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## LETTER TO THE EDITOR

**Highly enhanced orbital magnetism on cobalt cluster surfaces**

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**Abstract.** The ratio of the orbital to the spin magnetic moment has been measured for 2000-atom cobalt clusters in a copper matrix using magnetic x-ray dichroism. Averaging the result over all magnetic fields gives a value of 0.19(5) which is 2.2(6) times larger than the bulk value for face-centred-cubic cobalt. The orbital-to-spin ratio, at the cluster surface, is calculated from the measured high-field value of 0.16(2), using a simple surface model. The resulting value is almost twice that found for a plane surface and various possible reasons for this are given including changes in the nature of the cobalt–copper interface and an increase in the local density of states at the cluster surface (interface). The variation of the orbital-to-spin magnetization with the applied field provides the first evidence of changes in the surface magnetization of clusters in an external field.

**1. Introduction**

It is well known that the orbital magnetic moment is enhanced for atoms at the interfaces between magnetic and non-magnetic multilayers and this effect is predicted for Co/Cu systems by a number of theoretical studies [1–5]. Atoms at the interface have a lower coordination and this provides a symmetry axis where the (induced) orbital moment along this may differ from that in the orthogonal direction. Physically this amounts to an energy separation of the orbital states, defined by  $M_L$ , arising because of the differing Coulomb interactions with neighbouring electron charge distributions which make up the crystal field. In a thin film this gives rise to a surface magnetic anisotropy with a  $\cos^2(\theta)$  dependence with the easy axis either in-plane or out-of-plane, depending on the nature of the adjacent atomic layer. Experimentally it is found [1] that the increased orbital moment is mostly confined to a ‘few’ monolayers in the magnetic material at the interface. In embedded clusters we might therefore expect similar effects at the cluster surfaces but the nature of the geometry (each nanoparticle having crystal facets at various angles to the applied field) makes comparisons with thin films more difficult. The orbital-to-spin ratio is also directly dependent on the local density of states at the Fermi surface [1, 2, 6]. Spin-polarized states at the cluster surface (interface) are less bound because of the reduction in the total exchange interaction since they have fewer nearest neighbours. The net result is an increase in the LDOS at  $E_F$ . There may of course be other contributions to the enhancement of orbital moments from the intrinsic (nanoscale) nature of the clusters. One of the goals of the experiments described here was to ascertain whether the results could be explained by the same mechanism as operates in thin films.

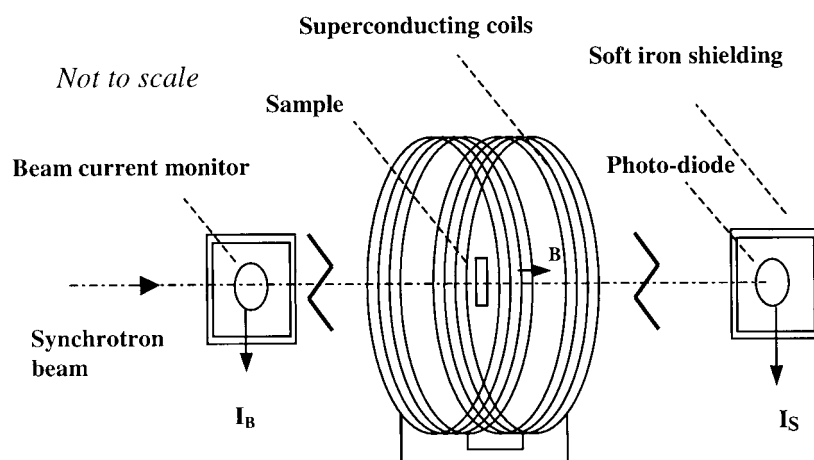
A primary requirement for obtaining meaningful results in these experiments is that the morphology of the material should be well defined, since it is well known that almost all surfaces give enhanced orbital moments simply because there are many atoms in sites with reduced coordination. In our experiments we have made the material by deposition of clusters at thermal energies and have also ensured that the density of clusters is very low, around 3%

by volume, thus making it likely that the possibility of sintering is small. Furthermore, we have established, by TEM studies [7], that it is very likely that the clusters are retained as spherical nanocrystals in the matrix. Recent measurements [8] of the residual magnetism in dilute samples of cobalt in copper indicate that the departures from spherical symmetry are small for material made by low-energy deposition.

## 2. Measurements

The measurements were made using the technique of magnetic x-ray dichroism using synchrotron radiation from beamline 1.1 at the SRS source at Daresbury. We have measured directly the changes in the *absorption* for circularly polarized radiation for thin samples of cobalt clusters. Samples were made by depositing cobalt clusters together with an atomic copper beam onto 20 nm thick carbon foils. These samples were made using the Daresbury Nanomaterials Machine [7] and were about 50–60 nm thick and contained about 3% by volume of cobalt clusters. The mass distribution of the clusters was measured prior to deposition using a large analysing magnet to separate the (charged) clusters. Each sample was capped with a copper layer of approximately 1.5 nm to prevent oxidation in the atmosphere.

Since it was very important to measure an average bulk value for the clusters we have used absorption spectroscopy rather than measuring the total electron yield. The latter has a varying sensitivity with surface depth because of the relatively small range of the escaping Auger electrons, and indeed may vary over the dimensions of the clusters (3.5 nm). Figure 1 shows the layout of the experiment.



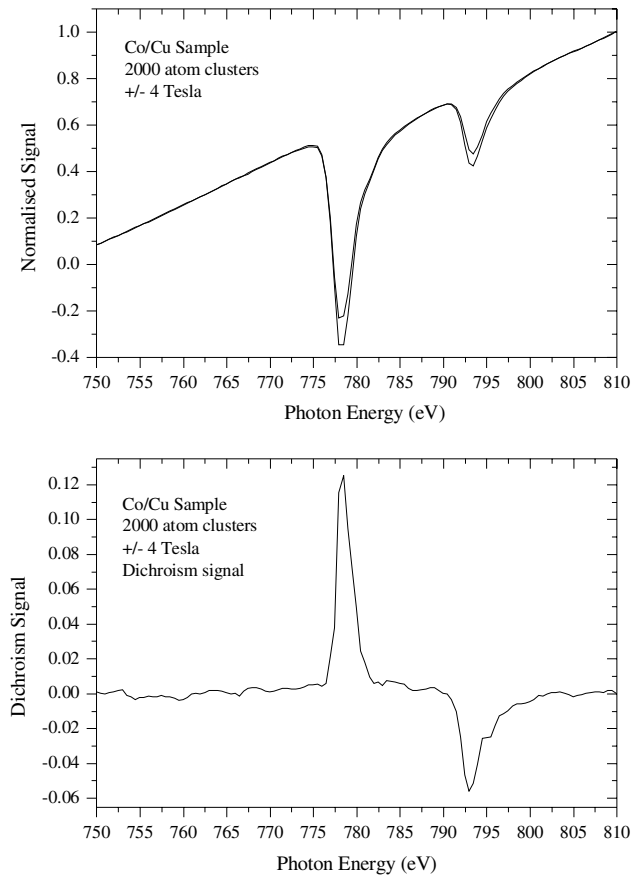
**Figure 1.** The arrangement for measuring magnetic x-ray dichroism.

A superconducting magnet was used to generate axial magnetic fields up to 4 T. The thin samples were positioned in vacuum in the centre of the coils and the absorption of synchrotron radiation measured by monitoring the current in a photo-diode ( $I_S$ ), downstream from the sample. A thin carbon foil was used to monitor the beam current ( $I_B$ ) and the diode current was recorded as a function of the magnitude and direction of the applied magnetic field. Since the diode was positioned 1 m away from the coil (diameter 0.1 m) and was magnetically shielded, the diode current from target electrons was insignificant compared to that from soft x-rays. Measurements were taken at room temperature in the photon energy range which spanned the L2 and L3 absorption lines of cobalt.

### 3. Results and discussion

At each field setting, two normalized absorption spectra ( $I_S/I_B$ ) were recorded, one with the field in the beam direction and the other with the field reversed.

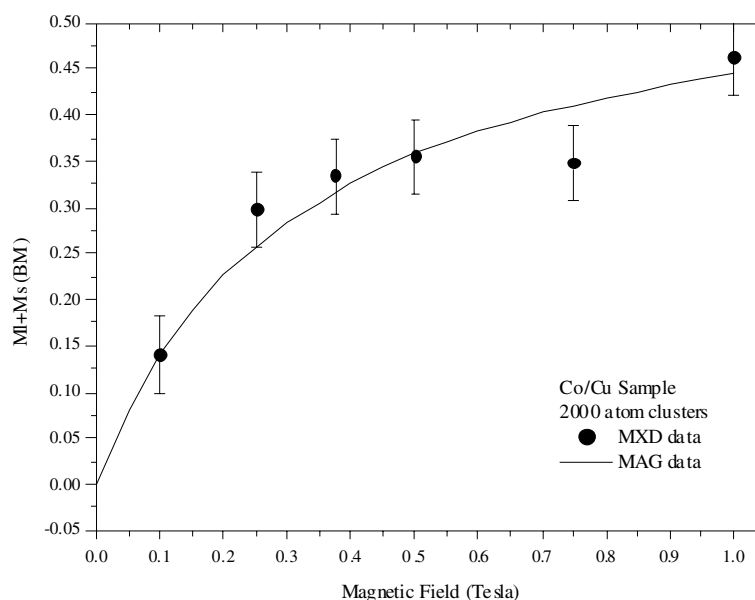
It was found that the spectra were identical for energy regions outside the absorption lines and so the difference spectrum ( $I_+ - I_-$ ) could be obtained with a high degree of accuracy. Figure 2 shows typical dichroism spectra for 2000-atom cobalt clusters in a copper matrix.



**Figure 2.** The top panel shows typical absorption spectra and the bottom one is the subtracted dichroism spectrum for the L2/L3 lines.

We then applied the standard sum rules [9, 10] to extract the spin and orbital atomic moments using the L-line integrated absorption. (A suitable correction was applied to account for any non-linearities with target thickness and for the small changes in efficiency of the detector as a function of energy.)

Figure 3 shows the total moment ( $M_S + M_L$ ) as a function of magnetic field at room temperature assuming that the number of holes in the d orbitals is 2. The solid line shows a separate measurement [8] of the superparamagnetic response made with a SQUID magnetometer. For no cluster-cluster interactions this curve should be a convolution of the size distribution and the Langevin function at least for field values where the cluster dipole energy is much larger than the magnetocrystalline anisotropy energy. The measured SQUID



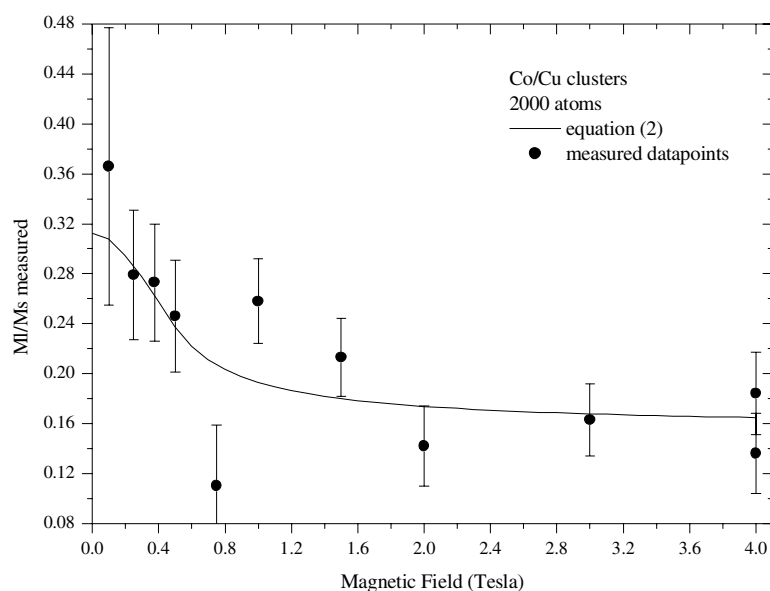
**Figure 3.** The total average magnetization spectrum per atom as obtained from the absorption spectrum. The solid-line curve is from SQUID measurements and can be fitted to  $M = 1.7 \mu_B/\text{atom}$ . Only the upper half of the symmetric curve is shown

curve (the solid line in figure 3) has been fitted to a calculated response assuming that the cluster magnetic moments are fixed at  $1.7 \mu_B/\text{atom}$ , close to that found for free clusters [11]. Furthermore, we have measured the residual magnetism [8] in the samples at temperatures down to 2 K. The temperature at which 50% of the particles become blocked is 5 K. This is strong evidence that the particles are all spherical and the particle interactions are weak dipole–dipole in origin. Indeed, measurements at 5% concentration where the dipole–dipole interactions are even smaller can be fitted to a single value for the anisotropy energy of  $4.0 \mu\text{eV}/\text{atom}$ . The total magnetic moment (per atom) from the MXCD measurements is much smaller than that obtained from the superparamagnetic response. The source of this paradoxical behaviour is not known but could be one of three things. The most likely is that there is a significant fraction of clusters which are non-magnetic. It is also possible (though unlikely) that the cluster beam contains atomic cobalt but this was not evident in earlier time-of-flight measurements [12]. Alternatively there may be strong antiferromagnetic coupling between the clusters. If the cause is atomic cobalt then the copper matrix will contain about 6% of cobalt. These atoms will have only an extremely small paramagnetic response at room temperature and whilst they significantly alter the total absorption they have no effect on the *change in absorption* that occurs when the magnetic field is reversed. This change, as the *measured* superparamagnetic response (solid line) of figure 3 shows, is completely attributable to clusters with an average size around 2000 atoms. However, the ratio

$$R = \frac{2(I_{L3} + I_{L2})}{3(I_{L3} - 2I_{L2})} \quad (1)$$

where  $I_{L3}$  denotes the integrated intensity of the L3 line in the *dichroism* spectrum, is equal to the ratio of the orbital to the spin magnetization. This is independent of the total absorption and does not depend on any assumption concerning either the number of hole states in the d band or the beam polarization. It does however assume that the tensor matrix elements  $\langle T_z \rangle$

can be ignored, which appears to be the case [9, 10] for cobalt thin films and is very likely to be true for clusters. The ratio of the orbital to the spin atomic moments for 2000-atom cobalt clusters embedded in copper is shown in figure 4. The errors in the individual points are estimated from the uncertainties in the procedure used to generate the dichroism spectra. Since the value of the ratio in FCC cobalt [1] is 0.078, these measured values represent a considerable enhancement of the orbital magnetization in clusters. However, the crystalline nature of the embedded clusters is not known though it is very likely that they are cubic. HCP cobalt can be eliminated as a possible structure because of the recent measurements of residual magnetism in these systems. There is also a possibility that the clusters are icosahedral (as found for free clusters of this size) but this group is not space filling and would result in a bigger mismatch with the cubic copper ‘lattice’.



**Figure 4.** The measured orbital-to-spin ratio as a function of magnetic field. The solid line is calculated assuming that the atomic spin direction is determined only by the external field and the surface anisotropy.

Similar increases in the average orbital-to-spin ratio have been found in deposited iron clusters [13], in cobalt clusters produced by ion implantation [14] and in self-assembled cobalt nanostructures [15, 16]. However, there are essentially two important differences in our work. Firstly, the band structures of cobalt and copper are very close and this may give the clusters unusual magnetic properties as suggested in recent theory [17]. Secondly, our method of preparation, which involves the deposition of pre-formed spherical nanocrystals, almost certainly results in material with a known morphology. Strong evidence for this is given by the magnetometry measurements discussed earlier and by many transmission electron microscopy measurements [8] of the structure of clusters in other matrices. Furthermore, we have developed a simple theory to relate the measured increases in orbital magnetism for spherical nanocrystals to those [1] for the same materials in planar geometry. Essentially this formulation is the same as that which gives rise to the  $1/d$  ( $d$  = thickness of sample) variation [18] of magnetic anisotropy in thin films. For clusters it gives rise to a variation of the measured orbital-to-spin ratio like  $1/R$  ( $R$  = cluster radius). (This is ignoring any changes in the LDOS

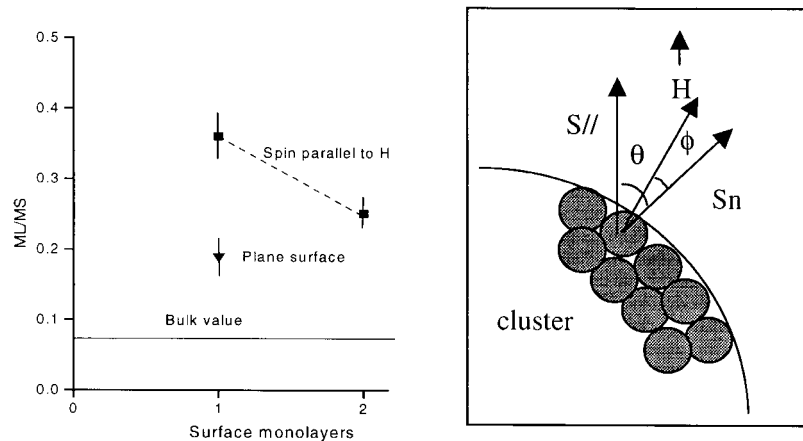
at  $E_F$  with cluster size. This point is discussed later.) The measured ratio of the orbital to the spin magnetization can be expressed as

$$\left(\frac{M_L}{M_S}\right)_{ME} = \left(\frac{M_L}{M_S}\right)_{BULK} + \left(\frac{M_L}{M_S}\right)_{SURF} f(N, i) \quad (2)$$

where

$$f(N, i, H) = \frac{1}{N} \sum_{\text{surface}}^i n_i \times 2 \int_0^{\pi/2} s(\theta) \sin(\theta) \cos^2(\phi) d\theta. \quad (3)$$

Here  $(M_L/M_S)_{SURF}$  is the *increase* of the ratio of the orbital to the spin magnetization at the surface and  $s(\theta)$  represents any spin variation over the cluster surface.  $\phi$  is the angle between the surface spin direction and the normal (figure 5) and is calculated as a function of  $\theta$  by minimizing the surface energy. This energy is a function of the field strength, the surface magnetic anisotropy and the exchange interaction. In the simplification here we assume that the magnetization is rather 'soft' and the exchange term can be neglected with  $s(\theta) = 1.0$ . (The latter is probably only true when the spin is along the field direction.) At low fields, when the spin might be normal if the exchange interaction allows a degree of canting, the integrand in equation (2) is 1. When the spin is constrained to lie in the magnetic field direction the integrand is  $1/3$ . The orbital-to-spin ratio is therefore particularly sensitive to changes in the surface spin direction. The summation (equation (2)) is over the number of surface monolayers, and we have calculated this term on the assumption that the surface orbital moment is contained within either one or two monolayers. A factor of 2 arises because the integral in equation (3) is over a single hemisphere only. Also it is assumed that the surface orbital-to-spin ratio is an average over all crystal directions.  $f(N, i)$  can then be calculated approximately by assuming spherical clusters and using the Wigner-Seitz radius for cobalt atoms. The results for the surface enhancement are shown in figure 5 and compared with the measured value [1] along the 100 direction for a cobalt-copper interface. Since the previous measurement shows that the surface orbital moment is mostly contained in the first monolayer it is clear that the enhancement on the cluster surface is significantly larger than that for a plane surface. Interestingly the variation of the measured values with magnetic field (figure 4) shows



**Figure 5.** The ratio of the orbital to the spin magnetization per atom at the surface as calculated from equations (2) and (3) using the measured high-field value of the ratio of the orbital to the spin magnetization and  $\phi = 0$ .

a trend that is predicted by a 'soft-magnetization' model, vis-à-vis these should be larger at low field than at high fields, presumably because the spin vector moves from normal to the surface to parallel to the field. The solid line is the variation computed assuming that the direction of spin is determined *only* by the applied field and the magnetic anisotropy. The fit is rather good considering that the only free variable apart from  $M_L/M_S$  is the surface magnetic anisotropy. Notice that the latter only affects the position at which the spin direction changes, so the asymptotic value at low field is not an independent variable once the value of  $M_L/M_S$  is chosen to fit the high-field region. Also the fit produces a positive value for the magnetic anisotropy, which is consistent with previous measurements [19]. The data therefore suggest that the exchange coupling at the surface is rather weak and allows a degree of spin canting between the surface monolayers and between atoms in the monolayer itself. (Note that the canting will be much larger on the cluster equator!)

Overall, the ratio of the orbital to the spin magnetization at the surface is a factor of 1.9 times larger than that for the plane surface when the spin is confined to the field direction. (This is calculated using the measured value at high fields and assuming that the integrand is  $1/6$  in equation (2).) The reasons for this large enhancement are not clear but some possibilities are:

- (1) In the case of thin films the cobalt was grown epitaxially on the copper substrate. It is most unlikely that the interface between the clusters and the copper matrix is well defined. Indeed it is likely that the clusters lie at grain boundaries between the copper nanocrystals. It is well known that along these dislocations [20] the atoms are not in a regular (or close-packed) arrangement.
- (2) The surface magnetization will differ along different crystal directions according to the surface structure. The measurements reported in [1] are for the 100 surface. Along the 111 direction, for example, the enhancement may be larger leading to a higher average value.
- (3) There may be considerable variation in the spin moment throughout the cluster with larger values at the surface, as has been modelled by a 'shell' magnetic structure model [11]. The comparison with a plane-geometry interface is not therefore valid. For example the second monolayer may have a low or reversed spin moment and this may make the interface between the first and second layer behave in a manner similar to the interface between cobalt and copper. Also the possibility of a second monolayer with much reduced spin would imply a small exchange coupling between layers and would therefore allow the spin at the surface to be normal at low fields. Again we note that this may not happen around the cluster equator.
- (4) Atomic sites, along or near to ridges on the cluster surface, will experience a different crystal field and may have larger orbital enhancements.
- (5) *The LDOS at  $E_F$  is a key issue in these measurements.* If changes in this value were the major contributing factor to the increase in the orbital-to-spin ratio over the plane surface, then the results would imply a doubling of the surface density of states for this size cluster. One result of this would be a steeper (than  $1/R$ ) fall-off in the surface contribution to the orbital-to-spin ratio as the cluster size is increased. Some evidence for this [21] has recently been found for iron clusters.

#### 4. Conclusions

The ratio of the orbital to the spin magnetism has been measured for 2000-atom cobalt clusters embedded in a copper matrix. This shows a considerable enhancement which is almost certainly associated with the reduced coordination of cobalt atoms at the cluster surface.



Several explanations have been given to explain why the surface enhancement is larger than found for the Co/Cu interface in a multilayer thin film. Two further experiments seem to be particularly salient in advancing these studies concerning the development of ferromagnetism in mesoscopic systems. Firstly the possibility of a soft magnetic structure could be confirmed (or otherwise) by further measurements of the orbital-to-spin ratio as a function of magnetic field. Secondly, it seems that measurements of the enhancement as a function of cluster size would help to establish that the increase in the spin-polarized LDOS at  $E_F$  was the primary factor in determining the difference between clusters and plane surfaces. However, it is extremely important that theoretical studies of these mesoscopic systems are carried out. It would appear that *ab initio* calculations (DFT) are now possible [22] on structures containing thousands of atoms.

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