Magnetization of compositionally modulated CuNi films

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We report static magnetization measurements on the compositionally modulated ferromagnetic alloy Cu/Ni, which, contrary to earlier ferromagnetic resonance measurements, show the moment per Ni atom is reduced relative to pure Ni. The low-temperature magnetization is found to vary linearly with modulation amplitude, but, surprisingly, the Curie temperature is found to be almost amplitude independent.

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The properties of artificially prepared layered materials have recently attracted much attention. This interest has been motivated by the production of semiconductor superlattices that have unique physical properties,[1] by the observation of unusual magnetic[2,3] and elastic properties[4] for compositionally modulated structures (CMS), and by the preparation of layered ultrathin coherent structures (LUCS)[5] from structurally dissimilar materials. We present in this letter static magnetization studies for a compositionally modulated structure made of the two elements Cu and Ni. We find that the saturation magnetization and the coercivity vary with composition modulation amplitude A and that the maximum magnetization per Ni atom is smaller than that of pure Ni. This is contrary to one of the interpretations of ferromagnetic resonance measurements,[3] which deduces a magnetic moment per Ni atom in the layered material exceeding that of pure Ni.

The magnetic behavior may be summarized as follows: (i) The magnetization of the CMS is smaller than that of pure Ni. (ii) The approach to saturation can be fitted using *standard* theories for magnetic materials. This fitting procedure indicates the absence of large uniform strains over a sample. (iii) The saturation magnetization varies linearly with composition amplitude in accordance with earlier results for the uniform alloy. (iv) The "Curie temperature" does not shift with composition amplitude A. This is a result peculiar to the CMS. (v) The Curie temperature T_C decreases with decreasing modulation wavelength λ, an effect which clearly is absent for uniform alloys where λ is not a meaningful parameter.

The CuNi samples (60-at. % Cu, 40-at. % Ni) were prepared using a dual electron beam gun system with a reciprocating shutter in vaccum of approximately 7×10^{-6} Torr. The shutter alternately exposed the cleaved mica substrate held at 350 °C to the flux of Cu or Ni. The total thickness of these samples are in the range 0.5–1μm. The structure of the films was determined by the use of standard $\theta - 2\theta$ x-ray diffraction techniques (Cu K_α radiation). From the position and amplitude of the Bragg peak and superlattice satellites a modulation wavelength and amplitude were obtained.[6] The distance over which the composition is repeated is denoted as the "modulation wavelength." From x-ray analysis of our films the composition ratio is found to vary sinusoidally perpendicular to the films rather than as a square wave which would result if there were no diffusion between layers. Such diffusion also reduces the amplitude of the composition modulation. The largest composition ratio is denoted as the composition amplitude A.

The samples were removed from the substrate and magnetization measurements performed using a Superconducting quantum interference device susceptometer[7] in fields up to 10 kG and in the temperature range 5–380 k. By annealing the samples at an elevated temperature for controlled times, it is possible to reduce A, while leaving the composition modulation wavelength λ unchanged. The annealing was performed in a high-vacuum furnace at temperatures of

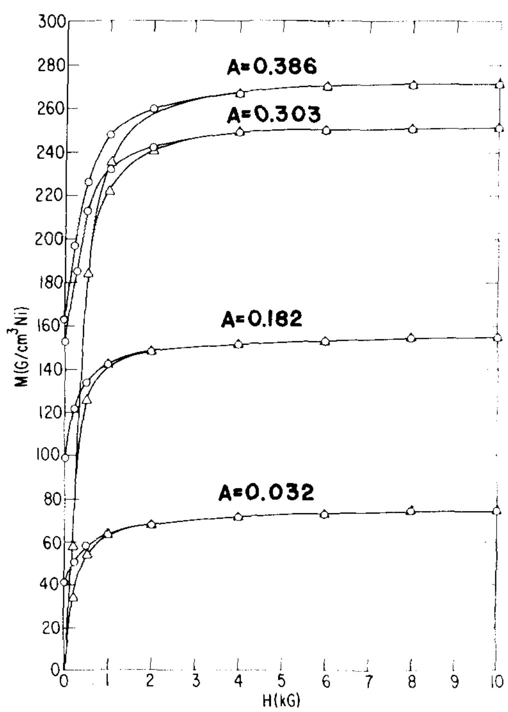

FIG. 1. Magnetization vs H for a 60% Cu/40% Ni sample with modulation wavelength 30.4 Å. The magnetization has been normalized to the total volume of Ni in the sample by using the bulk density value of 8.90 g/cm³. Four different composition amplitudes obtained from successive annealing, are shown. Δ increasing H, ○ decreasing H.

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400 °C.

Figure 1 shows the magnetization versus field H for a Cu/Ni (60 at. %) sample having a wavelength of 30.4 Å and for four composition modulation amplitudes obtained by successive annealings. In all cases H is in the plane of the sample. Notice that the saturation magnetization decreases with the composition amplitude as expected and that the magnetization curves are hysteretic as expected for a ferromagnetic material, although the uniform $Cu_{0.6}Ni_{0.4}$ alloy is nonmagnetic.[8] It should be pointed out that hysteresis in the magnetization for this material occurs at a substantially larger value ($\sim$4 kG) than it does for pure Ni ($\sim$500 G). It is customary[9] to fit the approach to saturation using an expression of the type

$$M = M_s - a_0/H - b_0/H^2 + \chi_0 H, \qquad (1)$$

where the a_0 term models the effects of dislocations or nonmagnetic cavities or inclusions, the b_0 term is attributed to in-plane magnetic crystal forces and to contributions arising from uniform strains, and χ_0 is a high-field susceptibility term. A fit of the experimental data to Eq. (1) for $M \gtrsim 0.9M_s$ is indistinguishable from the solid lines of Fig. 1. The saturation magnetizations obtained from these fits are higher by $\sim$5% than the experimentally measured magnetizations at 10 kG. The linear χ_0 term is small in measurement range ($<$ 10%), and the b_0 term is always a fraction ($<$ 30%) of the a_0 term, indicating that contrary to what is expected the material is not subject to large internal strains. Similar results were obtained for seven samples ranging in wavelength from 8 to 60 Å.

The measured saturation magnetizations obtained from these curves are plotted as a function of composition amplitude A in Fig. 2. As can be seen, the saturation magnetization varies linearly with composition amplitude. In fact, a plot of saturation magnetization for seven *different* wavelength samples shows a roughly linear dependence on A, independent of λ. This could be expected from the observations of linearly decreasing magnetizations as a function of Ni concentration in homogeneous alloys.[8]

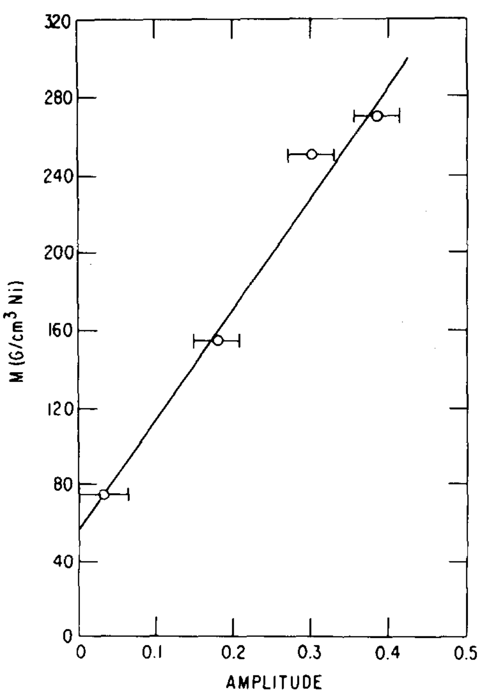

FIG. 2. Saturation magnetization as a function of composition modulation amplitude A for the sample shown in Fig. 1.

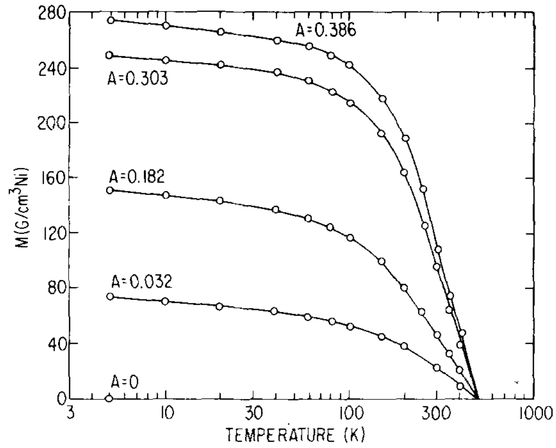

FIG. 3. Temperature dependence of the saturation magnetization for the sample shown in Fig. 1 and 2.

The largest magnetization obtained (0.36 μ_B/Ni atom) is from a sample having $\lambda = 28.4$ Å and $A = 0.42$. This value is within 15% of the magnetization determined from neutron diffraction experiments[10] and in good agreement with spin-polarized, supercell band-structure calculations for a (completely stratified) Cu/Ni LUCS system.[11] These results are in disagreement with the enhanced magnetization interpretation (relative to pure Ni) of Cu/Ni CMS ferromagnetic resonance data.[3] However, as discussed in Ref. 3, uniaxial anisotropy about an axis perpendicular to the film can produce an apparent magnetization shift. This interpretation was rejected by the authors of Ref. 3, since the required sign of the magnetostriction coefficient would have to be opposite to that of pure Ni. Our observations here suggest that this may indeed be the case.[12]

In recent paper White and Herring[13] have calculated the effect of a nonuniform magnetization, as exists in a CMS. In this model, if the ferromagnetic resonance frequency

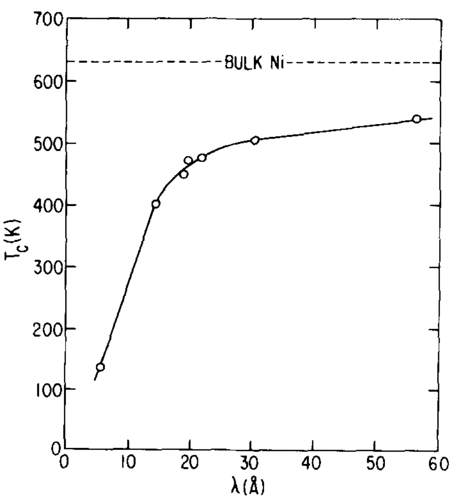

FIG. 4. Wavelength dependence of the Curie temperature as obtained from straight line extrapolations such as in Fig. 3.

shifts in a CMS are to be greater than those of pure Ni, there must be a complex magnetization distribution in the sample for example, with the direction of magnetization reversing sign several times within each layer. However, neutron diffraction measurements as well as the band structure calculations suggest the absence of such complex magnetization distribution. It should be pointed out that anomalous elastic properties as a function of wavelength have been observed earlier,[4] and we had expected this to manifest itself as a nonmonotonic dependence of the magnetization on wavelength.

The temperature dependence of the saturation magnetization for four composition amplitudes is shown in Fig. 3. This temperature dependence is in agreement with the temperature dependence obtained using ferromagnetic resonance.[3] It is interesting to note that the Curie temperature (as obtained from a straight line extrapolation of Fig. 3) does not change with decreasing modulation amplitude except for A equal to zero (after 6 h annealing at 500 °C) where the Curie temperature is less than 5 K. This unusual (nearly linear) behavior of $M(T)$ near the Curie temperature has earlier been atributed to the existence of regions of different concentration of nickel; as the temperature is decreased, regions of progressively smaller Ni concentration magnetize. Since the Curie temperature for homogenous alloys increases nearly linearly with Ni *concentration*,[14] a similar increase would be expected in the CuNi modulated structure as a function of *modulation amplitude*. The fact that the Curie temperature does not shift appreciably ($< 1\%$) with amplitude suggests the presence of a different physical mechanism which has not been taken into consideration.

Figure 4 shows the dependence of T_C on λ. Notice that the Curie temperature increases monotonically with λ, approaching the value of bulk Ni. This result is reminiscent of theories which predict a decrease of T_C for thin Ni films as a function of thickness.[15] It should be stressed that the Curie temperatures shown are obtained from extrapolations of the magnetization-temperature graphs. Since no attempt has been made to fit the magnetization curves to an equation of state, Fig. 4 is only intended to show the qualitative dependence of T_c on λ.

It has been suggested that the unusual magnetic properties might be explained[16] by clustering of the Ni atoms[17] in each plane. Since the laterally averaged magnetization is still assumed to vary sinusoidally perpendicular to the layers, the one-dimensional interpretation of the x-ray results would still be valid. On the other hand, the Curie temperature T_C would be given by the T_C of the Ni clusters, which does not depend strongly on cluster size but does depend on the thickness of the cluster "platelets." This would imply that the T_C dependence on wavelength should be similar to the dependence of a thin film on thickness. In addition, annealing of the samples might then decrease the lateral cluster size through diffusion. This would simultaneously result in a decrease of the average magnetization and of the x-ray satellites amplitude. The large values obtained for a_0 in Eq. (1) might also be indicative of clustering. We would like to stress that the clustering suggested by this experiment is rather unusual in that the Ni clusters independently in each layer unlike in an alloy.

In summary, we have measured the magnetization of the compositionally modulated system CuNi. The experimental data shows magnetizations reduced from that of pure Ni in agreement with neutron scattering experiments and band structure calculations. The saturation magnetization varies with composition amplitude independent of modulation wavelength. The "Curie temperature" is amplitude independent and decreases with decreasing wavelength. The field dependence of the magnetization implies that there is only a small magnetostrictive term, indicating the absence of large strains in this material. The temperature dependence of the saturation magnetization is in agreement with fmr measurements with a Curie point independent of modulation amplitude.

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