Enhanced Magnetization Density of a Compositionally Modulated CuNi Thin Film

Barry J. Thaler and J. B. Ketterson
Department of Physics and Materials Research Center, Northwestern University, Evanston, Illinois 60201

and

J. E. Hilliard
Department of Materials Science and Engineering and Materials Research Center,
Northwestern University, Evanston, Illinois 60201

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The magnetization density, M, of a CuNi thin film containing a 30-Å composition modulation has been deduced from ferromagnetic resonance data between 120 and 325°K. The data imply the existence of high-M regions in the modulated film. At 300°K, M is about 200 emu/cm^3, and increases as the temperature decreases. By 125°K, M is significantly larger than that of pure Ni. After most of the modulation was annealed out, M had decreased by an order of magnitude.

It has recently been demonstrated that the elastic properties of bimetallic films containing short-wavelength (less than 40 Å), one-dimensional composition modulations may be significantly different from those of the homogeneous alloys.[1,2] In this Letter we present the first measurements of the magnetic properties of such a system. We chose the CuNi system because a large enhancement in the biaxial elastic modulus has already been observed,[2] and also because good quality compositionally modulated films were readily available.

Magnetic studies of compositionally modulated films, like CuNi, have the potential to make significant contributions to our fundamental knowledge of ferromagnetism in metals. Studies of the dependence of the magnetic properties on both the wavelength and amplitude of the composition modulation add new variables to the alloy problem. Films containing alternating layers of different metals, with at least one metal being a couple of monolayers thick, may allow the production of contamination-free samples to test theories of surface magnetism. These films also offer the attractive possibility of producing nearly two-dimensional ferromagnets.

The compositionally modulated films were prepared using a technique described in detail elsewhere.[3] Briefly, this technique involves evaporating both Cu and Ni (from separate crucibles) through a rotating pinwheel shutter that alternately allows the particle flux from each source to reach the substrate. This technique produces samples having a composition profile somewhere between a square wave and a sine wave,[2] thus engendering the term "compositionally modulated" rather than "layered" thin films. Under normal operating conditions the evaporation rates were about 5 Å/sec, and the background pressure was about 2×10^{-7} Torr.

The compositionally modulated sample to be described in this Letter contained approximately 41 at.% Ni, was about 4500 Å thick, and had a modulation wavelength of about 30 Å, and the first Fourier component of its composition modulation was 0.41 ± 0.06 at. fraction. The film was deposited on a mica substrate heated to 300°C. Prior to deposition of the modulated film, a 1200–1300-Å Cu layer was evaporated onto the mica. The latter two procedures were necessary to give the crystallites a strongly preferred orientation of [111] normal to the plane of the film. The wavelength and amplitude of the modulation were determined from measurements of the position and integrated intensity of the x-ray diffraction patterns (made with Cu $K\alpha$ radiation) produced by the 111 Bragg peak, and its associated first-order satellites.[4] The Cu and Ni concentrations were determined by atomic absorption analysis, performed by the Argonne National Laboratory.

Because of the composition modulation the samples do not possess a uniform magnetization density; instead the magnetization density is an oscillatory function, $M(z)$, with the wavelength of the composition modulation. It is likely that $M(z)$ in the Cu-rich regions is essentially zero, thus significantly lowering the average magnetization of the entire sample when compared with the relatively high $M(z)$ of the Ni-rich regions. We employed the technique of ferromagnetic resonance (FMR) to probe the Ni-rich region, since we preferred a probe which favored the *local* magnetization densities, rather than the "reduced" averaged magnetization of the entire sample (as would be sensed by a magnetometer).

The FMR spectra were measured using a Varian model E-4 X-band EPR spectrometer with a 10-kG electromagnet. The samples were cut to a size of 4×6 mm^2 from much larger area films produced during the vapor-deposition process. A sample was held inside an open-ended quartz Dewar, which itself was placed in the microwave cavity. The temperature was regulated by passing temperature-regulated N_2 gas over the sample.

After an FMR spectrum is obtained, the resonance field must be converted to an effective magnetization density. Basically, FMR measures the precession frequency of the electron spins due to the combined effects of the external field H, the internal magnetization density M with its associated geometry-dependent demagnetizing fields, and the internal anisotropy fields either arising from intrinsic effects or induced by strain. For a ferromagnetic thin film of uniform magnetization and a negligible anisotropy field, the expression for the resonance frequency ω with H parallel to the film is[5]

$$\omega/\gamma = [H(H + 4\pi M)]^{1/2}, \tag{1}$$

and with H perpendicular to the film it is[5]

$$\omega/\gamma = H - 4\pi M, \tag{2}$$

where γ is the gyromagnetic ratio given by $\gamma = ge/2mc$, and g is the spectroscopic splitting factor. All calculations reported here assume $g = 2.21$, the value for pure Ni.[6] This assumption gains support from the fact that FMR studies of homogeneous NiCu[7] and NiCr[8] alloys are consistent with $g = 2.21$. If one were to correct Eqs. (1) and (2) for anisotropy fields, one would essentially add (or subtract) terms of the order of the anisotropy field to the applied field.[8]

A test of the validity of analyzing FMR data using Eqs. (1) and (2) (i.e., neglecting anisotropy fields) would be to obtain FMR spectra with H parallel and perpendicular to the film to ascertain whether the deduced values of M are in agreement with each other. In most cases a significant anisotropy field will cause a discrepancy between these two values of M. We tested our data in this way. Figure 1 shows values of M, obtained for H parallel and perpendicular to the film, as a function of temperature T. The data for the two directions are in quite good agreement, and so for most types of anisotropy we believe that the neglect of the anisotropy fields in the modulated film does not produce spurious results.

However, the above test will not detect the presence of the anisotropy field in a thin film having a uniaxial anisotropy axis *perpendicular* to the film. A thin film containing an isotropic stress in the plane of the film is an example of this type of anisotropy. In this case the resonance fields are shifted by amounts such that Eqs. (1) and (2) give the same, but incorrect, value of M. Macdonald[9] shows that Eqs. (1) and (2) may be corrected for this type of anisotropy by replacing $4\pi M$ by $4\pi[1 + (3\lambda\sigma/4\pi M^2)]M$, where λ is the magnetostriction coefficient and σ is the isotropic stress (positive for tension). The modulated CuNi films possess a coherent lattice,[2,10] and so it is quite likely that such stresses are present. Since the lattice parameter of bulk Cu is greater than that of bulk Ni, the Ni atoms (in the Ni-rich regions) must experience a tensile stress in the plane of the film. Combining this with the *negative* magnetostriction coefficient of Ni means that the values of M deduced from Eqs. (1) and (2) are too *low*. Stress may also be induced in the film by differential contraction arising from the difference in the thermal expansion coefficients of Ni and mica. Measurements by Macdonald, performed on Ni films deposited on mica, indicate that this stress also causes the values of M deduced from Eqs. (1) and (2) to be too *low*.[11,12] Since both of these stress mechanisms cause Eqs. (1) and (2) to underestimate M, the values that we report for this quantity deduced from Eqs. (1) and (2) are probably too *low*.

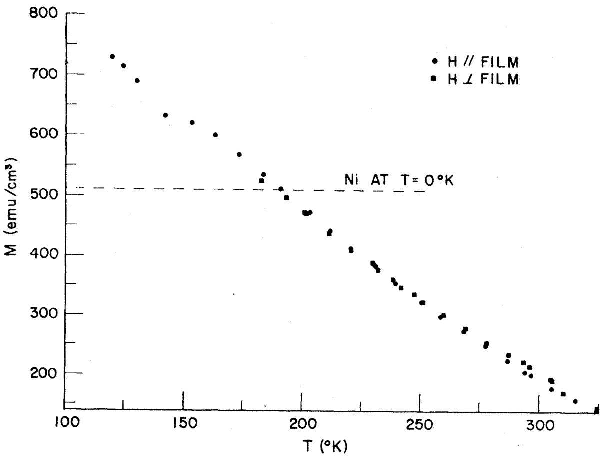

FIG. 1. The temperature (T) dependence of the magnetization M as determined from ferromagnetic resonance measurements in a compositionally modulated CuNi specimen with the magnetic field parallel and perpendicular to the sample.

From Fig. 1 we observe that M is approximately 200 emu/cm^3 at 300°K in the compositionally modulated CuNi sample; in contrast, homogeneous CuNi alloys[13] at this concentration level have Curie temperatures below 50°K.[14] Note that M increases as T decreases. In particular, by 185°K, M of the modulated sample is equal to that of pure Ni and, quite surprisingly, the data taken with H parallel to the film indicate that by 125°K, M of the compositionally modulated film is significantly larger than M of pure Ni. Because of magnetic field limitations we could not extend our FMR measurements with H perpendicular to the film below 180°K.

The linewidths ΔH (for the data shown in Fig. 1) with H perpendicular to the film were between 1175 and 1600 G, and ΔH increased as T decreased. For comparison, we measured ΔH of a thin Ni film prepared in the same vapor deposition system. ΔH of the modulated sample was about 5 times larger than that of the Ni film. This is not particularly surprising, since we remarked at the outset that the modulated sample possesses a distribution of magnetization densities $M(z)$ rather than a unique value as in Ni. Therefore the large ΔH may (at least in part) be a reflection of the periodic variation of M.

Finally we investigated the behavior of M as a function of the amplitude of the composition modulation. The amplitude of the composition modulation was decreased by annealing the sample *in vacuo* (~2×10^{-6} Torr) at 390°C for varying periods of time. After each anneal M vs T was measured, and the sample was also x rayed to determine the amplitude of the composition modulation.[15] As can be seen from Fig. 2, M uniformly decreases by an order of magnitude as the first Fourier component of the modulation A_1 decreases from 0.4 to 0.1 at. fraction. Since it was difficult to extract the high-angle, first-order 111 satellite from the tail of a peak due to the mica substrate (especially for the smaller values of A_1), we plotted M vs $(I_-/I_B)^{1/2}$, a quantity which should be proportional[2] to A_1; here I_B is the integrated intensity of the 111 Bragg peak and I_- is the integrated intensity of the low-angle, first-order 111 satellite. We determined the proportionality constant from measurements of both satellites in the unannealed state. The error bars on A_1 in Fig. 2 reflect the fact that we did not x ray exactly the same area after each anneal. This introduced a random error of about 5%. Any systematic errors in the proportionality factor connecting $(I_-/I_B)^{1/2}$ and A_1 are not included in these error bars; this error is reflected in our initial value of A_1 which was 0.41 ± 0.06 at. fraction.

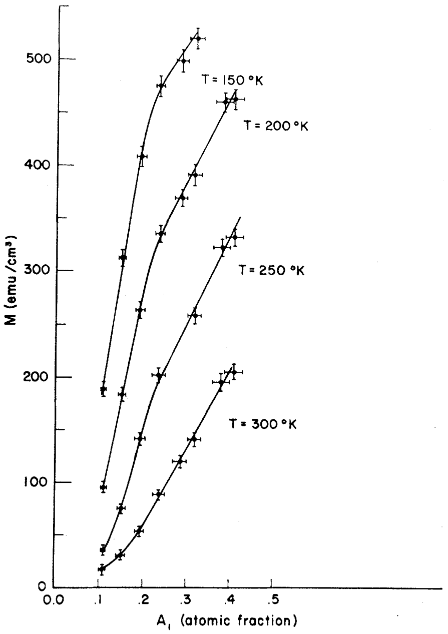

FIG. 2. The dependence of the magnetization M on the amplitude of the first Fourier coefficient of the composition modulation A_1 for various temperatures.

In summary, we have measured FMR spectra as a function of T for a CuNi thin film containing a 30-Å composition modulation. These spectra indicate that high-M regions exist in the modulated sample. At room temperature we deduce a value of M of about 200 emu/cm^3, in sharp contrast to homogeneous alloys containing (40–50)% Ni which have Curie temperatures below 50°K. As T is lowered, M increases, and by 125°K, M is significantly larger than that of pure Ni. When the composition modulation is removed by annealing, M decreases by an order of magnitude. The origin of the enhanced magnetization at low temperatures is not understood at this time; a similar situation exists with respect to the enhanced elastic modulii. However, the following points should be noted in this connection: (1) The composition modulation alters the electronic band structure through the appearance of additional Bragg planes; (2) at the crest of the Ni concentration wave, the interatomic distances differ substantially from bulk Ni, which might enhance the local magnetization; and (3) one-dimensional Ruderman-Kittel-Kasuya-Yosida oscillations might tend to be coherent in this system.

Some preliminary FMR measurements were earlier performed on the CuNi system by G. Horiuchi. We would like to thank Dr. A. Purdes for preparing the sample used in this study. The use of the Varian E-4 EPR spectrometer which is maintained by Mr. J. Anderson is also greatly appreciated. We would also like to thank Mr. G. Hénein for many helpful discussions throughout this investigation. This work was supported under the National Science Foundation–Materials Research Laboratory program through the Materials Research Center of Northwestern University under Grant No. DMR-76-80847.

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Complete Solution of the Korringa-Kohn-Rostoker Coherent-Potential-Approximation Equations: Cu-Ni Alloys

G. M. Stocks
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

and

W. M. Temmerman
H. H. Wills Physics Laboratory, University of Bristol, Bristol, United Kingdom

and

B. L. Gyorffy(a)
Brookhaven National Laboratory, Upton, New York 11973

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We report on calculations of the electronic states in disordered $\mathrm{Cu}_c\mathrm{Ni}_{(1-c)}$ alloys based on a complete solution of the coherent-potential approximation for a muffin-tin model of the alloy potential [Korringa-Kohn-Rostoker coherent-potential-approximation (KKR-CPA)]. The computational effort required is modest on the scale of that involved in band-structure calculations for many atoms per unit cell. The calculated densities of states are in good agreement with the results of photoemission and other experiments. The adequacy of previous approximate KKR-CPA and averaged t-matrix calculations is discussed.

Experience with simple models[1,2] over the past decade indicates that the coherent-potential approximation (CPA)[3] gives a sufficiently good description of electronic states in random alloys to warrant calculations based on first-principles crystal potentials similar to those used for perfect crystals. However, because of the computational complexities, until recently little progress has been made towards implementing such a scheme. In this Letter we present the first complete solutions of the CPA equations for a nonoverlapping muffin-tin model of the crystal potential [KKK (Korringa-Kohn-Rostoker)-CPA] for three $\mathrm{Cu}_c\mathrm{Ni}_{(1-c)}$ alloys. While correcting some