Detection of Magnetic Moments of Ni and Fe Atoms on the Surface of Pb

J. S. Moodera and R. Meservey
Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 23 August 1985)

A new, very sensitive method was used to study the existence of magnetic moments of Fe and Ni when deposited on a nonmagnetic metal. Evidence is presented that isolated Ni atoms possess a magnetic moment on the surface of Pb, contrary to previous results. At greater coverage of Ni and Fe the onset of ferromagnetism was found at the thickness observed in other experiments. The technique is sensitive to 10^{-6} of an atomic layer of Fe and can detect the existence of localized moments of magnetic materials on any metal substrate.

PACS numbers: 75.20.Hr, 73.60.Ka, 74.50.+r, 75.50.Cc

The question of when an impurity atom in a host metal has a magnetic moment is a classic problem.[1] At present, there is much current interest in the behavior of magnetic atoms and layers on nonmagnetic metal surfaces because powerful theoretical[2] and experimental[3] techniques have been developed recently to study these effects.[4] Ni, because of its importance in understanding itinerant-electron ferromagnetism, has been the material most extensively studied. Bergmann,[5] using the Hall effect, showed that ferromagnetism was suppressed for the first three atomic layers when Ni was deposited on various cryogenically deposited polyvalent common metals (Pb, Pb-Bi, Sn, In, Mg, and Al), but not on the noble metals Cu, Ag, and Au. Spin-polarized tunneling measurements[6] on Al and Au agreed with Bergmann's result and the results have been explained theoretically by the hybridization of *s-p* and *d* bands.[7] Bergmann[8] also concluded that with a coverage of less than three atomic layers, the Ni atoms had *no moment* on Pb-Bi, whereas for Fe a moment was detectable at a 2% coverage of Pb, In, or Sn films,[9] as determined by the temperature and field dependence of the Hall effect. The present Letter describes experiments which can examine the problem with greater sensitivity and from which we conclude that a small moment exists on Ni atoms on the surface of cryogenically deposited Pb, even though ferromagnetism only develops at about three atomic layers.[6,8]

The method, which has been partially described elsewhere,[10] uses a thin-film superconducting meander line as the inductive element of an *LC* oscillator circuit driven by a tunnel diode. The meander line is located on a sapphire substrate whose back is pressed against the copper bottom of a liquid-helium cryostat. The meander line faces the evaporation source located in an attached ultrahigh-vacuum system through a port in the liquid-nitrogen–cooled shroud. In addition to the room-temperature shutter, a shutter at near 77 K closes the nitrogen shroud. Another shutter protecting the substrate is cooled to near 4.2 K. When a thin film is deposited on an insulating layer in the near rf magnetic field of the meander line, it can change the effective inductance of the meander line and thus the frequency $f \approx (1/2\pi)(LC)^{1/2}$ of the oscillator circuit. The resonant frequency (≈ 14 MHz) can be measured with a counter to 1 part in 10^7. A particularly sensitive way of detecting the presence of magnetic moments is to deposit the magnetic material on a thin-film superconductor.

In the present experiments the typical method was to deposit 100 Å of SiO followed by 90 Å of Pb onto the 4.2-K substrate. The thickness was measured with a quartz-crystal thickness gauge. In order to prevent a large shunting capacitance between the lines of the Nb-meander pattern, a fine mesh screen with holes 110 μm^2 was used in the evaporation path so that the films to be measured were deposited in squares of this size. As the Pb was deposited there was no change in frequency until some Pb was deposited (13 to 25 Å), after which the frequency increased almost linearly with thickness until at 90 Å the total frequency change was 60 to 80 kHz (apparently depending on the exact threshold thickness at which the film became continuous). This increase in frequency corresponds to the decreased effective inductance of the Nb meander line caused by the currents induced in the neighboring superconducting Pb film. When the deposition of Pb was stopped, the frequency remained constant. If then Fe was deposited on the Pb (see Fig. 1), the superconductor became increasingly depaired and the frequency decreased approximately in proportion to the decrease of the superconducting order parameter Δ. At a certain critical thickness, d_c, the superconductivity is destroyed ($\Delta = 0$). At this point the frequency has returned to its value before the deposition of Pb. Further deposition of Fe does not significantly change the frequency. In Fig. 1 the value of d_c corresponds to a coverage of about 2.5% at which time we expect the Fe atoms to be acting as independent magnetic impurities. In such a case the effect on the superconductivity can be described by the Abrikosov-Gor'kov (AG) theory.[11,12] In fact, by finding the value of T_c as a function of the amount of magnetic impurity we have shown that the depression in T_c followed that predicted by the AG theory for paramagnetic impurities.[13,14] In Fig. 1 we also plot the frequency observed when Ni is deposited on a 90-Å-thick Pb film. The Ni film was deposited in the same manner. Since the frequency change for the Pb film used in the Ni deposition was about 10% higher than in the case of the one used for Fe, the frequency in Fig. 1 for the Ni film was decreased proportionally to compare the functional forms of the depairing effect. In addition, the thickness scales of the Ni and Fe were adjusted until the initial slopes of the two curves coincided. With these normalizations one sees that the change in frequency with thickness is very nearly the same for Ni and Fe if the equivalent amount of Ni is taken to be about 80 times greater than that of Fe. The curves diverge somewhat near d_c. It is possible that this divergence is caused by interactions between the Ni atoms at an average thickness of nearly two atomic layers, whereas with Fe at d_c, there should be no significant interactions at a 2.5% coverage. As a nonmagnetic (and nonsuperconducting) substance, Cu was also deposited to compare with Ni and Fe. There is a slight change in frequency, which is observed with any normal metal, caused by the proximity effect of the normal metal decreasing slightly the superconducting order parameter. The near coincidence of the functional forms of the Fe and Ni results suggests that the magnetic depairing process is the same in the two cases at least for low coverage. The rapid decrease in frequency for Ni is already apparent at 1% coverage where interaction effects between Ni atoms should be negligible.

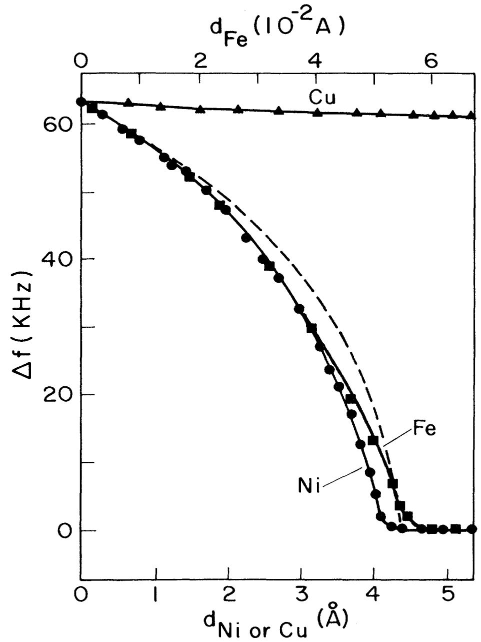

FIG. 1. The change in the oscillator frequency Δf for depositions of Fe, Ni, and Cu on 90-Å Pb films. The zero on the frequency scale is the frequency before deposition of the 90-Å-Pb films. The thickness scale of the Fe data has been adjusted to give the same initial slope as that of the Ni data. The Cu results are plotted on the same thickness scale as for Ni. The dashed line shows the dependence expected for Fe from the AG theory.

For Fe, the measurements of d_c varied by as much as a factor of 2. The cause of the variation is not certain, but the very slow evaporation rate is a probable cause. The rate ($\approx 10^{-2}$ Å/sec) leads to a 20% statistical error in the thickness measurement. In addition, the accommodation coefficient of the quartz monitor may be different from that of the low-temperature substrate. This large variation did not occur with Ni, for which the absolute values of d_c varied by about 10%. One concern in the measurement of surface effects is that of contamination. The base pressure of the vacuum system with an ion pump and a cryopump was $\approx 10^{-10}$ Torr. During evaporation of transition metals the pressure near the evaporation source was $(2\text{–}4)\times 10^{-8}$ Torr. Near the meander line within the cryogenic enclosure the vacuum was presumably much better. To test the possible effect of gases condensed on the Pb substrate, the Ni evaporations were delayed for 20 min instead of the usual 5 min between the end of the Pb evaporation and the start of the Ni evaporation. No significant change in the frequency was observed. In addition, no change was observed in the frequency when the Ni deposition was stopped for 10 min in the region where $d_{Ni} < d_c$, showing that significant contamination of the Ni was not present.

According to the AG theory,[11] the order parameter Δ is a known function of the depairing parameter (or the spin-scattering rate Γ) and the temperature T. This dependence has been calculated by Skalski, Betbeder-Matibet, and Weiss[13] and by Ambegaokar and Griffin.[14] Using the rf susceptibility we have measured T_c as a function of the Ni concentration on 90-Å Pb films and found that the decrease of T_c with impurity concentration fitted the AG theory. The spin-scattering rate has the form[13,15]

$$\Gamma = (\pi/2) n_i N(0) J^2 S(S+1).$$

Here n_i is the concentration of impurity atoms (that is, the ratio of the number of impurity atoms to the total number of impurity and Pb atoms in the film). $N(0)$ is the density of states at the impurity site, S the impurity spin, and J the exchange integral. In a simple screening model in which the magnetic field is everywhere parallel to the Pb film, the change of frequency Δf with n_i is proportional to λ^{-1} (where λ is the superconducting penetration depth). For small n_i, λ^{-1} is proportional to Δ, and using values of Δ obtained from Ref. 14, we calculated Δf as a function of n_i, which is proportional to the average thickness of the magnetic material. The calculated values of Δf vs d_{Fe}

are shown as the dashed line in Fig. 1. The fit to the data can be considered satisfactory since fields are actually at varying angles to the plane of the film. For this reason it is not useful at present to use the more general expressions for λ given by Maki.[16] Additional support for the essential validity of this model comes from the calculated absolute value of Δf which is 62 kHz for a reasonable value of $\lambda = 1.5\times 10^{-5}$ cm for cryogenically deposited Pb. Although a more exact calculation of Δf vs n_i is impractical, the AG theory implies that the transport properties of Pb films of the same dimensions and at the same temperature only depend on $\Delta(\Gamma)$. The fact that the functional dependence of Δf with Γ is the same for Ni as for Fe at low coverage is very strong evidence that the depairing mechanism is the same for Ni as it is for Fe. For Fe the depairing is known to be from independent moments of isolated atoms,[9] but for Ni at a coverage of 1.5 to 2.5 atomic layers, Bergmann[8] proposed that enhanced Pauli paramagnetism, but not isolated moments, could explain his Hall-effect measurements. In the present experiments at much lower coverage where interactions between moments are minimal, one would expect little effect from enhanced Pauli paramagnetism, in contrast to the observed rapid decrease of Δf with n_i at less than 1% coverage. Since the effect of this Ni moment is between 30 and 80 times less than the effect of the Fe moment, it is probable that it was too small to be observed in the Hall-effect measurements.

To investigate the effect of heavier coverage, Ni and Fe were deposited on a 1000-Å-thick Pb film (see Fig. 2). Since the coherence length in these cryogenically deposited lead films is probably about 100 Å, the Pb films never become completely normal even for very thick layers of a ferromagnet. In Fig. 2 we again adjust

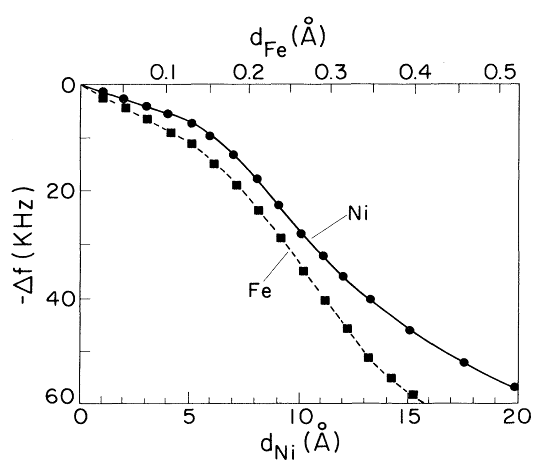

FIG. 2. Change in frequency with Fe and Ni deposited on 1000-Å Pb films. The thickness scale has been adjusted to show the similarity of the curves.

the length scales to bring out the similarity of the curves for Fe and Ni. For Ni the frequency change is proportional to the Ni thickness as expected for noninteracting moments. At a thickness of 5 Å the frequency starts to change much more rapidly. From previous experiments with the anomalous Hall effect and spin-polarized tunneling we identify this change with the onset of ferromagnetism. The gradual decrease in slope after a Ni thickness of 11 Å presumably reflects the increasing ineffectiveness of the added magnetic atoms in depairing the superconductor for thicknesses greater than the coherence length. For Fe the initial slope is constant, and at $d\approx 0.15$ Å the decrease of frequency with thickness accelerates, an effect which attribute to the onset of cooperative effects in agreement with other experiments.[9,17] At $d\approx 0.35$ Å the change of frequency starts to saturate for the same reason as for Ni. Again we see that the behavior of Ni and Fe is very similar both before and after the onset of ferromagnetism, if thicknesses which produce the same depairing are compared. In comparing the results for Fe and Ni, it should be remembered that for Fe, d_c is quite variable. From Figs. 1 and 2 the ratio of Fe thickness for the onset of ferromagnetism to the thickness d_c for the 90-Å film is about 2.4, whereas for Ni this ratio is only 1.2. However, because of the large variation of d_c for Fe, the Fe ratio was sometimes as low as 1.2 and we do not regard this difference as significant.

From these experiments we conclude that an isolated Ni atom on the surface of Pb has a magnetic moment. In addition, we conclude that the ferromagnetism in Ni and Fe takes place in essentially the same way under these circumstances: The existing localized moments are coupled by itinerant electrons to give the ferromagnetic ordering. The fact that the depairing parameter is still approximately proportional to the number of Ni atoms at two atomic layers may seem surprising. However, it apparently shows that the ferromagnetic interaction between Ni atoms is suppressed by the hybridization of the d and s-p electrons even though a small moment is present on the Ni atoms. Although we cannot determine the magnitude of the moment, we have shown that the spin-scattering rate of Fe is of the order of 50 times that of Ni on the Pb surface. Although the present results appear to conflict with the known absence of magnetic moments of Ni in dilute alloys of polyvalent common metals,[6] the much lower coordination number of Ni on the surface of cryogenically deposited Pb probably explains this difference.[4] It should be pointed out that the present method can be used to investigate a wide range of problems of surfaces and thin films. In particular, any metal may be deposited in a 10–20-Å-thick layer over the superconducting film and act as the host to the magnetic impurity. Because of the superconducting proximity effect, the sensitivity is still very great, but there is no constraint on the choice of metal to be the impurity or the host.

We wish to thank P. M. Tedrow, E. Maxwell, and J. Tersoff for useful discussions. This research was supported by the National Science Foundation under Grant No. DMR-8204337. The Francis Bitter National Magnet Laboratory is supported by the National Science Foundation through its Division of Materials Research under Contract No. DMR-8211416.

[1]J. Friedel, Nuovo Cimento, Suppl. **7**, 287 (1958); P. W. Anderson, Phys. Rev. **124**, 41 (1961); P. A. Wolff, Phys. Rev. **124**, 1030 (1961).

[2]C. L. Fu, A. J. Freeman, and T. Oguchi, Phys. Rev. Lett. **54**, 2700 (1985), and references therein.

[3]References leading to the literature are the following. *Photoemission:* R. J. Celotta, D. T. Pierce, G.-C. Wang, S. D. Bader, and G. P. Felcher, Phys. Rev. Lett. **43**, 728 (1979); A. M. Turner and J. L. Erskine, Phys. Rev. B **30**, 6675 (1984); E. Kisker, W. Gudat, E. Kuhlman, R. Clausberg, and M. Campagna, Phys. Rev. Lett. **45**, 2053 (1980). *Electron diffraction:* D. T. Pierce, R. J. Celotta, and J. Unguris, J. Magn. Magn. Mater. **31–34**, 369 (1983); A. Seiler, C. S. Geigerle, J. L. Pena, R. J. Celotta, and D. T. Pierce, J. Appl. Phys. **57**, 3638 (1985). *Mössbauer spectroscopy:* J. Tyson, A. Owens, and T. C. Walker, J. Magn. Magn. Mater. **35**, 126 (1983); N. K. Jaggi, L. H. Schwartz, H. K. Wong, and J. B. Ketterson, J. Magn. Magn. Mater. **49**, 1 (1985). *Magnetometry and Mössbauer spectroscopy:* G. Bayreuther, J. Magn. Magn. Mater. **38**, 273 (1983). *Secondary electrons:* M. Landolt, R. Allenspach, and D. Mauri, J. Appl. Phys. **57**, 3626 (1985). *Electron capture:* C. Rau and S. Eichner, Phys. Rev. Lett. **47**, 939 (1981). *Compositionally modulated structure:* Proceedings of the Thirtieth Annual Conference on Magnetism and Magnetic Materials, San Diego, California, 1984, J. Appl. Phys. **57**, No. 8 (1985). This technique potentially allows much greater sensitivity to interface properties so that techniques such as neutron scattering are practical.

[4]R. Richter, J. G. Gay, and J. R. Smith, Phys. Rev. Lett. **54**, 2704 (1985) give a summary of expermental results and references in this field.

[5]G. Bergmann, J. Magn. Magn. Mater. **35**, 68 (1983).

[6]J. S. Moodera and R. Meservey, Phys. Rev. B **29**, 2943 (1984).

[7]J. Tersoff and L. M. Falicov, Phys. Rev. B **26**, 6186 (1982).

[8]G. Bergmann, Phys. Rev. Lett. **41**, 264 (1978).

[9]G. Bergmann, Solid State Commun. **42**, 553 (1982).

[10]J. S. Moodera, R. Meservey, and P. M. Tedrow, J. Appl. Phys. **55**, 2502 (1984).

[11]A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960) [Sov. Phys. JETP **12**, 1243 (1961)].

[12]C. Rizzuto, Rep. Prog. Phys. **37**, 147 (1974), a review article on local moments including the effects on superconductivity.

[13]S. Skalski, O. Betbeder-Matibet, and P. R. Weiss, Phys. Rev. **136**, A1500 (1964).

[14]V. Ambegaokar and A. Griffin, Phys. Rev. **137**, A1151 (1965).

[15]R. M. White and T. H. Geballe, *Long Range Order in Solids* (Academic, New York, 1974), Chap. 7.

[16]K. Maki, in *Superconductivity,* edited by R. D. Parks (Dekker, New York, 1969), Vol. 2, p. 1059.

[17]R. Meservey, P. M. Tedrow, and J. S. Moodera, J. Magn. Magn. Mater. **35**, 1 (1983).