Reentrant magnetic behavior in fcc Co-Cu alloys

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Crystalline Co_xCu_{1-x} alloys, which cannot be obtained by equilibrium methods, have been fabricated by magnetron sputtering. The magnetic properties of the alloys, whose structure remains single-phase fcc up to $x=0.80$, is studied over the entire range of compositions. As in the case of other random magnetic systems such as Fe-Au, the metastable alloy is seen to evolve from a spin glass at low Co concentrations to a reentrant spin glass with evidence for both ferromagnetic and spin-glass ordering, and finally to a ferromagnet for $x>0.40$. A magnetic phase diagram for fcc Co-Cu is proposed.

I. INTRODUCTION

The magnetic properties of random magnetic alloys, in which a magnetic species is diluted into a nonmagnetic host, depend strongly on the relative concentrations of its constituents. For example, in the case of a ferromagnetic metal diluted in a noble metal, at least two distinct behaviors may be expected: a spin-glass behavior at low magnetic concentrations, when the random dilution of the magnetic species results in random interactions and frustration, and a ferromagnetic behavior at high magnetic concentrations. There is still considerable controversy, however, over the transition region between these two behaviors, the so-called reentrant spin-glass regime where evidence for both spin-glass and ferromagnetic orders is present.[1-4] Indeed, the issue of reentrant spin-glass phenomena has resulted in a vigorous debate among experimentalists and theorists, with many issues still unresolved, such as the role of magnetic clusters and short-range order in shaping the properties of these systems, the coexistence of ferromagnetic and spin-glass orders and the nature of any phase transitions.[5-8] Experimentally, the materials that have been most intensely studied, usually in very limited composition ranges, are binary alloys such as Fe-Au or Ni-Mn and various amorphous alloys containing Fe. It is tempting to generalize the results obtained for these systems to any random magnetic alloy. In practice however, few such alloys can easily be fabricated in an extended composition range due to the immiscibility or limited solubility of many of the likely candidates. Thus, little experimental evidence is available outside of a few cases. In particular, the transition from spin-glass behavior to ferromagnetism in face-centered cubic (fcc) Co alloys, to our knowledge, has never been studied, not only because of the lack of stable alloy systems, but also because the stable phase of Co at room temperature is the hexagonal close-packed (hcp) ϵ phase. However, using nonequilibrium deposition methods such as evaporation[9] or sputtering,[10] it is possible to obtain many metastable alloys not otherwise attainable. In recent years, sputtering has been shown to be the most versatile method in fabricating metastable alloys. During the sputtering process, the materials to be alloyed are atomized and can be quenched onto cooled substrates, resulting in metastable films of excellent homogeneity. A wide range of compositions can usually be obtained, making an accurate determination of concentration-related properties possible. In the case of Co-Cu, the equilibrium phase diagram permits only a small solubility ($<5\%$) at each end of the composition range. In between lies a large region where no alloys or compound exist. By sputtering, however, homogeneous alloys of hitherto unattainable compositions can be readily achieved and studied. In this paper we present the first complete results on the magnetic properties of metastable fcc Co_xCu_{1-x} crystalline alloys spanning a wide composition range ($0<x<0.80$ atomic concentration). Many of the properties characteristic of reentrant systems are found to occur in Co-Cu, and the study of this new system will constitute a useful addition to the experimental evidence concerning such phenomena.

II. EXPERIMENTAL METHOD

The Co-Cu samples were obtained by dc sputtering onto liquid-nitrogen-cooled glass or mica substrates, using homogeneous sputtering targets. The targets were presputtered prior to deposition, so that the film composition, in the steady state, can be taken to be equal to the composition of the target. The sputtering gas was 4 mTorr of argon, with a background pressure below 10^{-7} Torr. The films were deposited at a rate of about 6 Å/sec, resulting in final thicknesses of a few μm's, and were subsequently removed from the substrates for the magnetic measurements. Structural characterization was done using a θ-2θ x-ray diffractometer, while the magnetic measurements were performed with superconducting quantum interference device (SQUID) and vibrating sample magnetometers.

III. RESULTS

X-ray diffraction patterns of the as-sputtered Co_xCu_{1-x} films are shown in Fig. 1(a). All the samples with $0\leq x\leq 0.70$ are similar, showing a distinct fcc pat-

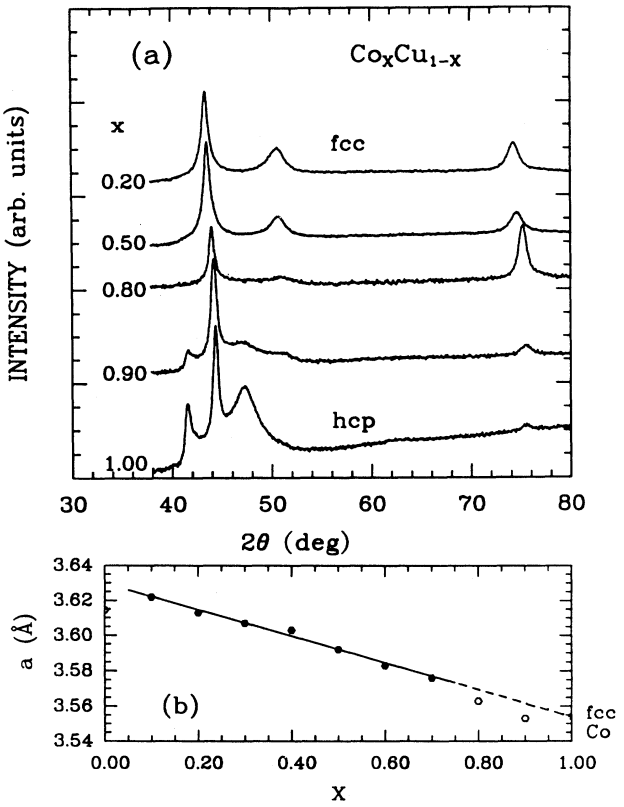

FIG. 1. (a) X-ray spectra of sputtered Co_xCu_{1-x} alloys. The Co hcp phase appears only above $x=0.80$. (b) Crystalline lattice spacing a obtained from fcc spectra as a function of x.

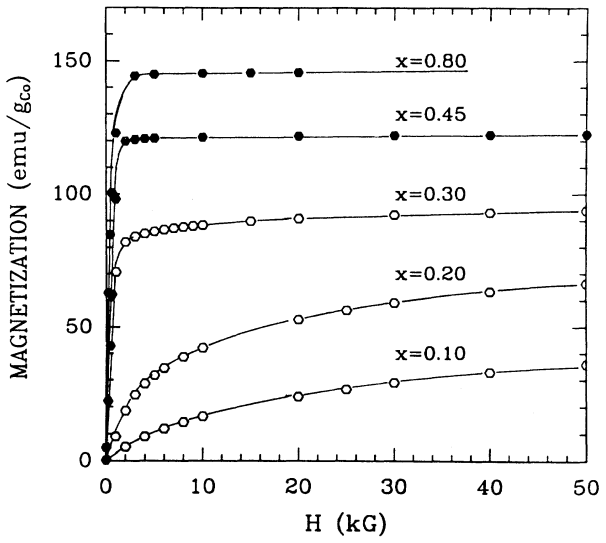

FIG. 2. Magnetization versus applied field for Co_xCu_{1-x}, in units of emu per gram of Co, at $T=5$ K. Full saturation is not reached at $H=50$ kG for $x \leq 0.30$ (open circles).

tern close to that of pure Cu. As the Co concentration is increased, the peak positions shift to higher 2θ values due to a decreasing lattice parameter. There is no evidence of the hcp phase until $x \geq 0.80$, at which point both fcc and hcp phases are found. The sputtering of pure Co only yields the hcp phase. Thus the sputtering method is extremely successful is stabilizing the metastable fcc alloy in a very large composition range. The lattice spacing extracted from the fcc phase [Fig. 1(b)] is found to decrease smoothly with increasing Co concentration, with deviations from linearity apparent only after the transition to a multiphase material. Extrapolating to $x=1$ yields the known[11] bulk fcc Co value of $a=3.544$ Å.

The magnetization curves for various samples at $T=5$ K are shown in Fig. 2. For the samples with $x>0.30$, the magnetization was found to be easily saturated using fields of just a few kG, indicative of established ferromagnetic order. For the samples with low Co concentration ($x \leq 0.30$), the magnetization does not saturate, even in fields up to 50 kG. This hints at a breakdown of long-range magnetic order below $x=0.30$. The saturation magnetization of the ferromagnetic samples ($x>0.30$), or the magnetization at 50 kG ($x \leq 0.30$), at $T=5$ K, in units of emu per gram of Co, is shown in Fig. 3, as a function of Co content. For the ferromagnetic samples with fcc structure ($0.30<x<0.80$), the saturation magnetization is not constant but scales closely with x, demonstrating that Co does not retain its full moment upon dilution. An extrapolation of this trend to $x=0$ yields a moment of about 80 emu/g, approximately half of the bulk hcp magnetization of 162 emu/g (or 1.7 μ_B per Co atom). The magnetization in the fcc phase extrapolated at $x=1.00$ from data below $x=0.80$ is approximately 175 emu/g, slightly higher than the bulk hcp Co magnetization, and would represent the magnetization of fcc Co at 5 K. This is consistent with the enhancement of magnetization seen in bulk Co upon transformation to the fcc phase at 700 K.[12] A small decrease in magnetization is

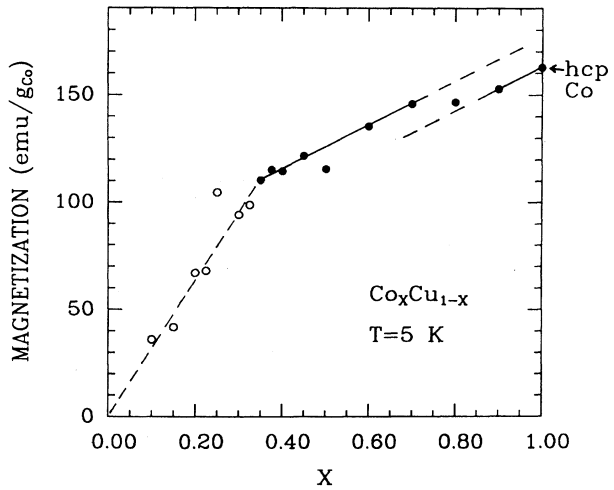

FIG. 3. Solid circles: Saturation magnetization of sputtered Co_xCu_{1-x} alloys as a function of x, in units of emu/g of Co. Open circles: Magnetization under an applied field of 50 kG.

thus seen as the hcp phase appears for $x \geq 0.80$. At low Co concentrations ($x \leq 0.30$), since the magnetization does not saturate, the data in Fig. 3 (open circles) does not yield information on the Co moment. But the magnetization at 50 kG seems to extrapolate to zero at $x=0$. Because of the more complex magnetic ordering in the low Co samples, a more detailed study of their magnetic behavior as a function of temperature is necessary.

Figure 4 shows the zero-field-cooled (ZFC) and field-cooled (FC) magnetizations of samples with $x=0.10$ and 0.20, measured as a function of temperature in a small field $H_{ext}=50$ G and 10 G, respectively. The results are what is typically expected of spin glasses, with a sharp cusplike peak in the ZFC magnetization at the spin-freezing temperature T_g and strong divergence below T_g of the FC and ZFC branches. As the Co concentration is increased, T_g shifts towards higher temperatures, from 7 K and 21.5 K for $x=0.10$ and $x=0.20$, respectively, to a maximum of 24 K for $x=0.23$. Above this concentration ($x>0.23$) an abrupt change in behavior is seen, as shown in Fig. 5. Two distinct transitions are now present in the magnetization curves. The sharp rise in the magnetization, at temperatures much higher than the above freezing temperatures, is characteristic of a Curie transition, with the Curie temperature defined as the inflexion point of the curve. Below this temperature, the magnetization exhibits a plateau, and ultimately a sharp decrease in the magnetization at low temperature, similar to the behavior seen in the spin-glass regime. Thus, evidence for both ferromagnetic and spin-glass transitions are simultaneously present (in this case T_g is defined as the temperature at which the extrapolation on the low-temperature side reaches the plateau level, as shown on Fig. 5). To gain further insight into the nature of these double transitions, and their possible dependence on the external field, the sample of $Co_{0.30}Cu_{0.70}$ was measured under different applied fields. As shown in Fig. 6, both transition temperatures remain well defined, and are not dependent on the value of the small applied dc field. However, in the region between the two transitions, the features found in the magnetization curves are strongly field dependent. For example, the data taken under $H_{ext}=10$ G shows a sharp rise in the magnetization at about 90 K. When the

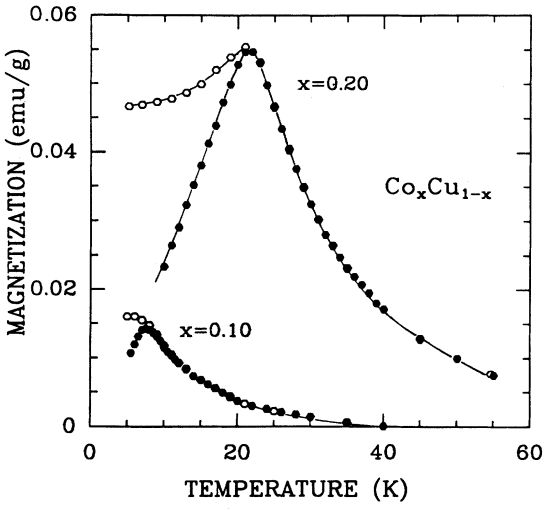

FIG. 4. Typical zero-field-cooled (solid circles) and field-cooled (open circles) magnetization curves for Co_xCu_{1-x} in spin-glass regime, with $H_{ext}=50$ G and 10 G for $x=0.10$ and $x=0.20$, respectively.

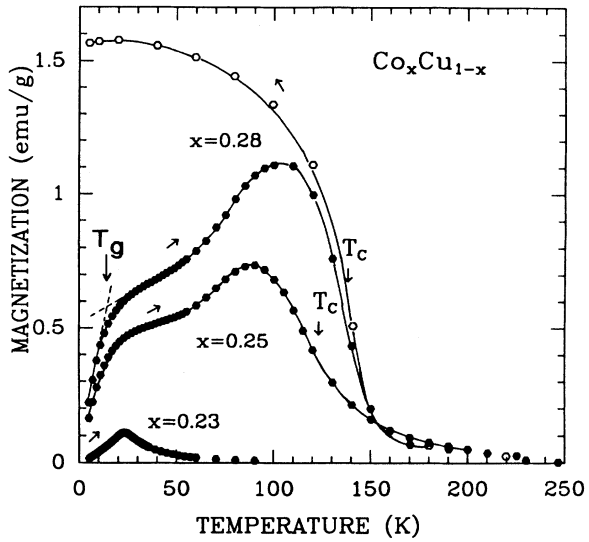

FIG. 5. Typical zero-field-cooled magnetization curves (solid circles) for Co_xCu_{1-x} in reentrant regime, with $H_{ext}=10$ G. The field cooled data is also shown for $x=0.28$ (open circles).

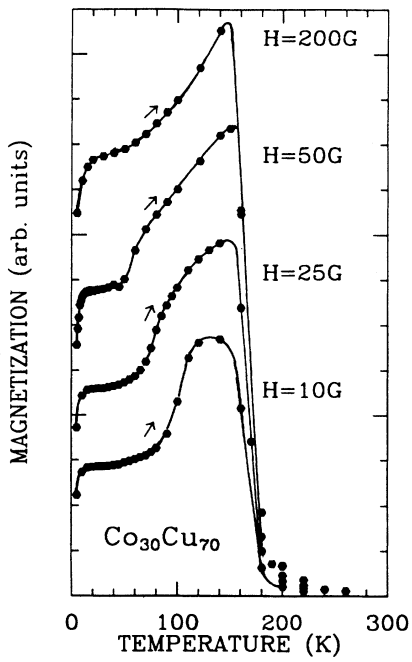

FIG. 6. Zero-field-cooled Magnetization of $Co_{30}Cu_{70}$ as a function of temperature, for different values of the external field H_{ext}.

field is changed to $H_{ext}=25$ G and 50 G, the rise occurs at 70 and 40 K, respectively. A similar behavior is seen in all other samples which display a double transition. It has not yet been determined whether these features represent any real change in the state of the magnetization, such as the so-called canting transition to a state with frozen transverse spin components, as suggested by Mössbauer measurements on Fe-Au alloys.[13] As the Co concentration is increased above $x=0.40$, no further evidence of spin-glass behavior is seen at low temperature, while T_C becomes too high to measure without causing irreversible segregation of Co and Cu.

From the data gathered on all the alloy compositions, a magnetic phase diagram is proposed, as shown on Fig. 7. At low Co concentrations ($x \leq 0.23$), only the spin-glass phase is present at low temperatures. In that region, T_g scales with the Co concentration, reaching a maximum of 24 K. Ferromagnetic order appears above a critical concentration $x_c \approx 0.24$, with the value of T_C increasing sharply with Co concentration at a rate of approximately 23 K per atomic %. Additionally, for samples up to $x=0.40$, there is also a spin-glass transition at low temperatures. In this case, T_g decreases with increasing Co content, and becomes zero at about $x=0.40$, above which only a ferromagnetic transition may be observed. In Fig. 7, the deviation of data points along the paramagnetic-ferromagnetic line at low concentrations is due to the difficulty of determining T_C in that region, as the transition becomes broad due to the convergence of T_C and T_g. Coexistence of spin-glass and ferromagnetic orderings thus begins around $x=0.24$ and remains until the spin-glass freezing temperature reaches zero, around $x=0.40$. Although no high-temperature measurements are possible above this concentration, T_C is expected to increase towards the known value of 1400 K for bulk fcc Co.

The onset of ferromagnetism in random alloys can be treated as a site percolation problem. For the fcc lattice in three dimensions, with nearest-neighbor interactions only, the percolation threshold cannot be calculated exactly, but is estimated to be in the range $x_c^t \approx 0.16-0.19$.[14] The value of $x_c=0.24$ observed in our Co-Cu alloys is close but definitely higher than this theoretical value. By contrast, for vapor-quenched Fe-Cu, a similar metastable fcc alloy, the critical concentration was found to be 0.19,[10] within the range of x_c^t. Similarly, for Fe-Au alloys, the percolation threshold is about 0.16.[15] Thus a dependence of x_c upon interaction strength (i.e., Fe moments in Cu or Au, versus Co moments in Cu) may be inferred. In particular, if, as it has been suggested,[16] the Co atom requires at least two other close Co neighbors to acquire a moment, then the percolation problem is not simple site percolation, and the modified model[17] results in a higher x_c^t, in qualitative agreement with our results.

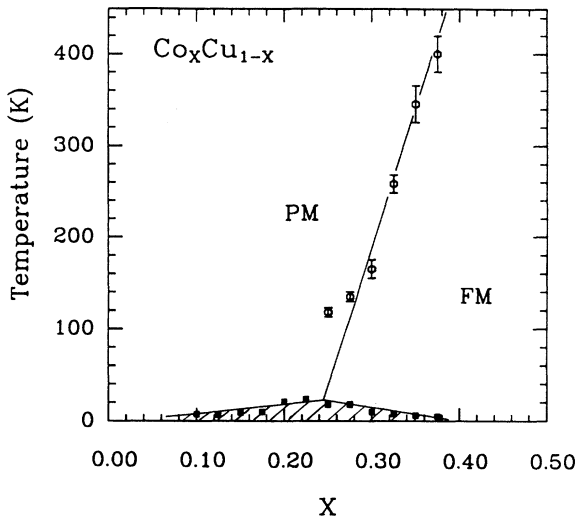

FIG. 7. Magnetic phase diagram of fcc Co_xCu_{1-x} showing paramagnetic (PM), ferromagnetic (FM) and spin-glass (shaded area) phases.

In conclusion, we have studied for the first time the magnetic properties of metastable fcc Co_xCu_{1-x} alloys obtained by magnetron sputtering. In addition to spin-glass and ferromagnetic behaviors, we find a large reentrant spin-glass region ($0.24 \leq x < 0.40$) where evidence for both spin-glass and ferromagnetic behaviors are present. Thus fcc Co-Cu is a new, simple system in which reentrant magnetic phenomena may be investigated. A magnetic phase diagram, similar to those of other diluted ferromagnet systems such as Fe-Au, is obtained.

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