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An investigation of the electrodeposited inhomogeneous alloyed film $Cu_{0.94}Co_{0.06}$ by means of SQUID magnetometry

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Abstract. The magnetic behaviour of the inhomogeneous alloyed film, $Cu_{0.94}Co_{0.06}$, produced by electrodeposition has been investigated in the temperature range 2 to 300 K and in magnetic fields of up to 5 T using SQUID magnetometry. The films exhibit either hysteretic or reversible behaviour depending upon the temperature. This is interpreted as being due to the presence of small, FCC, Co-rich particles of FCC Co in the non-magnetic matrix, giving rise to superparamagnetism at higher temperatures. With the help of low-field susceptibility measurements made on samples cooled in zero field we have been able to determine the distribution of blocking temperatures and thus make an estimate of the size distribution of the particles in the Cu matrix; these have been found to range in diameter from 6 to 12 nm. These results have been compared with values obtained from a measurement of the temperature dependence of the remanence. We have found that, even in such a relatively dilute magnetic system as $Cu_{0.94}Co_{0.06}$, interactions between magnetic clusters are not negligible. The interaction energy is estimated to be of the order of 1.7×10^{-3} eV.

1. Introduction

In recent years, interest has been focused on the properties of magnetic multilayers, nanostructures and inhomogeneous (heterogeneous or cluster-based) alloys. Amongst the many interesting properties of these materials, it seems likely that the phenomenon of giant magnetoresistance (GMR) will be the first which, in the near future, will find practical application.

In order to be able to optimize the parameters which control GMR, it is essential to have a basic understanding of the physical properties of these systems. Also, for any potential application, it is a great advantage if the system is not only relatively easy to fabricate, but also consists of readily available elements. The CuCo system is one which exhibits GMR and, in the past, this system has been widely investigated. More recently, there have been a number of measurements reported on thin films of granular or multilayer CuCo samples. These, however, have almost all been prepared by such techniques as sputtering [1–6], melt spinning [7, 8], laser ablation [9] or various types of deposition involving high-vacuum conditions. All these above-mentioned preparation methods are relatively complicated or expensive. In contrast to this, up to the present time, almost no one has used electrodeposition (ED) for the preparation of thin films of inhomogeneous alloys, despite the great advantages of simplicity and cost.

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In an earlier paper [10] we have demonstrated the possibility of producing heterogeneous $Cu_{1-x}Co_x$ alloyed films by the technique of ED using conditions of constant current, i.e. the non-pulsed regime. These films were heterogeneous immediately after deposition and no post-deposition annealing was necessary. This fact is in marked contrast not only to films produced by other techniques, but also to films produced using ED by other workers [11], where it has been necessary to subject samples to a heat treatment before they were in an inhomogeneous state. It should also be mentioned, perhaps, that recently Alper *et al* [12] have observed GMR in short-period Cu/Co–Ni–Cu superlattices grown by ED. Our films [10] consist mainly of Co-rich particles in the Cu matrix for $x \leqslant 0.06$–0.50 and Cu particles in a Co matrix for $x \geqslant 0.50$ [13].

In the present paper we report magnetic measurements on the alloy $Cu_{0.94}Co_{0.06}$. In view of the results of other workers on similar systems with comparable Co concentrations [8, 14, 15], it seemed likely that we could expect to produce a film which exhibits pure superparamagnetism (SPM). However, we find this not to be the case and have to consider interaction effects. These interactions will clearly increase with increasing Co concentration.

2. Experimental technique

The $Cu_{0.94}Co_{0.06}$ films, which were prepared in Minsk, were electrodeposited onto either Al, Cu or ceramic substrates; the ceramic substrates had previously been coated with a non-magnetic layer of NiP. The electrolytic composition was

$CuSO_4 \cdot 5H_2O$	30 g l^{-1}
$CoCl_2 \cdot 6H_2O$	3.3 g l^{-1}
H_3BO_3	6.6 g l^{-1}
$MgSO_4 \cdot 7H_2O$	23.3 g l^{-1}
$CoSO_4 \cdot 7H_2O$	10 g l^{-1}
$Na_3C_6H_5O_7 \cdot 5H_2O$	120 g l^{-1}
$C_6H_4SO_2NHCO$	1 g l^{-1}.

The electrolyte had a pH of 6.0 and deposition was performed at 20 °C with a current density of 5 mA cm^{-2}. The metallic substrates were, in general, of thickness $\simeq$0.1 mm and films were typically of order 1 μm thick. The film composition was determined by both x-ray and chemical analysis [10]. TEM measurements confirmed that the film was composed of Co-rich, FCC particles dispersed in a polycrystalline, FCC, Cu-rich matrix; this had a grain size of typically 50 nm.

Magnetic measurements, which were confined mainly to films on Cu substrates, were performed in the temperature range 2 to 300 K and in fields of up to 5 T using a Quantum Design SQUID magnetometer. Fields could be set to an accuracy of $\pm 10^{-6}$ T and temperatures could be controlled to within $\pm 10^{-2}$ K. Measurements of magnetic moment as a function of field for various temperatures were made, together with the technique of zero-field-cooled (ZFC) and field-cooled FC) low-field susceptibility measurements [16–21]. Since we wished to make a precise check on the samples to see whether they satisfied the criteria of SPM, careful measurements were also made on identical Cu sheets on which no films had been deposited and also on the actual substrates used for deposition after mechanically removing the CuCo film. These results were used to correct for the effects of the substrate, which made a small contribution to the SQUID signal, especially at high fields and low temperatures.

In order to investigate whether the films exhibited any anisotropy due to the directional nature of their growth, measurements were also made at 300 K whilst rotating the sample from an orientation with the field in-plane to that with it perpendicular to the plane of the sample.

3. Results and discussion

Magnetization loops were measured over the temperature range 2 to 300 K, although, for reasons of time, complete loops were not always measured at every temperature. Figure 1 shows the high- and low-field hysteresis loops measured at 5 K. It is important to note that, even at a temperature of 5 K and an applied field of 5 T, the sample could not be magnetically saturated.

Figure 2 shows the temperature dependence of the remanence as determined from the hysteresis loops. An extrapolation of this curve to zero remanence gives a value of 55±5 K for T_B, the maximum blocking temperature of the sample. This result is in excellent agreement with a previous value quoted for an identically prepared film [10] and is a good indication of the reproducibility of our samples.

Figure 3 gives the magnetization measurements for a sample measured at 150, 200, 250 and 300 K, temperatures which are well above the maximum blocking temperature of the film. These data have been corrected, as mentioned earlier, for the diamagnetic contribution of the Cu substrate. At these temperatures, no hysteretic effects were observed and, again, saturation is not achieved. This non-saturation, even at 5 K, we interpret as being evidence for the existence of a wide range of particle sizes in the sample. At low temperatures and high fields, the relatively large particles will saturate, but if very small Co clusters and isolated Co atoms are present in the Cu matrix, they will give rise to the observed non-saturation, even in a field of 5 T.

As is well known, there are two experimental conditions which have to be satisfied for true SPM: firstly, there must be no hysteresis loop above the maximum blocking temperature, and secondly, the magnetization curves must superimpose when plotted as a function of reduced field, i.e. as a function of H/T. In order to test this second criterion, in figure 4 we plot such curves. It can be seen that the curves do not superimpose, even after correction for the diamagnetic contribution of the Cu substrate. We thus conclude that here we are not dealing with a sample which exhibits pure SPM. This means that we have to consider magnetic interactions between particles.

An analysis of the remanence curve of figure 2 gives us a further method of obtaining information about our sample. By taking the derivative of this curve, we are able to gain information about the energy barrier distribution within the sample [16] which, in turn, is related to the particle size distribution. Figure 5 shows the derivative of the remanence of curve of figure 2. This indicates a wide distribution of energy barriers. These energy barriers to magnetic reversal of moments in real systems are influenced by effects such as interactions between SPM particles, the presence of interacting spin-glass structures, and variations in K_A due, for example, to localized strain at defects and boundaries. However, the experimental points show no evidence of a peak within the temperature range of our measurements and presumably the maximum occurs below the lower limit of the measurements. This suggests that the peak in the curve representing particle size distribution corresponds to a blocking temperature below 2 K.

As a further means of investigating the range and distribution of blocking temperatures, we have measured the moment (effectively the initial susceptibility) in a small, constant applied field, in this case 5 mT, after zero-field cooling the sample from well above the

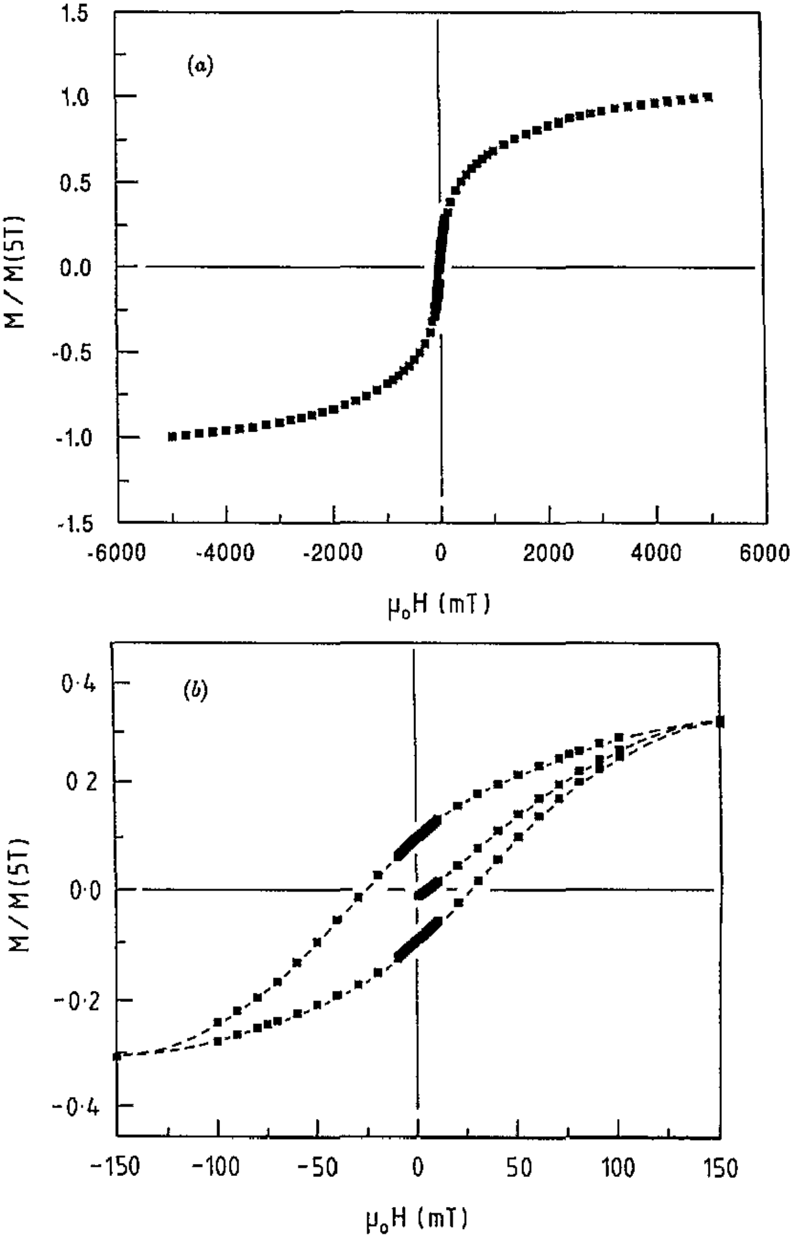

Figure 1. Hysteresis loop for a $Cu_{0.94}Co_{0.06}$ film measured at 5 K. (*a*) High field. (*b*) Low field. The magnetization has been normalized to its value at 5 T.

maximum blocking temperature. Measurements were then made at increasing temperatures from 5 to 300 K. We then field cooled the sample, still in 5 mT, measuring from 300 to 5 K. Such measurements have been found to be extremely sensitive to particle interactions [18–21] and are also a good method of investigating the energy barrier distribution. The results of these measurements are shown in figure 6. The position of the bifurcation between the two curves (250 K) is an indication of the maximum blocking temperature, whereas the

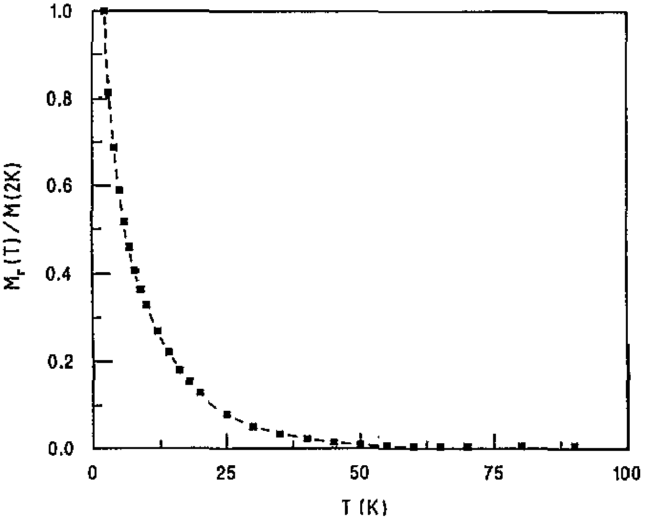

Figure 2. Temperature dependence of the remanence for a $Cu_{0.94}Co_{0.06}$ film as derived from the corresponding hysteresis loops where a field of 5 T was applied at each temperature. The remanence is normalized to its value at 2 K.

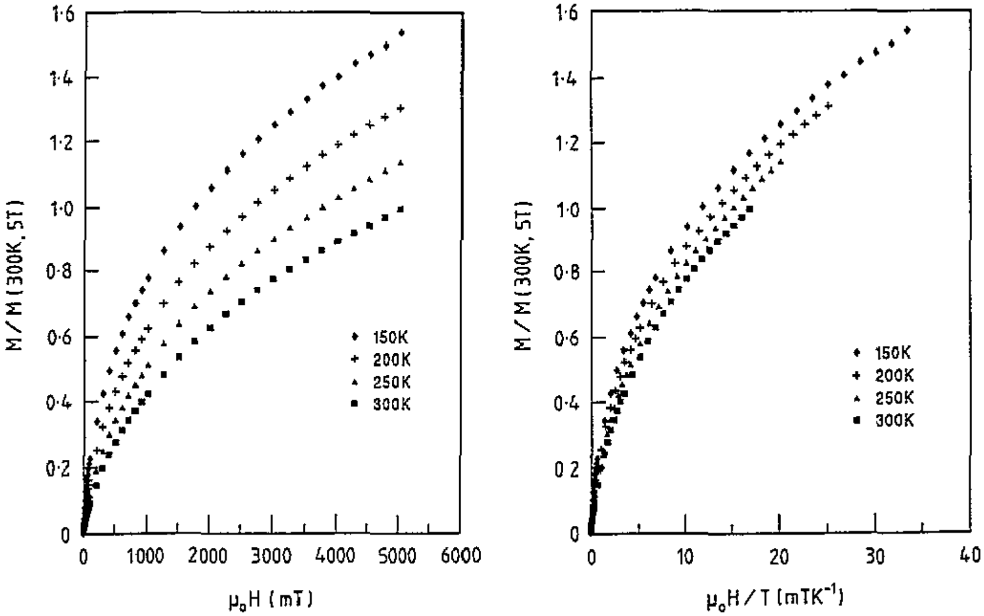

Figure 3. Magnetization of a $Cu_{0.94}Co_{0.06}$ film as a function of the magnetic field. The results have been corrected for the contribution of the diamagnetic Cu substrate and are normalized to the value of the magnetization at a temperature of 300 K and a field of 5 T.

Figure 4. Magnetization of a $Cu_{0.94}Co_{0.06}$ film plotted as a function of reduced field; the magnetization has been normalized to its value at a temperature of 300 K and a field of 5 T. The data are from figure 3.

position of the peak in the ZFC curve gives us a value of 35 K for the mean blocking

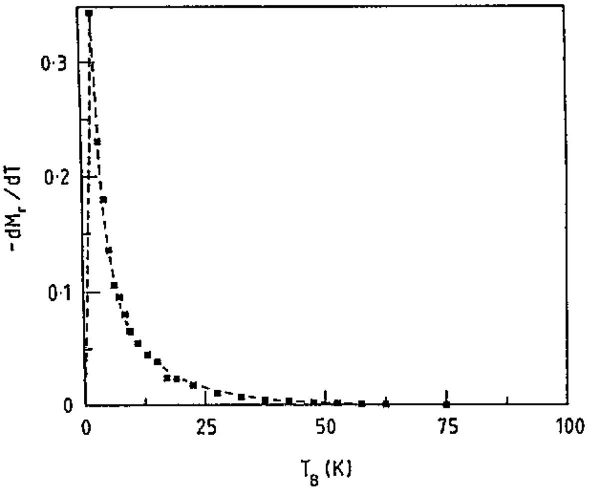

Figure 5. Derivative of the temperature dependence of the remanence for a $Cu_{0.94}Co_{0.06}$ film; the data are from figure 2. The curve given is a guide for the eye only.

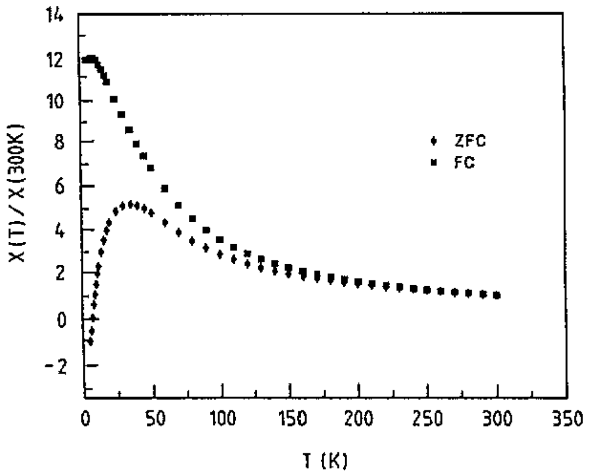

Figure 6. Magnetization of a $Cu_{0.94}Co_{0.06}$ film as measured in a field of 5 mT. The lower curve is for the film initially cooled to 5 K in zero magnetic field (zero-field-cooled, ZFC), while the upper curve is for the sample cooled in the measuring field 5 mT (field-cooled, FC). The results are normalized to the value of the magnetization at 300 K.

temperature.

According to Bean and Livingstone [22], we may use the now well-known expression $K_A v = 25k_B T_B$ to make an estimate of particle size. This expression assumes that the particles, of volume v, exhibit uniaxial anisotropy and is based on a measuring time of 100 s, which is of the same order of magnitude as the SQUID measuring time. If we now assume that the Co-rich particles are present in the matrix as an FCC phase [10] and take a value for K_A of 5.55×10^{17} eV cm^{-3} [23] (the exact value of K_A is somewhat arbitrary, since it is strongly temperature dependent and also presumably shape and strain anisotropies play an important role), we are able to estimate the particle diameter corresponding to the maximum blocking temperature of 55 K, derived directly from the remanence curve (figure

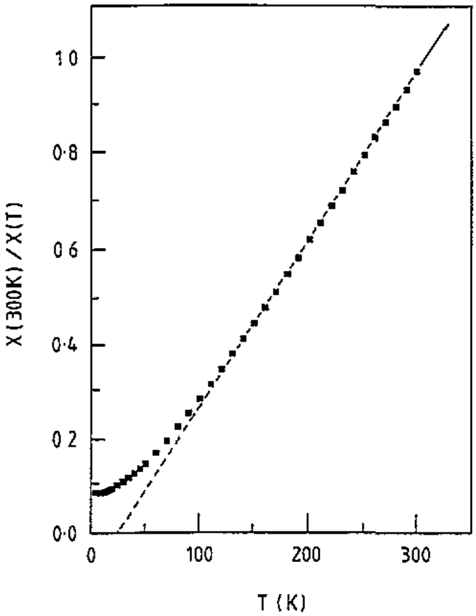

Figure 7. Temperature dependence of the reciprocal of the FC susceptibility, normalized to its value at 300 K, for a $Cu_{0.94}Co_{0.06}$ alloy; the data are from figure 6.

5), to be 7 nm, whereas the mean particle diameter, which is related [17] to the peak in the ZFC curve (35 K), we find to be 6 nm. Finally, the maximum particle diameter, according to the position of the bifurcation in the ZFC/FC curves, is found to be 12 nm. This discrepancy is not unexpected, since we are applying different measuring techniques and also both the shape of the ZFC curve and the temperature at which the bifurcation occurs are dependent upon measuring field. A similar variation has also been observed by other workers [16]. The present results are in good qualitative agreement with the measurements of Dieny *et al* [8] on melt-spun CuCo samples.

The apparent wide range of particle sizes, according to the ZFC/FC measurements, may be due to the fact that, in the present system, we have to take particle interactions into account. Such interactions may effectively increase the particle size via a coupling mechanism between particles, i.e. two particles, whilst metallurgically separate, may experience a ferromagnetic coupling, thus behaving magnetically as a single particle. There is also the possibility, as a consequence of the method of film preparation, that we have non-spherical particles which are elongated in the direction of the film growth. This seems unlikely, however, as an investigation of the variation of magnetization of the film as a function of the angle between film plane and applied field showed the magnetization to be independent of orientation when demagnetizing effects had been allowed for.

The origin of the peak of the ZFC curve lies in the increase in the fraction of particles that become unblocked with increasing temperature, whilst simultaneously their value of susceptibility decreases due to thermal fluctuations. This ZFC curve is reproducible but irreversible, in contrast to the FC curve which is both reproducible and reversible. This is because, whereas the shape of the ZFC curve is determined by blocking effects (and is also, strictly speaking, dependent on both field and time) plus the effects of particle interactions, when we cool the sample in a field and measure in a steady field, as the temperature is reduced the particles are blocked so as to be aligned in the field. Thus, even though a particle is below its blocking temperature, it will still make its full contribution to the magnetic moment of the sample. Hence, we are able to use the FC curve to investigate the influence of particle interactions in the absence of blocking effects.

The temperature dependence of the reciprocal of the initial susceptibility as measured in a field of 5 mT and after FC is shown in figure 7. At high temperatures there is an almost linear dependence on temperature and, by extrapolation of the high-temperature region to zero, we obtain a positive interaction temperature, T_{int}, of 20 ± 2 K. Following the remarks of O'Grady *et al* [16] we treat this determination with some caution. However, it does indicate that of the two distinct contributions of particle blocking and interactions, the latter is the dominant process. We have obtained an estimate of 1.72×10^{-3} eV for the interaction energy simply by equating it to $k_{\mathrm{B}} T_{\mathrm{int}}$. This value is comparable with the value of 4.3×10^{-2} eV for the anisotropy energy assuming the value of K_{A} quoted earlier.

Childress and Chien [2] have also investigated the $\mathrm{Cu}_{1-x}\mathrm{Co}_x$ system, producing samples using magnetron sputtering. For values of x in the range 0.10 to 0.20, the ZFC/FC curves are very similar to our present results, apart from the fact that our ZFC/FC curves do not coalesce, due to the presence of blocked SPM particles. The nearly flat FC curve below 15 K observed by Childress and Chien is very similar to the FC curve found in the present work and this generally constitutes the signature of a spin-glass transition. Any regions of the matrix exhibiting spin-glass behaviour will, of course, contribute to the remanence below this temperature and effect energy barrier distribution measurements. At the moment, we are unable to explain the two negative points on the ZFC curve at low temperatures. However, we do not believe the effect to be due to the substrate but, on the other hand, it seems unlikely that it is an instrumentation effect.

For more concentrated alloys, it is expected that the interaction temperature, T_{int}, and the corresponding interaction energies will be considerably enhanced. Such investigations on $\mathrm{Cu}_{1-x}\mathrm{Co}_x$ with values of x in the range 0.08 to 0.85 are currently in progress and will be reported in due course [13], together with measurements of the influence of annealing on the Mössbauer spectrum, TEM and GMR measurements. Preliminary magnetoresistance results indicate that the CuCo system is a very promising one from the practical point of view of GMR since, in a $\mathrm{Cu}_{0.94}\mathrm{Co}_{0.06}$ sample prepared by ED, we have recently observed a GMR value of about 15% at room temperature and in fields of less than 1.3 T after annealing [24]. The value of the GMR exhibited in saturation fields for these films ($\mu_0 H > 5$ T) is expected to be considerably greater.

4. Conclusions

We report the first detailed magnetic measurements on the inhomogeneous alloy, $\mathrm{Cu}_{0.94}\mathrm{Co}_{0.06}$, produced by electrodeposition. The alloy exhibits superparamagnetism with a maximum blocking temperature, as determined from the disappearance of hysteresis loops, of 55 K. Despite measurements made well above this temperature range, the samples do not show pure superparamagnetism and magnetic interactions have to be taken into account. Measurements of the temperature dependence of the remanence have been made in order to determine particle size distributions and the results have been compared with those obtained from zero-field-cooled and field-cooled experiments. From these measurements we have determined an interaction temperature of 20 K. The values obtained for the maximum blocking temperature depend upon the type of measurement, but we find particle sizes ranging up to 12 nm in diameter. These particles have been found to be Co-rich FCC particles in an FCC matrix. Further measurements on the influence of anneal and also varying the Co concentration are in progress; measurements to investigate the origin of the magnetic interactions are also planned in the near future.

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