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LETTER TO THE EDITOR

Quenching of ferromagnetism in cobalt clusters embedded in copper

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Abstract. Magnetic x-ray circular dichroism has been used to measure the room-temperature magnetization of cobalt clusters embedded in a copper matrix. It is found that the magnetization depends on the average cluster size and concentration but, in all cases, is significantly less than that of a thin cobalt film even at magnetic fields of 4 T. Various mechanisms for this behaviour are discussed including the possibility that there are significant cluster–matrix and cluster–cluster exchange interactions. Anomalously large values of the ratio of the average orbital to spin moment, measured for some samples, may be a signature of antiferromagnetic exchange coupling. Antiferromagnetic coupling of clusters would necessitate a stronger interaction than can be predicted with RKKY theory and the possibility that this coupling is a 'superexchange' mechanism is discussed.

This letter reports on the first magnetic x-ray circular dichroism measurements (MXCD) on mesoscopic thin films made from deposited clusters, which are buried within a non-magnetic matrix. The results show that the magnetic structure of this material is significantly modified by the presence of discrete clusters.

Cobalt–copper nanocomposites can be made by a variety of other techniques including spin melting, mechanical alloying and atomic deposition. Previous measurements have been made of their magnetization [1] and their giant magnetoresistance (GMR) [2]. Because the unusual behaviour, reported here, has not been previously published it is probable that the morphology of these 'atomically engineered' materials is different from that made by other techniques. The samples here were made using the Freiburg magnetron cluster source [3]. Cobalt clusters of a variable mean size of about 200–15 000 atoms were generated by combining an improved magnetron sputtering with a gas aggregation tube at liquid nitrogen temperature [3], and deposited at room temperature on Si(100) substrates simultaneously with an atomic copper beam from a conventional sputter source. The cluster concentration in the resulting films is adjusted through the ratio of the cluster and atomic beam deposition rates, as measured *in situ* with a rotatable quartz microbalance in the deposition chamber. The cluster size distribution was monitored by a high-resolution time-of-flight (TOF) mass spectrometer, and could be well fitted to a log-normal distribution. Samples were made with volume concentrations of cobalt of 10% and 50% giving rise to the average geometries listed in table 1. All the samples were approximately 50 ML thick and were capped with 15 ML of copper to allow transfer in the atmosphere. At this thickness the cluster samples are essentially two dimensional.

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Table 1. Cluster sizes and average spacings for the samples measured in these experiments. The dipole–dipole energy is shown in column 5 and is to be compared with the energy of the dipole in the external field. In the last column the value of the field required to give $\langle m\rangle/\langle m_{st}\rangle = 0.65$ is shown. (Because the clusters have a log-normal size distribution the values of $\langle m\rangle/\langle m_{st}\rangle$ will be larger than 0.65 at the stated fields.)

Cluster size (atoms)	Concentration (%)	$R_{cluster}$ (Å)	Cluster spacing (Å)	dip–dip energy (meV)	$\boldsymbol{\mu}\cdot\boldsymbol{H}$ ($H = 1$ T) (meV)	$H(\langle m\rangle/\langle m_{st}\rangle = 0.65)$ (T)
300	10	9.3	32.6	−0.14	−35	2.0
FWHM = 500	50		19.0	−0.91		
1 000	10	14.0	48.6	−0.47	−116	0.6
FWHM = 1 000	50		28.4	−2.35		
9 000	10	29.1	101.1	−4.22	−1040	0.07
FWHM = 10 000	50		59.2	−21.0		

Experiments to fully characterize these samples are being developed but there are strong reasons to believe that they resemble spherical (large cuboctahedral or icosohedral) cobalt clusters embedded in a copper matrix. Firstly, copper and cobalt are mutually insoluble at temperatures below 400 °C [4] so the deposition, particularly of cooled clusters, is unlikely to cause diffusion.

Secondly, molecular dynamic calculations [5] have been used to simulate the deposition of different-energy clusters onto a substrate. These show that at thermal energies the clusters retain their shape on deposition and it is not until the energy reaches about 5 eV per atom that the clusters fuse significantly. Some confirmation of this comes from measurements of the mechanical properties of the films. Although the low-energy deposition produces stable films, they are very weak compared with the hard films [6] produced when high-energy clusters are deposited. It is also likely that the presence of an immiscible matrix of copper between the cobalt helps to preserve the cluster shapes.

Room-temperature MXCD measurements [7–9] of the materials were carried out on station 1.1 of the Daresbury synchrotron. Samples were placed in a magnetic field (normal to the surface) and the total yield of electrons [10] measured at wavelengths spanning the L2 and L3 edges. The field was then reversed and the spectrum again recorded. These two spectra can then be subtracted to obtain the dichroism. Sample dichroism spectra are shown in figure 1. It is found that the original spectra, i.e. before subtraction, contain no extra peaks resulting from chemical core shifts of the p-states indicating that there is little or no contamination of the cobalt.

General sum rules [10, 11] have been used to obtain the average local spin and orbital components of the magnetism. In principle it is only possible to obtain the orbital component, since the sum rule for spin also contains the unknown $\langle T_z\rangle$. However for the special symmetry in cluster material the latter unknown vanishes. Notwithstanding this, it would appear that the value of $\langle T_z\rangle$ in cobalt is small [10, 12] and can generally be ignored for cobalt thin films without causing large errors. We are aware that the uncertainties about the application of sum rules particularly regarding the contribution of diffuse moments to the dichroism can cause uncertainties in the absolute values. However, we are primarily concerned with relative changes in magnetism, from a thin cobalt film, for which the sum rules can be shown [13] to be accurate.

The value for the total average magnetism per atom ($\langle m\rangle = \langle m_S\rangle + \langle m_L\rangle$) has been plotted in figure 2 assuming that the number of d holes is two for all the systems under study. This is an estimated value used to make a comparison between the relative values

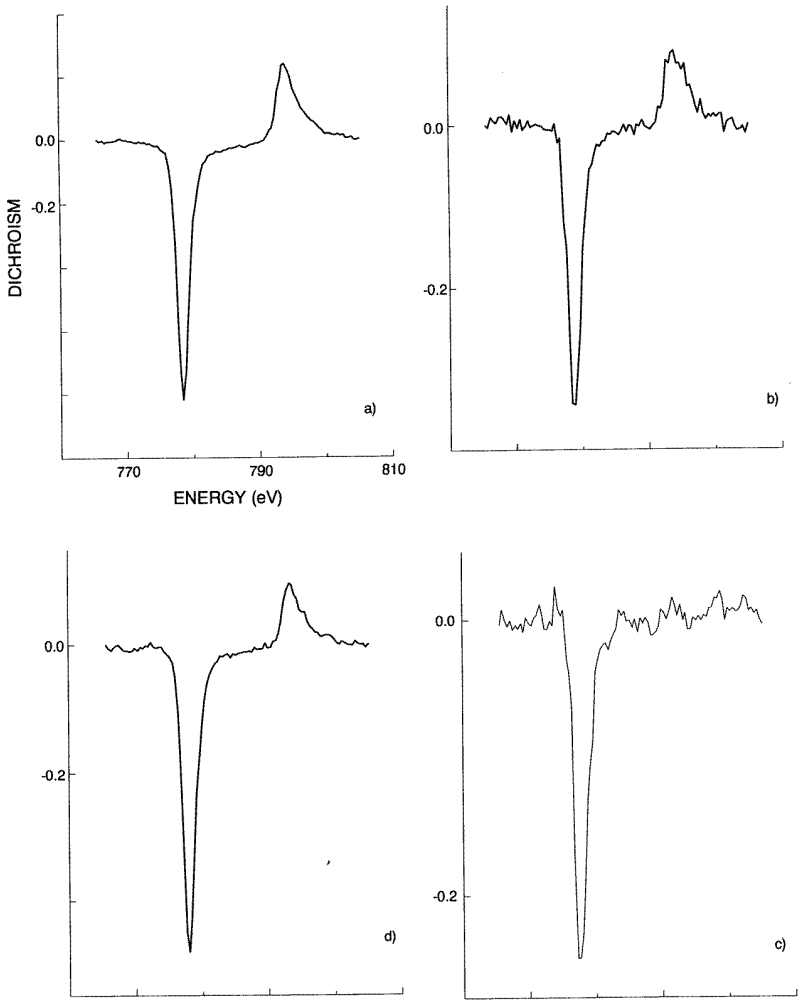

Figure 1. Dichroism spectra for the cobalt cluster samples. (a) Cobalt film; (b) Co cluster of 300 atoms at a concentration of 50%; (c) 1000 atoms at 10%; (d) 9000 atoms at 10%.

of the magnetism for each case. We have also ignored the small changes in n_h (number of holes) caused by charge transfer between the copper and the cobalt. The most notable feature of the data† is the dramatic reduction in magnetization from the pure cobalt film particularly for the clusters with average size of 1000 atoms.

For a superparamagnetic ensemble with no interactions between particles, or between the particles and the matrix, one can calculate the magnetic fields which give a particular ratio of the average magnetization to the saturation value ($\langle m \rangle / \langle m_{st} \rangle$). This is just determined by the Langevin function. The values of field required to give 65% of the saturation magnetization are given in table 1 for a uniform particle size equal to the average size of the clusters. (Because the distribution of particle sizes is skewed to larger sizes the magnetic field to

† Preliminary MOKE measurements indicate that the magnetizations of the 1000-atom samples are much smaller than those of the 10 000-atom samples.

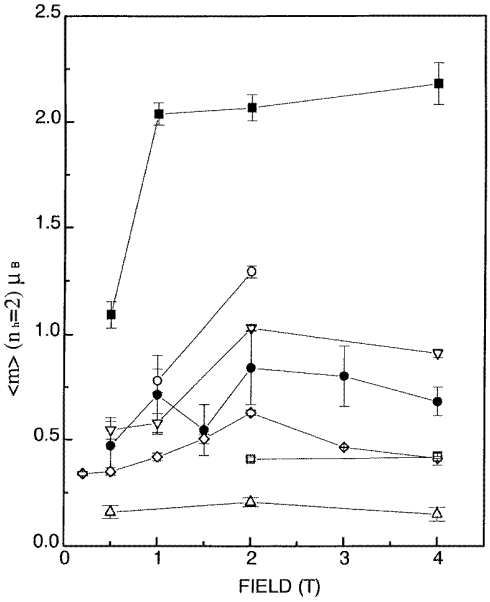

Figure 2. Values of the average magnetization per cobalt atom for the assumption $n_h = 2$. Data points are: ■, 90Å Co film; ●, 300 Co atoms/cluster at 10% concentration; ◇, 300 at 50%; ○, 8500 at 50%; ▽, 9000 at 10%; □, 1000 at 50%; △, 1000 at 10%.

give this degree of alignment will be smaller than this quoted value.) Also there are no significant increases in the magnetization between 2 and 4 T, with most curves showing small decreases in this range.

There are several possibilities to consider in order to explain this quenching. The first is that the cobalt clusters have significantly lower moments than free clusters [11] because of the presence of the copper. This would seem to contradict the experimental observations on Co–Cu thin films [13] and also one might expect significant increases between 2 and 4 T which are not observed. The larger magnetization for the 300-atom cluster sample over the 1000-atom sample would also be difficult to explain unless there were some dramatic 'shell' effects in the magnetic properties of the individual clusters.

Screening due to the presence of localized, exchange coupled, electrons in the surrounding copper is another possibility to consider. If this is the cause then the total average magnetization per atom of the cobalt should increase with the field and eventually reach values similar to that of the cobalt film. (This difference between cluster–matrix and cluster–cluster interactions can only be revealed by an element specific technique such as MXCD.) The expected response here is therefore just one of a superparamagnetic ensemble [14] with reduced moments resulting from the cluster–matrix interactions. However, there will only be any change in the response of the system, apart from possible blocking effects, if the copper becomes ferromagnetic. This can be seen by considering the difference between the spin up and spin down electrons in all of the copper. If this is zero then the presence of the copper cannot influence the overall response of the cobalt to the external field. Since it is unlikely that the copper is significantly ferromagnetic we believe that cluster–matrix interactions can probably be ignored as a separate reason for our anomalous results. (Of course the matrix may be an essential element in mediating the exchange interaction between clusters.)

A third possibility is that there is significant antiferromagnetic coupling between the cobalt clusters. For this to show up in these measurements, the coupling energy must be similar to or greater than the dipole energy, $\boldsymbol{\mu} \cdot \boldsymbol{H}$. (The dipole energy is comparable to the thermal energy, kT, for the smallest clusters.) In table 1 we list the dipole–dipole (antiferromagnetic) coupling energy and compare it with $\boldsymbol{\mu} \cdot \boldsymbol{H}$. RKKY calculations of the exchange coupling of clusters have been made by Altbir *et al* [15] and these show contributions to the coupling energy of similar magnitude to the dipole–dipole term. From table 1 it would appear therefore that neither of these mechanisms is strong enough to cause observable antiferromagnetic behaviour at these high magnetic fields. Even if there is a phase transition to the antiferromagnetic state, as might be the case for our 1000-atom sample, the size of these two contributions seems insufficient.

If antiferromagnetic behaviour is responsible for our observation then the exchange coupling must be significantly greater than can be predicted with the RKKY model. There are a number of calculations which show non-oscillatory antiferromagnetic exchange coupling. One is when the interface layer is an insulator. Calculations for Fe–C–Fe [16], which consider the insulator as a non-magnetic electron tunnelling barrier, show that the coupling can become antiferromagnetic. A different approach which encompasses the relevant cobalt–copper–cobalt multilayer is calculated by Barnas [17] in one dimension. The s–d coupling is represented by a spin-dependent barrier at the interface to represent the interaction strength. When the interaction is strong, the RKKY oscillations largely disappear and the coupling can become antiferromagnetic at short ranges. The average strength of the interaction at short ranges can increase by a factor of 50 which would certainly cause the effects described here. The existence of discrete levels near the Fermi surface in the clusters may give rise to a strong 'superexchange' mechanism. Lacroix and Gavigan have made calculations [18] for the Co–Cu system when the d-state band is replaced by two discrete levels (of opposite spin) at the Fermi energy. They show that the antiferromagnetic coupling can become large when the d-electron levels are close together. It is thus possible to envisage that the density of states in the clusters at the Fermi surface may have sharp structures resembling discrete levels. This DOS may be strongly size dependent (i.e. these are magnetic quantum well states or resonances) and hence explain the differing behaviour of our samples. One further possibility, which cannot be ignored, is that there are significant surface impurities in the clusters or copper which provide vacant levels near the Fermi surface. These could then give rise to conventional superexchange between clusters. However, the absence of core level shifts in the cobalt edge spectra and the larger magnetization of the 300-atom cluster sample over the 1000-atom sample would tend to cast doubts on this mechanism being the cause.

A striking feature of the results is the large values for the ratio of orbital to spin magnetization for the 1000-atom samples at 10%. Whilst the cobalt thin film gave results similar to those observed previously [13], values for $\langle m_L \rangle / \langle m_S \rangle$ of 0.84(18) at 0.5 T, 1.05(15) at 2 T and 0.57(19) at 4 T were obtained, from measurements on two different samples. These values, which are more than twice any previously observed, have an obvious effect on the shape of the dichroism as shown in figure 1. Significant antiferromagnetic cluster–cluster interactions would be expected to give enhancements of the orbital to spin ratio. This is simply because the exchange coupling quenches directly only the spin contribution to the magnetism. A further feature of our data which supports antiferromagnetic coupling of clusters as a likely cause is the almost flat response, particularly for the 1000-atom samples, between 0.5 and 4 T. This would be expected if the exchange coupling between two clusters were significantly larger than the energy of the individual cluster dipoles in the external field.

Detailed calculations of the magnetic coupling of clusters are in progress [19], and these should help to further elucidate the mechanisms underlying this behaviour. These calculations should also indicate the important regions of temperature and magnetic field where further measurements are most likely to provide answers to these intriguing effects.

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