Magnetic Properties of Compositionally Modulated Cu-Ni Thin Films

E. M. Gyorgy, J. F. Dillon, Jr., D. B. McWhan, L. W. Rupp, Jr., and L. R. Testardi
Bell Laboratories, Murray Hill, New Jersey 07974

and

P. J. Flanders
Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104
(Received 14 April 1980)

The magnetic properties of modulated Cu-Ni films with Ni thickness ranging from 6 to 60 Å and for various Cu thickness have been measured at room temperature, 77°K, and 4.2°K. The results show that the magnetic properties do not depend on the Cu thickness but only on the surface to volume ratio of the Ni. The Ni behavior is interpreted in terms of a large surface anisotropy, and not in terms of an enhanced moment.

PACS numbers: 75.70.-i, 75.50.Cc

Stimulated by the pioneering observations of the elastic and magnetic properties of modulated films by Hilliard and co-workers,[1,2] we have measured the magnetic properties of compositionally modulated CuNi thin films from 300 to 4.2 °K. The low-temperature results are interpreted in terms of a somewhat reduced magnetic moment and a large in-plane anisotropy, rather than the enhanced moment proposed by Thaler, Ketterson, and Hilliard.[2] The new anisotropy results from the thinness of the Ni layers and does not depend on their spacing. Here and in what follows the moment is defined in terms of the volume of the Ni present and not the total volume.

The magnetization and anisotropy were determined with a vibrating sample magnetometer[3] (VSM) (0–15 kG) or with a force method[4] (0–50 kG) and from microwave resonance measurements.

Films were prepared by evaporation of Cu and Ni from separate alumina crucibles onto mica substrates at 250–300 °C at pressures of 3 to 10 $\times 10^{-8}$ Torr. The deposition rate was from 1 to 6 Å/sec. Film thicknesses were determined by standard quartz monitors and confirmed (to ± 5%) by substrate-weight-gain measurements. Signals from the thickness monitors were also used to properly sequence the mechanical shutters for the alternate deposition of Cu and Ni. For all films 2×10^{3} Å of Cu were initially deposited, and for the resonance measurements this Cu layer was removed by preferential etching. The films were removed from the mica substrates before all magnetic measurements. Electron diffraction and TEM studies show clear lamella structure and diffraction sidebands with the expected spacing.[5] The films show varying amounts of [111] preferred orientation with the best ones approaching single crystals containing a few stacking faults. The degree of texture and the amplitude of the composition and strain modulation were determined from x-ray diffraction measurements following those of Segmüller and Blakeslee.[6] The full width at half maximum (FWHM) of the rocking curve of the (111) reflection was taken as a measure of the texture and only films with FWHM of about 5° or less were used for the magnetic measurements reported here. The sample with 8 Å Ni–8 Å Cu (Ref. 7) (3135 layers of Ni) was studied in more detail and showed all the Bragg peaks expected for a fcc crystal with $a_0 = 3.577$ Å. The FWHM was 0.4° and up to three harmonics were observed around (000), (111), and (222) reciprocal-lattice points. The chemical modulation is from 82% Ni to 26% Ni and the corresponding interplanar spacing modulation is from $0.984a_0/\sqrt{3}$ to $1.012a_0/\sqrt{3}$ (Å).

Magnetization curves typical of modulated films with small FWHM rocking curves are shown in Fig. 1. As a reference, Fig. 1(a) shows the magnetization of a 1.02×10^{-4}-cm-thick Ni film at 77 °K with the applied field ($\vec{H}$) in the plane ($H_{\parallel}$), and $\vec{H}$ perpendicular to the plane ($H_{\perp}$). Figure 1(b) shows the same measurement for a 10-Å-Ni–10-Å-Cu film (2440 layers of Ni). Figures 1(a) and 1(b) were obtained with the VSM. The high-field behavior of this sample measured using the force method is shown in Fig. 1(c).

From Fig. 1(a) it may be seen that the Ni data closely approximate the magnetic behavior expected for a thin, defect-free film with only a small anisotropy. The magnetization for $H_{\perp}$ increases linearly with H until $H \cong 4\pi M_0$ and then remains constant. The remanence for $H_{\perp}$ is very small. The slight deviation from saturation at $4\pi M_0$ and the low remanence for $H_{\parallel}$ are attribut-

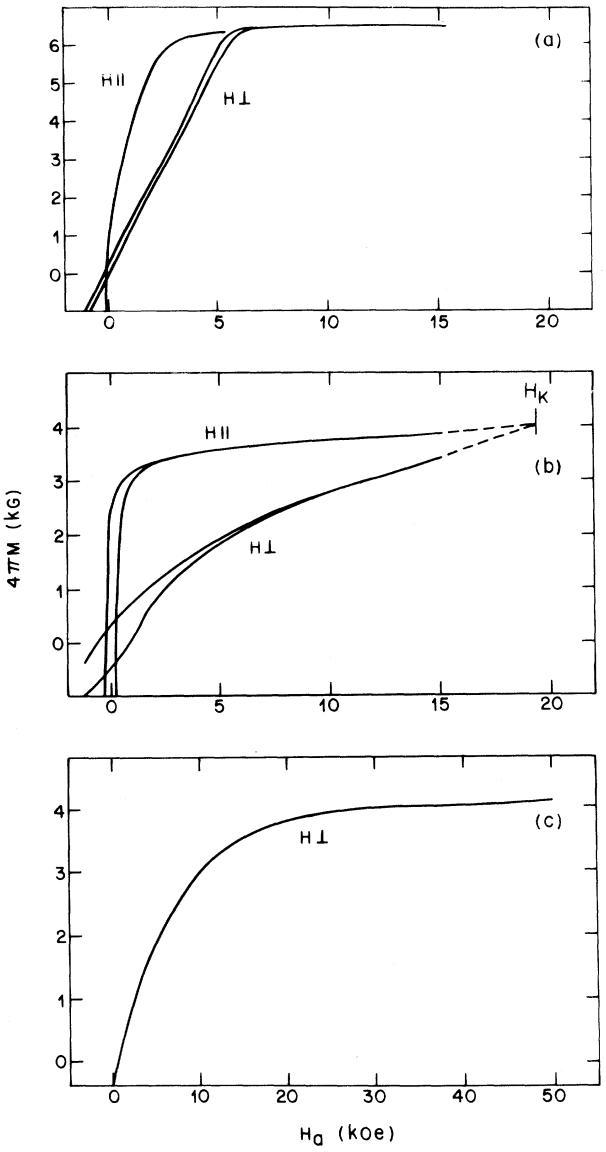

FIG. 1. (a) The magnetization for $\vec{H}$ parallel and $\vec{H}$ perpendicular to the film plane for a 1.02×10^{-4}-cm-thick Ni film at 77°K. (b) Same as (a) for a 10-Å-Cu modulated film. The sample contained 2440 layers of Ni. The dashed segments represent the extrapolation used to determine H_K. (c) The high-field data with $\vec{H}$ perpendicular for the film used for (b).

ed to the [111] texture, which coupled with the negative crystalline anisotropy constant (K_1), yields an easy axis perpendicular to the plane. Figures 1(b) and 1(c) indicate that the 10-Å-Ni–10-Å-Cu sample deviates somewhat from the ideal-thin-film behavior in that the approach to saturation for $H_\perp$ is not quite linear and that there is some remanence. The large flat region at high fields shown in Fig. 1(c) demonstrates that these films are totally saturated and that they do not show any super paramagentic effects. The lack of these effects implies that, if the nickel is distributed in clusters, the minimum size of such clusters is approximately 10 Å × 200 Å × 200 Å.[8] In this sense the magnetization curves show clearly that the samples behave as thin films. {By measuring the product of M and H, the force method [Fig. 1(c)] tends to suppress the remanence.} It should be remarked that films with large FWHM rocking curves generally have a large remanence for $H_\perp$, showing that these samples are not well described by a thin-film model.

With $H_\parallel$, the extrapolation of the high-field data back to $H=0$ is the magnetization of the Ni. With $H_\perp$, the intercept of the magnetization with the saturated region of the $H_\parallel$ curve is the anisotropy field (H_K). For thin films $H_K = 4\pi M_0 + 2K_u/M$, where K_u (for K_u positive) is any anisotropy tending to keep M in the plane. If microwave resonance[2] is used, values of H_K may be extracted from the fields for resonance with $H_\perp$ and $H_\parallel$.

So far we have tacitly assumed that M is uniform through the Ni thickness. If this is not the case, the magnetization measurement with $H_\parallel$ yields the average magnetization, $\langle 4\pi M\rangle$. If we take $K_u = 0$, the measurement with $H_\perp$ gives the maximum value, $4\pi M_{\max}$. The microwave resonance technique, again for $K_u = 0$ and $M \geq 0$ through the film, results in a value of M that is less than or equal to $4\pi M_{\max}$.[9]

In Fig. 2(a) we plot $\langle 4\pi M\rangle$ vs $1/t$ at 4.2 °K for films t-Ni–t-Cu, where t is the thickness in angstroms. Figure 2(b) shows $\langle 4\pi M\rangle$ vs t for 10-Å-Ni–t-Cu. For the films on which Fig. 2 is based, the total Ni thickness ranged from 0.8×10^{-4} to 2.5×10^{-4} cm. Figures 2(c) and 2(d) give H_K for the same samples. If H_K is determined by the area between the magnetization curves for $H_\parallel$ and $H_\perp$ rather than the intercept of the two curves, the value obtained is somewhat lower but the general behavior is the same. With the exception of the film with $t = 6$ Å, all the films that are shown in Fig. 2 have the ratio of remanence for $H_\perp$ to $\langle 4\pi M\rangle$ less than 0.16. For the 6-Å film this ratio is 0.3, and this larger deviation from ideal-thin-film behavior may account for the low value of H_K observed. Otherwise this film has the magnetic properties of a continuous film in as much as for $H_\parallel$ it saturates in less than 1 kG.

The results obtained at 77 °K are only slightly reduced from those shown in Fig. 2. Extrapola-

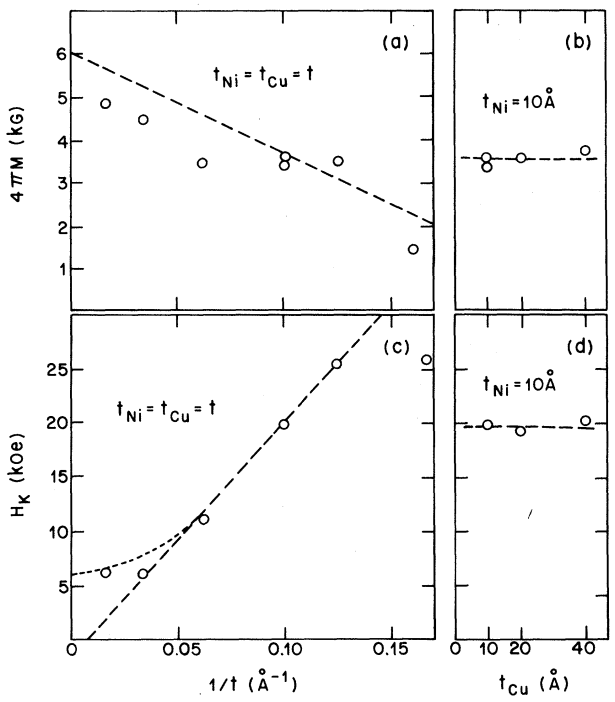

FIG. 2. (a) The average magnetization at 4.2°K as a function of $1/t$, where t is the thickness in angstroms, for films t-Ni$-t$-Cu. (b) The average magnetization at 4.2°K as a function of the Cu thickness in angstroms (t) for films 10-Å-Ni$-t$-Cu. (c) The anisotropy field (H_K) at 4.2°K vs $1/t$ for films t-Ni$-t$-Cu. (d) H_K vs t at 4.2°K for 10-Å-Ni$-t$-Cu.

tion of the data of Ref. 2 to 77 °K gives $H_K = 1.1 \times 10^4$ Oe for $t = 12$ Å which is in very good agreement with our static measurements. Our rf results for a $t = 10$-Å sample at 77 °K are also in good agreement with the static data.

Figure 2 clearly demonstrates that $\langle 4\pi M\rangle$ and H_K depend only on the Ni thickness and not the Cu thickness. That is the Ni properties are determined by its area to volume ratio and not by modulation effects.

In Ref. 2 it is assumed that K_u is small and negative and that therefore H_K is essentially a measure of $4\pi M_{max}$. However, our measurements of $\langle 4\pi M\rangle$ make this assumption appear unreasonable. For example, at 4.2 °K the sample with $t = 8$ Å would, with this assumption, have $4\pi M_{max} = 2.5 \times 10^4$ G and $\langle 4\pi M\rangle = 3.5 \times 10^3$ G. If we make the reasonable assumption that $M \geq 0$ through the film, the magnetization would be confined to only 1 Å or $\frac{1}{2}$ an atomic layer. For the $t = 6$ Å film only 0.17 of an atomic layer could be magnetic. A magnetization of 2.6×10^4 G confined in such a small thickness does not appear plausible. Rather, it is necessary to postulate a large anisotropy that tends to keep M in the plane and a magnetization that is less or equal to that of bulk nickel.

The origin of this anisotropy is at present uncertain. The behavior shown in Fig. 2(c) suggests a surface anisotropy. In fact the line in Fig. 2(c) is $H_K = 2 \times 10^5/t$ Oe, which implies a surface anisotropy of 0.3 ergs/cm^2. While no experimental values of the surface anisotropy of the Ni-Cu interface are available, it may be noted that values of this order of magntiude but opposite sign have been obtained for NiFe alloys on Cu.[10] To account for the zero intercept there must be some volume anisotropy that cancels the effect of $4\pi M$. This added anisotropy quite possibly arises from magnetostrictive effects. In fact, the measured strain modulation combined with λ_{111} for bulk Ni leads to an anisotropy contribution which approximately balances the $4\pi M$ term due to shape. For large t, this term should disappear since in this case the lattices are no longer coherent and H_K should approach 6×10^3 Oe as $1/t$ goes to zero.

The decrease of $\langle 4\pi M\rangle$ with thickness shown in Fig. 2(a) may arise from a decrease in magnetization with thickness or from nonmagnetic (dead) layers. The line in Fig. 2(a) represents the behavior the samples would have if the value of $4\pi M$ is that of bulk Ni and there is a 2-Å-thick dead layer at each Ni-Cu interface. The magnetic data presented here do not permit us to choose between the two alternatives. However, the measured amplitude of the chemical modulation suggests that the results are best explained by a reduction of magnetic moment and not by the presence of dead layers. If a nonmagnetic layer does exist, it probably arises from chemical mixing of Ni and Cu over the imperfect interface. For discussion of intrinsic dead layers see Ref. 10.

We have profited from stimulating discussions with E. I. Blount, S. Nakahara, and L. R. Walker. We thank E. Y. Chen for assistance in sample mounting and data handling. This work was supported in part by the National Science Foundation, Materials Research Laboratory Program under Grant No. DMR 76-80994.

[1]W. M. C. Yang, T. Tsakalakos, and J. E. Hilliard, J. Appl. Phys. 48, 876 (1977).

[2]B. J. Thaler, J. B. Ketterson, and J. E. Hilliard, Phys. Rev. Lett. 41, 336 (1978).

[3]S. Foner, Rev. Sci. Instrum. 30, 548 (1959).

[4]P. J. Flanders and C. D. Graham, Rev. Sci. Instrum.

50, 1564 (1976).
[5]S. Nakahara, R. Schutz and L. R. Testardi, in Proceedings of the International Conference on Metallurgical Coatings, San Diego, 1980 (to be published).
[6]A. Segmüller and A. E. Blakeslee, J. Appl. Cryst. 6, 19 (1973).
[7]The films here will be specified by the ideal Ni-Cu thicknesses. However, this is not meant to imply that sharp boundaries were achieved in the films.
[8]I. S. Jacobs and C. P. Bean, in *Magnetism III*, edited by G. Rado and H. Suhl (Academic, New York, 1963), p. 276. G. P. Felcher, J. W. Cable, J. Q. Zheng, J. B. Ketterson and J. E. Hilliard (private communication) have recently discussed clustering in these materials.
[9]R. M. White and C. Herring, to be published.
[10]U. Gradman, J. Magn. Magn. Mater. 6, 173 (1977).

Theory for the Dielectric Function of Granular Composite Media

Ping Sheng
Theoretical Sciences Group, Exxon Research and Engineering Company, Corporate Research Science Laboratories, Linden, New Jersey 07036
(Received 28 March 1980)

A new theory for the dielectric function of composite solids is formulated which displays both the optical dielectric anomaly and the percolation threshold, thereby providing a basis for a unified understanding of the optical and percolation transport properties of granular materials. The results of the theory are shown to be in good agreement with experimental data.

PACS numbers: 77.90.+k

Recent interest in the optical and transport properties of granular composite materials has spurred renewed theoretical investigation in the calculation of the dielectric function[1-3] for a heterogeneous composite medium. There are at present two prevalent theories for the dielectric constant of composite materials. One is the Maxwell-Garnett theory[3] (MGT), which is usually preferred for the calculation of optical properties, because it predicts the existence of the optical dielectric anomaly observed in granular metal films. However, because of the inherently asymmetrical treatment of the two constituents of the composite, MGT predictions grossly disagree with experimental optical and transport results in cermets when the volume fraction of the dispersed phase (in MGT) becomes comparable to or greater than that of the matrix phase.[3] In particular, the theory does not produce the observed percolation threshold in granular metals. The effective medium theory (EMT) proposed by Bruggeman[4] is the other widely used approach to the calculation of the dielectric constant for composite materials. The EMT does give a percolation threshold, but, unlike the MGT, it yields no dielectric anomaly. Moreover, the predicted value of the percolation threshold is low compared with the experimental result.[5]

In this Letter I present a new theory for the dielectric constant of granular composite (also known as cermet films). The theory displays both the optical dielectric anomaly and the percolation threshold, thereby providing a basis for the unified understanding of the optical and percolation transport properties of granular composite media.

The study of hopping conductivity in grangular metals[6-8] has indicated that the microstructure of composite films is primarily determined by the grain formation process through surface diffusion of sputtered or evaporated molecules. The resulting composition homogeneity on the scale of the surface diffusion length has been shown to be responsible for the characteristic temperature and electric field dependence[8] of granular metal hopping conductivity. As the starting point of the present theory, consider a spherical region with the dimension of a diffusion length inside the material. Within such a region a fraction p of the volume is taken by the molecules of component 1 and the rest by component 2. Here p is the macroscopic volume composition of component 1. When a grain is formed inside this region by diffusion and coalescence. there are two possible outcomes: Component 1 forms the grain and component 2 the coating, which we denote as a type-1 unit; or component 2 may form the grain and component 1 the coating, which is denoted as a type-2 unit. The relative probability of occurrence for the two cases can be estimated by counting the number of equally possible final configurations (corresponding to

