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Superparamagnetism in small Fe clusters on Cu(111)

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Abstract. Fe clusters of 105 ± 2 atoms/cluster were mass selectively deposited onto Cu(111) at cryogenic temperatures. XMCD was used to measure temperature and direction dependent magnetization curves. The clusters are superparamagnetic at the lowest temperature measured (10 K). Their magnetization curves are consistent with magnetic moments of $\approx 2.5\mu_B$ per atom which are thus enhanced over the bulk values. Within experimental accuracy, the clusters do not present magnetocrystalline anisotropy in the temperature range of 10 K to 60 K.

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1 Introduction

For ensembles of small magnetic particles to display intrinsic ferromagnetism, it is necessary for them to possess either large magnetic anisotropy or to be held at very low temperatures. This is because the ratio of anisotropy energy to thermal energy governs the orientational stability of the cluster magnetic moment. Above the blocking temperature, a cluster ensemble is thermally demagnetized, despite the fact that the atomic moments within each individual cluster are still ferromagnetically coupled. The intrinsic magnetic anisotropy in each cluster is related to anisotropy of the spin orbit interaction and is generally relatively small in $3d$ transition metal ferromagnets. Typical blocking temperatures of 4 nm diameter particles would be 15 K or less, if only the bulk magnetic anisotropy energy density were to be considered, however, small magnetic clusters may possess an increased magnetic anisotropy energy density since both spin and orbital magnetic moments are strongly enhanced at small cluster sizes [1–3]. Furthermore, local contributions to magnetic anisotropy energy may occur at the particle surface. Macroscopic ferromagnetic order may alternatively arise in ensembles of otherwise superparamagnetic particles provided there is sufficiently strong coupling between them. Dipolar coupling between densely arranged magnetic particles could be a source of such collective blocking.

Deposition of iron clusters has been reported several times. Lau et al. [2] deposited small clusters (2–9 atoms) onto a Ni/Cu(001) surface magnetized out of plane. They report a strongly size-dependent enhancement of magnetization (with respect to bulk iron). Binns et al. [4] also report a magnetization enhancement for mid-sized clusters (180–700 atoms) when deposited on non-magnetic HOPG, when additionally coated with cobalt or when embedded in a silver matrix material. Bansmann and Kleibert [5] report that larger clusters (6–12 nm) on magnetized Co/W(110) surfaces also show enhanced moments. Though this trend of enhanced moments is a constant, the properties of the cluster systems are strongly dependent upon size, interparticle distances and substrate choice. This is maybe best exemplified by the reduction of magnetic moments below detection threshold in small Fe clusters when changing their environment from a rare gas matrix to a graphite surface [6]. Only the largest of the clusters in these studies exhibit room temperature ferromagnetism.

Surprisingly high ferromagnetic critical temperatures were recently reported [7,8] for small Fe nanoclusters (diameters of 2.4 to 3.7 nm) prepared on Cu(111) by means of buffer layer assisted growth [9]. These clusters displayed strong magnetic anisotropy with a hard magnetic axis found along the surface normal. Dipolar interaction could safely be ruled out as the origin of both, collective blocking and anisotropy. Experimental evidence appears to support the view that the Cu(111) surface electrons mediate the magnetic interactions and thus are responsible for collective order in the two-dimensional particle ensemble. Since exchange interactions are essentially isotropic, they cannot be the source of the observed anisotropy. This anisotropy must result from individual, albeit effectively

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coupled particles. Interaction at the cluster substrate interface is a likely candidate to produce such an anisotropy.

In the present work we investigate magnetic properties of small mass selected $Fe_{105\pm2}$ clusters deposited onto Cu(111) at low temperatures and small kinetic energies. X-ray magnetic circular dichroism (XMCD) is used as a sensitive probe of magnetization. Magnetization curves were measured in applied magnetic fields of up to 2 T at normal and oblique incidence to probe the occurrence of magnetic anisotropy. Since the clusters were superparamagnetic at temperatures as low as 10 K we analyze their total moments in terms of Langevin superparamagnetism.

2 Experiment

Cu(111) was prepared by repeated cycles of sputtering and annealing until a sharp LEED pattern indicated high surface quality. Fe clusters were generated by a laser vaporization cluster ion source and deposition setup similar to the one described in [10]. Mass selection is achieved by means of a quadrupole mass filter which was set to accept clusters in the range of Fe_{103} to Fe_{107}. The clusters were deposited at low kinetic energy ($\ll$1 eV/atom) while the substrate was maintained at a temperature below 100 K until a coverage of $1.5(5)\times10^4$ clusters/μm^2 was achieved, correspoding to an average distance of 8.3(7) nm between clusters, well comparable to the conditions in [7,8]. The total amount of material corresponds to 0.1 monolayers.

X-ray absorption spectra were recorded at the PM3 soft X-ray bending magnet beam line for circular polarization of the BESSY-II synchrotron radiation facility in Berlin, Germany. XAS and XMCD data as well as XMCD magnetization curves [11] were measured by recording the sample drain current (total electron yield) under X-ray illumination in applied magnetic fields of up to 2 T, both at normal X-ray incidence and at an incidence angle of 60° with respect to the surface normal.

3 Results and discussion

The inset to Figure 1 shows the Fe L_3 absorption curves of a $Fe_{105\pm2}$ cluster sample, measured at a temperature of 65 K in applied fields of $\pm$1 T. The absorption lineshape is characteristic of metallic Fe. At the low coverage, the peak absorption amounts to about 2.5% of the substrate signal. All XMCD magnetization curves discussed in the following were recorded at the excitation energy at which the largest magnetic circular dichroism is obtained (arrow).

Magnetization curves, measured at temperatures of 10, 30 and 60 K, at both normal and oblique incidence (60°), are all given in the main panel of Figure 1. Clearly, the clusters are superparamagnetic at all temperatures, i.e. remnant magnetization cannot be observed at the temperatures that we reach in our experiment. At low applied fields, the slope of the measured curves clearly depends on temperature. Measurements at normal and oblique incidence essentially fall right on top of each other. Thus we

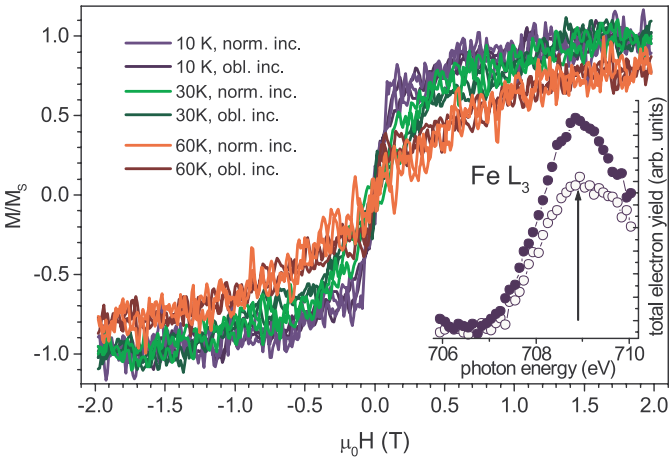

Fig. 1. Superparamagnetic XMCD magnetization curves, measured at normal X-ray incidence and oblique X-ray incidence (60°), respectively, at temperatures of 10 K, 30 K and 60 K. The inset shows Fe L_3 absorption spectra, measured at applied fields of $\pm$1 T at a temperature of 65 K. Magnetization curves were measured at the photon energy of largest difference (XMCD) between the two spectra (arrow).

do not observe significant magnetic anisotropy. This result is very different from the claims of Pierce et al. who find essentially zero out of plane magnetization at an applied field of 0.25 T. To substantiate this statement we have analyzed the experimental magnetization curves within the model of classical Langevin paramagnetism.

Figure 2 displays the resulting total magnetic moments of the clusters as a function of temperature as evaluated from individual magnetization curves as in Figure 1. While there is some scatter in the experimental data, we see that the atomic magnetic moments are consistently enhanced ($2.5 \pm 0.3\mu_B$) with respect to their bulk counterparts ($2.2\mu_B$), in both normal and oblique incidence, particularly at low temperature. This enhanced magnetization in the clusters is well in line with observations of gas phase Fe clusters [1,12]. Gas phase measurements, however, yield even higher magnetic moments per atom at this cluster size. Thus hybridization with the Cu(111) substrate must have the effect of reducing the cluster magnetic moments, compared to the values of free particles. In this respect the present results are well in line with earlier findings on deposited iron clusters [2,4,5]. Despite the moment enhancement, any effective anisotropy energy is clearly too small to be observed at a temperature of 10 K.

Given the fact that the clusters investigated here are considerably smaller than those of Pierce et al. in [7] while being deposited at comparable density, we can estimate from their results an expected critical temperature. To do this we assume that the suspected indirect interaction is well represented by an effective Heisenberg Hamiltonian, $H_{eff} = -J_{ij}\boldsymbol{S}_i\boldsymbol{S}_j$, where in general the effective exchange interaction will depend on interparticle distance. Simplifying the problem to a regular lattice and nearest neighbour interaction the critical temperature is proportional

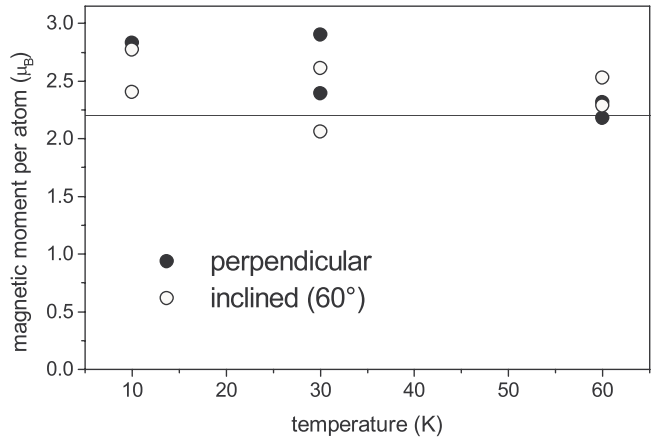

Fig. 2. Magnetic moments per atom, as determined from the magnetization curves by least squares fit of Langevin paramagnetic response. Full symbols correspond to out of plane (normal incidence) magnetization measurements, open symbols to data taken at oblique incidence. The atomic magnetic moment of bulk bcc iron ($2.2\mu_B$) is indicated by the horizontal line.

to the square of the average cluster size at constant distance between particles. Appropriately downscaling the critical temperatures observed in [7], we are lead to expect collective blocking to occur below 3 K, outside our currently accessible temperature range. Therefore, our observation of superparamagnetic response in the case of $Fe_{105\pm2}$ clusters is not at odds with the results of Pierce et al.

Next we consider the observation of the essentially isotropic magnetization response even at the lowest temperatures reached in our experiments. In the superparamagnetic regime, uniaxial anisotropy will be appreciable in the form of anisotropic magnetization curves when the anisotropy energy is of the order of thermal energy or above. Based on this criterion, we determine an upper bound to the effective uniaxial anisotropy energy of roughly 1 meV per cluster or, equivalently, $\approx 10\,\mu$eV per atom. Thus, although in a deposited 100 atom cluster there is necessarily a high proportion of atoms participating in the interface between clusters and surface, the effective anisotropy energy enhancement on a per atom basis is enhanced by less than a factor three with respect to the bulk value for bcc Fe [7].

Calculations [13] find a large magnetic anisotropy energy of 0.9 meV per atom for Fe dimers on Cu(111). However, the magnetic anisotropy is strongly reduced when the dimer is embedded within the surface or subsurface layer. It is therefore conceivable that local atomic arrangements at the cluster substrate interface should play an important role in determining magnetic anisotropies observed in systems of clusters at surfaces. Thus, the conditions at which clusters are grown or deposited may prove decisive for the outcome of magnetic experiments. Besides cluster size the method of sample preparation is indeed an important difference between the experiments in [7] and the present work and could be the origin of the different magnetic anisotropies observed.

4 Conclusion

In conclusion, the finding of superparamagnetism in $Fe_{105\pm2}$ clusters deposited onto Cu(111) at temperatures as low as 10 K shows that their intrinsic anisotropy energy is smaller than 10^{-5} eV per atom. Analyzing the magnetization curves in terms of Langevin superparamagnetism, we find the atomic magnetic moments to be enhanced by 10–20%. The apparent lack of significant magnetic anisotropy in the present experiments suggests that the recent observation of high ferromagnetic critical temperatures in Fe nanoparticle ensembles on Cu(111) might derive from interface formation specific to buffer layer assisted growth. Experiments to compare magnetic clusters of similar sizes and densities, generated under various conditions, are presently in preparation to further elucidate this aspect of nanomagnetism at surfaces.

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