so sensitive that even the paramagnetic behavior of $\frac{1}{6}$ of a monolayer of Fe on top of a 250-Å-thick $Pb_{75}Bi_{25}$ can be easily detected.

The evaporation cryostat which I use is first evacuated to 10^{-7} Torr and then inserted into the He bath of a superconducting magnet.[16] All walls are at liquid He temperature with exception of the evaporation source. The latter is cooled with liquid N_2. As discussed below I conclude from the experiment that the vacuum is better than 10^{-11} Torr. In this vacuum I condense first the metallic substrate. Generally I choose a film of amorphous $Pb_{75}Bi_{25}$ with a thickness of 250 Å.

The Ni (Co, Fe) is sublimized from a wire (1 mm diam), heated by an alternating current. The metals have—according to Johnson and Matthey and Koch-Light—a purity of 99.998%. For Ni the only impurity which I found in a spectroscopic analysis was 8 ppm Al. The evaporation rate is about 1 atomic layer/min [the coverage is 1 atomic layer if $(L\rho/A)^{2/3}$ atoms per unit area are condensed, where $L = 6.02\times10^{23}$ cm^{-3}, ρ is density of the solid, and A is the atomic weight]. The amount of condensed metal is measured by a quartz balance. The quartz is also at liquid He temperature. This has two important advantages: (i) The accommodation coefficient for the metals is equal to 1 and the same as for the substrate; (ii) the frequency drift is negligible, due to the constant temperature. The accuracy of the thickness determination is $\frac{1}{30}$ atomic layer. During the condensation the conductivity of the film is monitored *continuously* on an x-y recorder. The general behavior is the following. The conductivity first decreases slightly, goes through a minimum at about 0.2 atomic layer of the Ni (Co, Fe), and then increases with a slope corresponding to the resistivity of the amorphous metal.

(As a sensitive and direct test of the clean vacuum conditions I interrupted the condensation for two hours. The conductivity remained the same—within the accuracy of a few 10^{-5}. During a further condensation it increased linearly with the same slope as before.)

The low condensation temperature suppresses the diffusion at the surface and into the substrate and any clustering besides the statistical one. After the measurement of the Hall curve and the transition temperature (if the substrate is a superconductor) the next evaporation takes place about 15–20 minutes later.

Except for small corrections one can treat the sandwich as a shunt of the $Pb_{75}Bi_{25}$ and the Ni films. Within this model one obtains after an elementary calculation for the anomalous Hall angle of the sandwich,[11]

$$\varphi_{ex} = \varphi_1(R_0^{\square} - R^{\square})/R_0^{\square} \approx \varphi_1 R_0^{\square} D_1/\rho_1,$$

where $R_0^{\square} = \rho_0/D_0$ is the per-square resistance of the first metal, $R^{\square}$ is the per-square resistance of the sandwich, $\varphi_{ex} = R_{xy}/R^{\square}$ is the measured anomalous Hall angle of the sandwich, and φ_1 is the anomalous Hall angle of the Ni (Co, Fe) film. This means that the Hall angle of the ferromagnetic film is reduced because of the shunt with the first metal by a factor $\Delta R^{\square}/R_0^{\square}$. Corrections occur because asymmetrically scattered conduction electrons propagate also into the normal metal. Since the mean free path in amorphous $Pb_{75}Bi_{25}$ is short these corrections are small.

In Fig. 1 the Hall curves for a sandwich of $Pb_{75}Bi_{25}$/Ni are plotted. The temperature of the film is about 10 K. The number by each curve gives the coverage of the substrate with Ni in units of atomic layers. The original $Pb_{75}Bi_{25}$ shows a linear Hall curve with negative slope as is typical for amorphous metals.[17] A superposition of the $Pb_{75}Bi_{25}$ film with Ni of a thickness of 0.4 and 1.0 atomic layer leaves the Hall curve almost unchanged. The coverage with 1.5, 2.1, and 2.5 atomic layers Ni increases the slope of the Hall curve progressively. However, the Hall curves remain linear and they are temperature

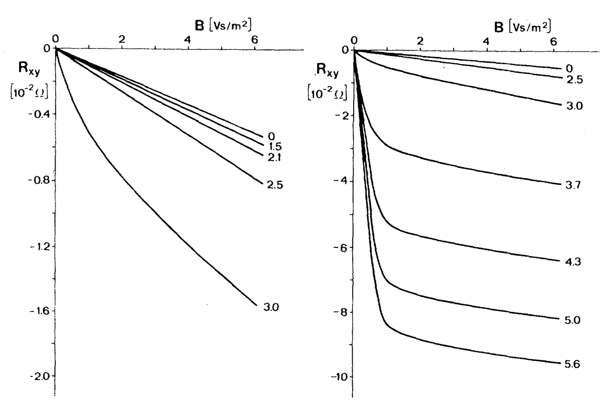

FIG. 1. The Hall curves of $Pb_{75}Bi_{25}$ (250 Å) on which Ni films of increasing thickness are condensed. The number by each curve gives the averaged Ni thickness in units of atomic layers.

independent between 5 and 20 K. This shows definitely that the Ni atoms do not possess a magnetic moment. Otherwise the Hall curves would (i) be field dependent and (ii) change their additional slope by a factor of 4 if one varies the temperature from 20 to 5 K. This becomes very clear if one superimposes the $Pb_{75}Bi_{25}$ instead of Ni with Fe. A coverage of only $\frac{1}{6}$ atomic layer Fe yields a nonlinear temperature-dependent Hall curve and the initial slope is changed almost by 100%. On the other hand the superposition with a few layers of the simple metal Pb leaves the Hall curve unchanged. Therefore the increased slope of the linear temperature-independent Hall curves of the $Pb_{75}Bi_{25}$/Ni sandwich is of magnetic origin but not due to local moments. It is caused by an enhanced Pauli susceptibility which is temperature independent. For a coverage with 3.0 atomic layers Ni the Hall curve is nonlinear. This indicates the formation of a magnetic moment in the Ni film. With increasing Ni thickness the magnetic moment increases. The thicker Ni films ($D>3.7$ atomic layers) show the typical behavior of a ferromagnetic film. The linear slope in the low-field region is due to the high demagnetization factor of the thin film. The point of inflection occurs when the saturation magnetization is reached.

Extrapolating the high-field part of the Hall curve to zero field yields the anomalous Hall resistance of the sandwich, $R_{xy}(0)$. The latter is proportional to the magnetic moment of the sandwich and is plotted in Fig. 2. In the left part of Fig. 2 I show the slope of the (linear) Hall curves. It is proportional to the susceptibility of the Ni and diverges between 2 and 3 atomic layers Ni ($\Delta R_{xy} \propto \chi B$).

After the Ni film has reached a total thickness of 5.6 atomic layers I superimpose $Pb_{75}Bi_{25}$ on it. As Fig. 2 demonstrates, this coverage suppresses in addition the magnetic moments at the top of the Ni film.

I used also crystalline Pb, Cu, and the semimetal Bi as substrates for the Ni. For these substrates the sensitivity of the measurement is much less since the Ni grows on top of the crystalline substrate in the crystalline state with a strongly reduced anomalous Hall effect. Nevertheless I find that the first two layers of Ni do not show ferromagnetism.

Additional evidence for the loss of the magnetic moment of the Ni atoms in the first two layers is the dependence of the superconducting temperature of the sandwich on the Ni film thickness.

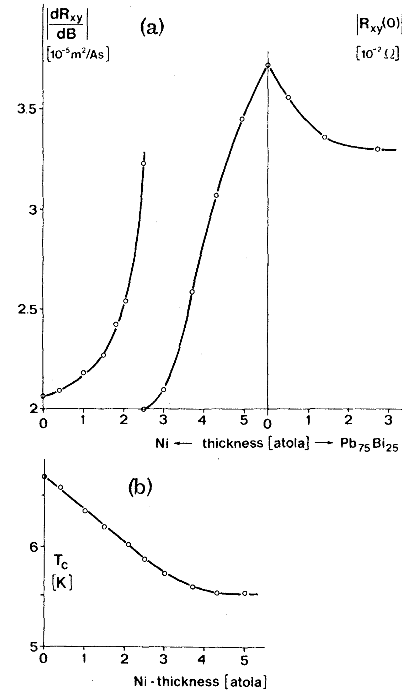

FIG. 2. (a) dk_{xy}/dB and $k_{xy}(0)$ as functions of the Ni thickness. The first corresponds to the susceptibility of the Ni film and the second to the magnetic moment. To the right of the figure $R_{xy}(0)$ is shown for an additional condensation of $Pb_{75}Bi_{25}$ on top of the thickest Ni film. (b) The superconducting transition temperature of the sandwich as a function of the Ni thickness.

The transition temperature decreases rather slowly as Fig. 2(b) shows. The depression of T_c is saturated when the Ni becomes ferromagnetic. I superimposed for comparison Fe on top of a $Pb_{75}Bi_{25}$ film. A coverage of only $\frac{1}{6}$ atomic layer yields the total depression of the superconducting transition temperature. Co, evaporated on top of the $Pb_{75}Bi_{25}$ film, also exhibits a magnetic moment immediately. The results are similar to those for Fe.

Bulk Ni is among the magnetic elements the best example for an itinerant-election ferromagnet.[18] The product UN_0 (N_0 is the density of states and U is the exchange constant) is larger than 1 and the $d_\uparrow$ and $d_\downarrow$ sub-bands are split. If the thin Ni film is in contact with the surface of a simple metal the magnetic d states hybridize with the conduction electrons of the simple metal. The density of states is reduced. This is in strong analogy to the Anderson model of a magnetic impurity.[19] For $D<2-3$ atomic layers the product UN becomes less than 1 and the magnetic moment of the Ni disappears. The susceptibility is, however, enhanced by the Stoner enhancement factor $1/(1-UN)$. With increasing Ni film thickness the density of states approaches the bulk value N_0. For a thickness of about 2–3 atomic layers, UN crosses the value 1 and the susceptibility diverges. Thicker Ni films possess a magnetic moment and approach the properties of bulk band ferromagnet Ni.

As a result of these considerations, I doubt that this problem of "two-dimensional" magnetism can be described by the theory of Jaccarino and Walker.[20] According to this theory, a Ni atom builds up a magnetic moment, when the number of its nearest Ni neighbors exceeds a critical number. Taking into account the second-nearest neighbors[21] one might expect that the first atomic layer of Ni possesses a magnetic moment. The loss of magnetic moments in the second layer clearly contradicts this theory. We assume that the delocalization of the d-wave functions within the Ni plane is of great importance.

The result stimulates several interesting questions. What is the magnetic behavior of an isolated Ni monolayer? Going from a single magnetic Ni atom[22] to the ferromagnetic bulk, one may consider two intermediate states: the linear chain and the two-dimensional plane. As to their magnetic behavior, one has a sensitive balance between the increasing delocalization of the Ni d states and the increasing interatomic exchange interaction. Since the band calculations are at present rather successful in determining the magnetic moment of the ground state,[23] an extension to these reduced dimensionalities should be feasible.[24]

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