The magnetization and Curie temperature of compositionally modulated Cu/Ni films

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We report detailed measurements of the magnetization of Cu/Ni composition modulated foils as a function of temperature, magnetic field, composition wavelength, and composition amplitude. We find a Curie temperature that initially increases rapidly with wavelength but quickly saturates. We also find that the Curie temperature is independent of composition amplitude which we ascribe to the existence of disk-like Ni clusters.

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I. INTRODUCTION

The study of artificially layered materials has recently attracted much interest as it opens a path to the development of new materials that do not exist in nature. Such materials are prepared by alternately depositing two constituents with a repeat distance, or wavelength, which varies from a few atomic plane spacings to hundreds or thousands of Angstroms. Since at long wavelengths behavior typical of bulk materials in contact occurs, it is generally the properties at shorter wavelengths which are of the most interest. Hilliard and co-workers have systematically studied interlayer diffusion for compositionally modulated foils (CMF)'s of the Cu/Au,[1] Au/Ag[2], and Cu/Pd[3] systems. They have also observed an appreciable increase in the elastic modulus of modulated Au/Ni and Cu/Pd foils[4] relative to that of homogeneous foils having the same average composition. Thaler *et al.*[5] and Gyorgy *et al.*[6] have studied the magnetization and the magnetic anisotropy for CMF's of the Cu/Ni system. Brodsky *et al.*[7] have observed an enhanced magnetic susceptibility at low temperature for the Pd/Au system. Schuller and Falco[8,9] have prepared a new class of films termed layered ultrathin coherent structures (LUCSs) from the structurally dissimilar materials niobium and copper, where an epitaxial like registry may occur at the interface. The superconducting properties of these materials have also attracted wide attention.[8–13]

In this paper we report the static magnetization of a series of Cu/Ni (60 atomic % Cu, 40 atomic % Ni) compositionally modulated alloys. We find that the saturation magnetization and the hysteretic magnetization scale with composition amplitude A and that the maximum magnetic moment per Ni atom is smaller than that of pure Ni. The approach of the static magnetization to saturation can be fitted by standard theories, and these fits indicate the absence of large strains in the layers. For our samples we find the interesting result that the Curie temperature, which is less than that of bulk Ni, is essentially independent of the amplitude A and only depends on the wavelength λ.

The Cu/Ni system is a familiar one whose bulk physical properties are relatively well known. Cu and Ni are both f.c.c. with nearly identical lattice parameters ($a_{Cu} = 3.61$ Å, $a_{Ni} = 3.52$ Å). A complete Cu/Ni solid solution can be obtained over a wide temperature range at all compositions. In the crystalline state pure Ni is ferromagnetic having a spontaneous magnetic moment of 0.61 Bohr magnetons (μ_B) per atom while copper is slightly diamagnetic. The average atomic magnetic moment and the Curie temperature of uniform Cu/Ni alloys decreases linearly with decreasing Ni concentration.[14,15] On a fractional basis, the magnetic moment of Ni decreases by about 0.1 μ_B for each 10 atomic percent Cu added. Thus the moment and the Curie temperature both approach zero for a uniform Cu/Ni (40 atomic % Ni) alloy. (See Fig. 1.)

II. EXPERIMENTAL PROCEDURE AND X-RAY DIFFRACTION ANALYSIS

The compositionally modulated Cu/Ni films used in this study all had an average Ni concentration of 40 atomic

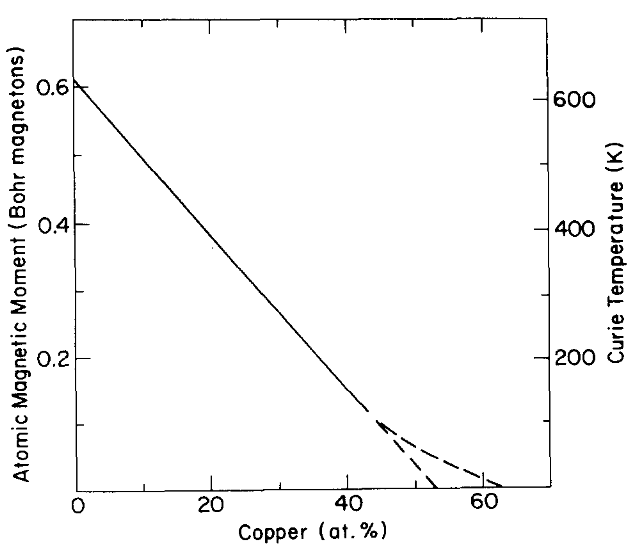

FIG. 1. The magnetic moment and Curie temperature of uniform Cu-Ni alloys as a function of concentration.

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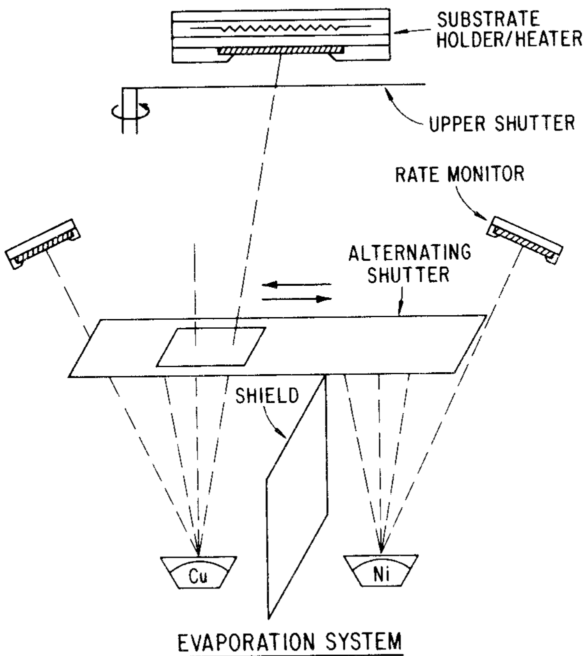

FIG. 2. A schematic drawing of the dual *e* gun evaporation apparatus used to prepare the Cu/Ni composition modulated films.

% with wavelengths ranging between 8 and 57 Å. Samples were prepared by electron beam evaporation in an oil diffusion pumped high vacuum system with a liquid nitrogen cooled Meissner trap surrounding the sample region. The pressure was typically 7×10^{-6} Torr during the evaporations.

The actual modulation of the composition is carried out by an electromagnetically actuated reciprocating shutter which produces a modulation of the vapor flux impinging on the substrate from each source (Fig. 2). The films were deposited on mica substrates heated to 350°C by an infrared lamp. The substrates were first cleaned with a detergent, rinsed in distilled water, and finally vapor cleaned with ethyl alcohol.

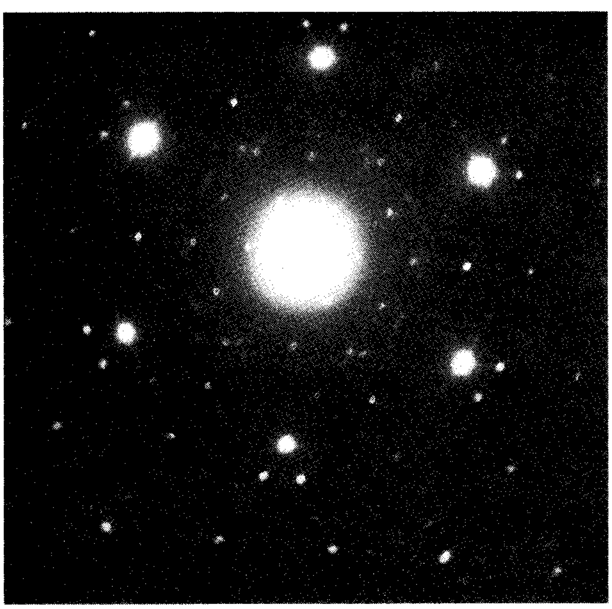

FIG. 3. Electron diffraction pattern for a typical Cu/Ni modulated film.

Prior to initiation of the modulation, an epitaxial Cu layer of about 800 Å was deposited to ensure that the Cu/Ni modulated films grew in a highly orientated [111] texture. The deposition rates of Cu and Ni were 30 and 20 Å/sec, respectively, and were controlled by a feedback system using quartz crystal oscillators as monitors. For given fluxes, the wavelength of the CMFs are controlled by the frequency of the electromechanical shutter. The overall thicknesses of our Cu/Ni CMFs were in the range of 0.5–1.0 μm.

The structure of our CMFs was determined using both transmission electron microscopy, Laue x-ray diffraction and $\theta - 2\theta$ x-ray diffraction with Cu $K\alpha$ radiation. The electron diffraction patterns clearly show that CMFs can be grown very well on a Cu epitaxial layer which is, in turn, deposited on mica (Fig. 3). The results of these TEM studies of our CMFs are the same as those of x-ray diffraction. Figure 4 shows Laue diffraction results from pure Cu as well as a

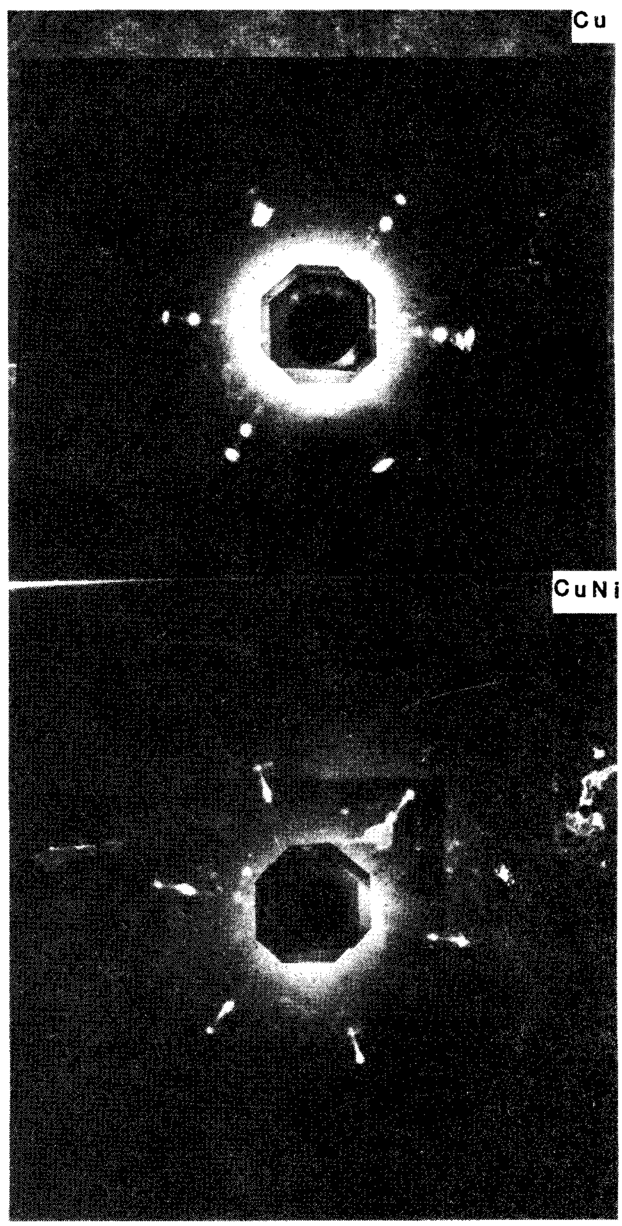

FIG. 4. The transmission Laue x-ray diffraction patterns for a pure Cu and a Cu/Ni modulated film.

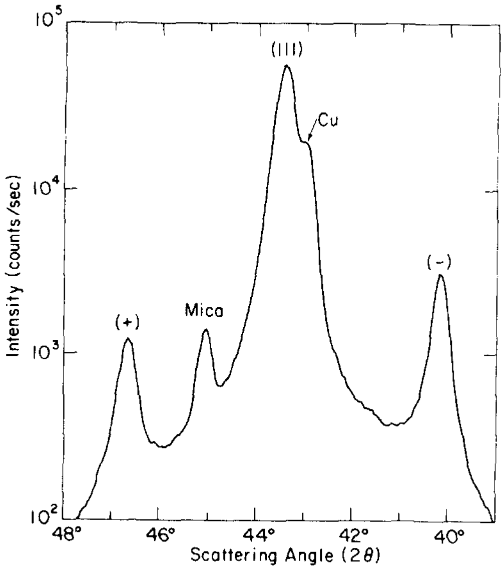

FIG. 5. The θ-2θ x-ray diffraction tracing for a typical Cu/Ni CMF with a wavelength of 30.4 Å.

Cu/Ni modulated film. These indicate the high quality of the films, as well as twinning of the crystal structure. Figure 5 shows $\theta - 2\theta$ x-ray results from a typical CMF with a wavelength of 30.4 Å. Note the strong central Bragg peak associated with the [111] (preferred) texture and the satellite peaks which appear on either side of the main peak.

The modulation wavelength λ and the composition amplitude A can be obtained from the positions and intensities of the central Bragg peak and the two superlattice satellite peaks[16] by the relation

$$S^{\pm} = S^{B} \pm 1/\lambda, \tag{1}$$

where $S^B = 2\sin\theta^B/\lambda_x$ and $S^{\pm} = 2\sin\theta^{\pm}/\lambda_x$; here S^B is the reciprocal of the [111] interplanar spacing, θ^B and $\theta^{\pm}$ are the angles of the central and satellite peaks, λ is the wavelength of the CMF, and λ_x is the x-ray wavelength. The presence of the composition modulation results in a periodic variation of both the atomic scattering factor and the lattice parameter.[16] For a sinusoidal profile the atomic scattering factor of the nth plane is assumed to be given by:

$$f_n = f\left[1 + \left(\frac{\Delta f}{f}\right)\mathrm{A}\sin\left(\frac{2\pi na}{\lambda}\right)\right], \tag{2}$$

where f_A and f_B are the atomic scattering factors of the A and B atoms, $\Delta f = f_B - f_A$, $f = c_A f_A + c_B f_B = c_A f_A + (1 - c_A) f_B$, a is the interplanar spacing and A is the amplitude of composition modulation.

The position of the nth plane is assumed to be given by:

$$x_n = na + \Delta x_n = na - \frac{\lambda\epsilon}{2\pi} A\cos\left(\frac{2\pi na}{\lambda}\right), \tag{3}$$

where ϵ is the strain amplitude which determines the positions of the atoms in succesive planes.

The diffracted amplitude is

$$F(S) = \sum_n f_n \exp(-2\pi i S x_n), \tag{4}$$

and the intensity is $I = F^*F$. Substituting Eqs. (2) and (3) into Eq. (4), and making a Taylor expansion of the exponential, we find that a pair of satellite peaks appears located $\pm 1/\lambda$ around the central Bragg peak. The ratios of the intensities of the satellites to the Bragg peak are given by:

$$I^-/I^B = \left[\frac{A}{2}\left(\lambda\epsilon S^- + \left(\frac{\Delta f}{f}\right)\right)\right]^2 \tag{5}$$

and

$$I^+/I^B = \left[\frac{A}{2}\left(\lambda\epsilon S^+ + \left(\frac{\Delta f}{f}\right)\right)\right]^2, \tag{6}$$

where $S^{\pm} = n/a \pm 1/\lambda$.

The ratio of the integrated intensities of the satellites to the Bragg peak $I^{\pm}/I^B$ are measured by a planimeter after each annealing treatment. The amplitude of the composition modulation determined in this way reduces with the annealing time at a fixed anneal temperature, presumably since the sample is forming a homogeneous alloy as A approaches zero.

The amplitude of the composition modulation A and lattice parameter ϵ, after a correction of the measured intensities I_m as discussed below, are expressed as follows:

$$A = \frac{S^+(I^-/I^B)^{1/2} - S^-(I^+/I^B)^{1/2}}{(\Delta f/f)S^B}, \tag{7}$$

$$\epsilon = \frac{(I^-/I^B)^{1/2} + (I^+/I^B)^{1/2}}{\lambda S^B}. \tag{8}$$

The corrected intensity I_c is given by

$$I_c = I_m(LP\epsilon D). \tag{9}$$

Here L is the Lorentz factor, which for a single crystal is given by $L = 1/\sin 2\theta$. For monochromatic radiation the polarization factor is

$$P = [1 + \cos^2(2\theta)]/2. \tag{10}$$

The absorption factor is given by $\alpha = [1 - \exp(-2\bar{\mu}t/\sin\theta)]$ with t the total thickness of the modulated film, and $\bar{\mu}$ the average linear absorption coefficient. $\bar{\mu}$ can be calculated from $\bar{\mu} = c_A\mu_A + (1 - c_A)\mu_B$, with $\mu_{Cu} = 475$, $\mu_{Ni} = 407$[14] yielding $\bar{\mu} = 447.8$. $D = \exp[1 - 2\bar{B}(\sin\theta/\lambda_x)^2]$ is the Debye-Waller factor, involving the average "temperature" coefficient $\bar{B} = c_A B_A + (1 - c_A)B_B$, with $B_{Cu} = 0.35$, and $B_{Ni} = 0.55$ yielding $\bar{B} = 0.47$ for our concentration. The atomic scattering factor is 21.94 for Cu and 20.62 for Ni.[17] We should stress at this point that the $\theta - 2\theta$ diffraction measurement only gives information perpendicular to the layers.

In order to reduce strains when our samples were cooled to low temperatures and to eliminate the effect of substrate magnetic moment, the samples were removed from the mica. The magnetization measurements were performed using an SHE Model VTS 10 susceptometer for fields up to 10 kG and in the temperature range 5–380°K. The direction of the magnetic field is parallel to the plane of the films for all measurements reported here; no demagnetization correction is required for this geometry. To study the amplitude dependence under otherwise identical conditions, the samples were annealed after each magnetization measurement to reduce the amplitude of modulation. As expected, only the amplitude of the x-ray satellites changed after each annealing while their positions remained unaltered, indicating that the wavelength λ was unchanged. The amplitude of modulation decreased exponentially with annealing time; the time constant being related to the diffusion constant. Annealing of the samples was performed in a high vacuum furnace heated by an infrared lamp at temperatures up to 400°C and for times ranging from a few minutes to a few hours. When the desired annealing time was reached helium gas was introduced to the vacuum chamber, rapidly cooling the samples to room temperature. Finally, the samples were annealed at 510°C for 6 h to produce an essentially uniform alloy.

III. EXPERIMENTAL RESULTS

We have performed magnetization measurements for seven samples with wavelengths from 8 to 57 Å. Figure 6 shows a typical curve of the magnetization M versus magnetic field H for a 30.4-Å CMF sample. Data are shown at a temperature 5 K for four different composition modulation amplitudes A obtained by successive anneals. Similar results were obtained for the other samples. The data exhibit magnetic saturation and hysteresis properties typical of common magnetic materials. It is observed that the hysteresis effects extend to higher fields (<3 kG) than in pure Ni (~ 500 G) and that the saturation magnetization reduces with decreasing composition amplitude, as expected. We should stress at this point that a homogeneous alloy with same 60% Cu-40% Ni average composition as our CMFs is nonmagnetic.

When the sample magnetization is approaching the saturation region, the curve can be fitted with an expression of the form[15]:

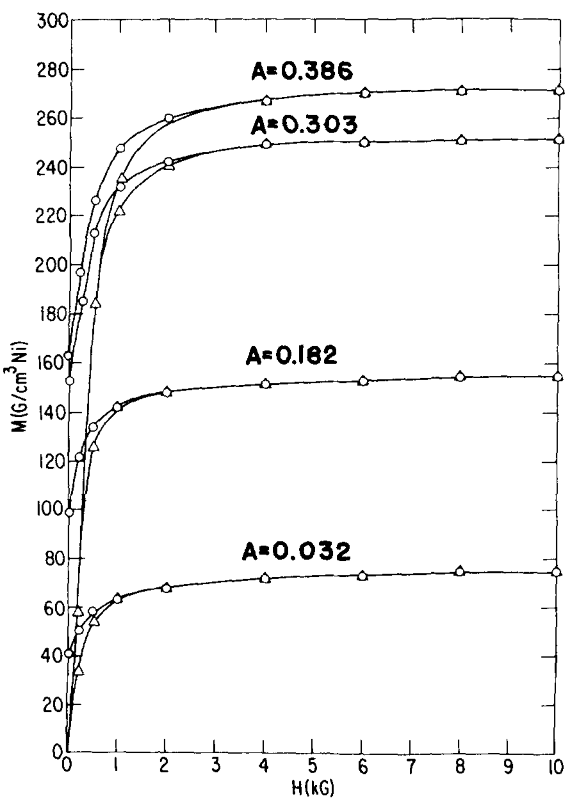

FIG. 6. A typical plot of magnetization M as a function of field H; the line is a least squares fit to Eq. 10.

$$M = M_s\left(1 - \frac{a}{H} - \frac{b}{H^2}\right) + \chi_0 H. \tag{10}$$

Here, the second term, a/H, models the effects of dislocations and nonmagnetic inclusions which may prevent the perfect alignment of moments; the third term, $-b/H^2$, is attributed to in-plane magnetic crystal forces and to contributions arising from strains; the last term, $\chi_0 H$, represents the paramagnetic contribution. A fit of the experimental data to Eq. (10) for $M > 0.9\, M_s$ is indistinguishable from the solid lines of Fig. 6. The saturation magnetizations obtained from these fits are higher by $\sim 5\%$ than the experimentally measured magnetizations at 10 kG. The linear χ_0 term is small throughout the measurement range. The third term is always a fraction ($<30\%$) of the second term. This implies that there are no large strains in the plane of the CMFs.

The largest value observed for the magnetization was $0.36\mu_B$/Ni atom, obtained from a sample having $\lambda = 28.4$ Å and $A = 0.42$, and is smaller than that of pure Ni ($0.61\,\mu_B$/Ni atom). This value is within 15% of the magnetization determined from a neutron diffraction experiment[18] on similar samples, and is in good agreement with spin-polarized supercell band structure calculations for a completely stratified Cu/Ni CMF system.[19]

The measure saturation magnetizations obtained from the fit described above are plotted as a function of the composition amplitude A in Fig. 7. As can be seen, the saturation magnetization scales roughly linearly with the composition amplitude. In fact, a plot of M_s versus A for the other six samples shows the same behavior as Fig. 7, i.e., a roughly linear dependence on A. Thus the saturation magnetization reduces monotonically with decreasing amplitude. This amplitude dependence could be expected from the behavior of uniform Cu/Ni alloys: as A decreases the maximum concen-

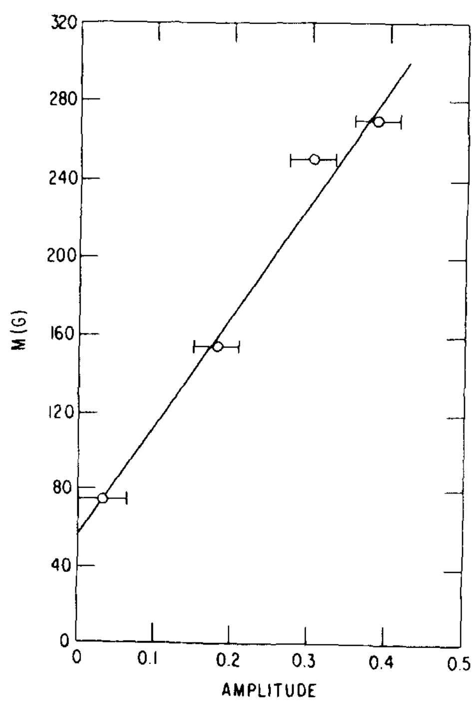

FIG. 7. The saturation magnetizations at 10 kG as a function of composition amplitude.

tration on Ni-rich material in each layer decreases. Thus, as Fig. 1 shows the magnetization should decrease.

In Fig. 7 it appears that M_s is finite for $A = 0$. We interpret this behavior as evidence that there is a cluster structure existing in the Ni layers which is contributing to the magnitude of the magnetization and which largely determines the Curie temperature of our CMFs. When the samples are annealed at a lower temperature, for example 400°C in one case, the amplitude A reduces to a very small value, but is not exactly zero. In this case, the CMF might still appear weakly magnetic and have the *same* Curie temperature as the unannealed sample; if the clusters were highly anisotropic and if the Curie temperature were dominated by the *smallest* dimension of the clusters (which is presumably some fraction of the composition wavelength). The result of the annealing process may then be to reduce the larger dimensions of the clusters and therefore the magnetization, which depends on the *total* cluster volume. It is only when the sample is completely annealed to form a uniform alloy that the amplitude A becomes truly zero. In this limit the sample becomes nonmagnetic down to the lowest temperature employed in these measurements (5 K). We speculate that these anisotropic Ni clusters are formed by our method of using two vapor sources to alternately deposit Cu and Ni layers on substrates maintained at temperatures less than 350°C. Films formed in this manner might be expected to exhibit cluster characteristics (and associated magnetic behavior) which are radically different from those obtained in bulk samples cooled from the melt. The substrate temperature is likely an important factor with lower substrate temperatures favoring a higher degree segregation; the effect of substrate temperature on the satellite structure was not systematically studied in this work.

The temperature dependence of the saturation magnetization for a sample having a 30.4-Å wavelength is shown in Fig. 8. We find that the saturation magnetization for a given amplitude decreases with increasing temperature, falling to zero at the Curie point T_c. This observed temperature dependence is in agreement with FMR measurements.[5] Perhaps the most striking thing to be observed in these experiments is that decreasing the amplitude A does not affect the Curie temperature (as obtained from extrapolations) to within a few percent. This result supports the existence of clusters in our CMFs. Apparently these clusters are quite stable and determined the Curie temperature. A similar phenomenon has been observed earlier by Gerlach[20] in the Ni-Au system. He reports that if the specimen (obtained by quenching bulk materials from 950°C) was initially composed of a two-phase mixture, the Curie temperature becomes higher after subsequent annealing at 400°C; additional annealing at that temperature leaves the Curie temperature unchanged and only reduces the saturation magnetization values. In our case the existence of clusters in an otherwise uniform alloy is analogous to the mixture of two phases in the Ni/Au system. The above discussion illustrates that the picture of a Cu/Ni CMF as a modulation on an otherwise uniform alloy is an oversimplification, and that nonuniformity within the superlattice planes is important.

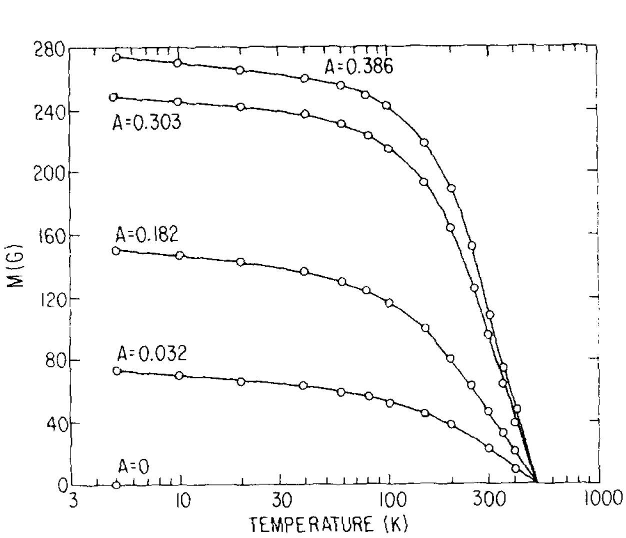

FIG. 8. The temperature dependence of the saturation magnetization.

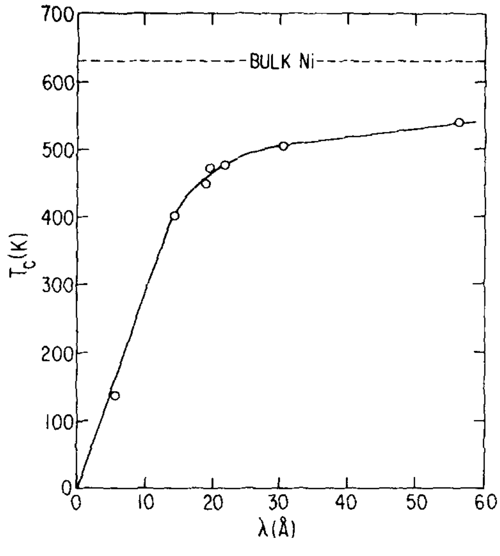

FIG. 9. The Curie temperature T_c as a function of wavelength λ.

Figure 9 shows the Curie temperature T_c (as obtained from extrapolation in Fig. 8) as a function of wavelength λ. These results are only intended to show the qualitative behavior of the Cu/Ni system. Precise determination of T_c's should be obtained from an Arrot plot. Notice that T_c increases monotonically with wavelength λ approaching, but remaining less than, the value of bulk Ni (627 K). In our model T_c does not depend on the radius of the cluster "disc," but does depend strongly on its thickness. This would imply that the dependence of T_c on wavelength should be similar to the dependence of the T_c of a thin film on thickness. We note that the shortest wavelength sample the satellites were very weak; this point which has the lowest T_c, may thus be misleading. Annealing of samples appears to decrease the lateral cluster radius through diffusion. This would simultaneously result in a decrease of the average magnetization and of the x-ray satellite intensities. We would like to stress that the clustering suggested by this experiment is rather unlike that in the "uniform" alloy case.

In summary, we have measured the magnetization of Cu/Ni compositionally modulated foils as a function of temperature, magnetic field, composition wavelength, and amplitude. We find a maximum magnetization of 0.36 μ_B/Ni atom in agreement with neutron scattering results[18] as well as with band structure calculations.[19] We find some evidence for Ni clustering within the layers; suggesting that, at least samples, the picture of Cu/Ni CMFs as compositionally modulated uniform alloys is an oversimplification.

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