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Surface Spin Polarization of Fe Nanoclusters

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The spin polarization at the surface of Fe nanoclusters has been probed using a spin-polarized metastable helium beam. The clusters, produced in a gas aggregation source, display a lognormal size distribution with a peak centered at ~11 nm. Varying coverages of both spheroid- and cuboid-shaped particles were concomitantly deposited onto clean Si(111) substrates for investigation with the extremely surface sensitive technique of metastable de-excitation spectroscopy (MDS). A nominal cluster coverage of 8 Å yielded a maximum asymmetry of ~10 % in the ejected electron yield for He spins aligned parallel and anti-parallel to the magnetization direction of the clusters. When compared to values obtained from epitaxial Fe films on various substrates, the measured asymmetry suggests an enhancement in the surface spin polarization, as theoretically proposed. The atomic structure of the clusters and their topography on the Si(111) substrates were studied with transmission and scanning electron microscopy.

Index Terms— Nanoclusters, spin polarization, surface magnetism, metastable de-excitation spectroscopy

I. INTRODUCTION

THE continued effort to understand the properties of magnetic nanoparticles derives largely from their potential to enable miniaturization beyond the thermal limit in magnetic storage devices [1]. As the size of the particles reduces, so does the coordination of the surface atoms resulting in significant changes to fundamental electronic, optical, and magnetic properties. This departure from bulk-like behavior also renders nanoparticles attractive candidates for functionalized nanostructured materials in catalysis and magnetic sensing.

The increasing dominance of surface effects in nanoclusters leads to a narrowing of the valence band and an associated increase in the density of states (DOS) at the Fermi level [2]. The spin and orbital magnetic moments are also greatly enhanced when compared to bulk values. This has been observed in particles as large as 12 nm in diameter where the fraction of surface atoms is 23 %, and has been attributed to the increasing orbital moment of the outer two shells which contain a greater proportion of surface atoms as the particle size decreases [3]. Understanding the role the surface of the nanoclusters plays in determining their material properties is essential if they are to be used in technical applications. This is especially true given that in such an application it will be necessary to deposit the clusters onto surfaces or embed them in matrices further modifying their properties. For example, as the surface coverage of Fe clusters approaches saturation, the orbital moment dramatically reduces to approach that of bulk Fe [3].

Studying the surface of nanoclusters in isolation requires surface specific techniques which are also magnetically sensitive, such as those routinely used to measure the spin polarization of magnetic thin films. Of these, spin-polarized metastable de-excitation spectroscopy (SPMDS) is the most surface sensitive as de-excitation of the metastable atoms occurs on the vacuum side of a surface resulting in an ejected electron energy spectrum that is characteristic of its magnetic,

electronic, and chemical properties.

SPMDS is particularly sensitive to the surface valence band so that size-dependent electronic properties may be studied such as *d*-band narrowing. Due to this narrowing, any asymmetry in the spin-split density of states at the Fermi level is exaggerated. This can be probed directly by spin-polarizing the electrons of the incident He 2^3S atoms as, due to the dynamics of the de-excitation process, the yield of electrons emitted depends on whether the He 2^3S spins are aligned parallel or anti-parallel to the sample magnetization.

This paper outlines an electron microscopy and SPMDS study of the atomic structure and surface magnetism of Fe nanoclusters deposited onto clean Si(111) substrates.

II. EXPERIMENTAL METHOD

Nanoclusters were produced using a gas aggregation source coupled to a UHV surface analysis facility that includes a He 2^3S beamline for metastable de-excitation spectroscopy (MDS) [4]. As is typical for these sources, the size distribution of the clusters follows a lognormal distribution with a most probable particle width of around 11 nm. Clusters were deposited onto either carbon TEM grids or clean Si(111) substrates that were prepared by flashing to 1200 °C with a subsequent slow cool to produce a 7×7 reconstruction, as confirmed by low energy electron diffraction. Samples were then either removed from the UHV chamber for analysis by TEM or SEM or transferred to a surface analysis chamber for investigation by SPMDS.

To obtain SPMDS spectra, a beam of He 2^3S atoms was incident on the cluster-covered substrates at 45° to the surface normal. The yield of electrons at a specific kinetic energy emitted in the normal direction due to de-excitation of the metastable atoms was measured with a hemispherical energy analyzer (Omicron, EA 125). A spin polarization of >95 % in the He 2^3S beam was achieved using optical pumping of the He $2^3S_1 \rightarrow 2^3P_2$ transition. The quantization axis of the He spins was set to be collinear with the in-plane magnetization direction of the sample. SPMDS spectra were acquired with the orientation of He 2^3S atom spins and the sample

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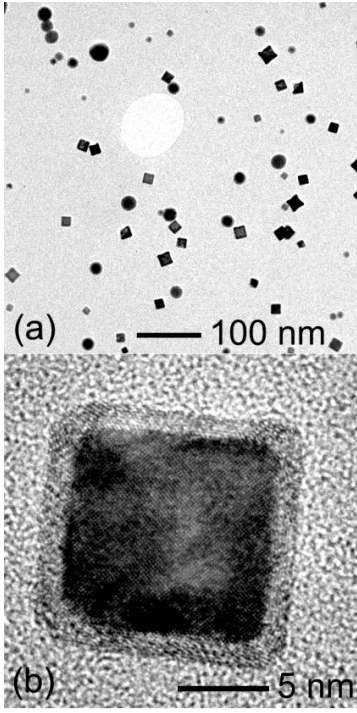


Fig. 1. (a) TEM image of Fe nanoclusters deposited on a carbon film. (b) A cuboid Fe nanocluster consisting of approximately 100000 atoms and surrounded by a ~ 1.5 nm oxide layer.

magnetization direction parallel (\uparrow) and anti-parallel (\downarrow) and the asymmetry $A(E)$ calculated using the standard definition:

$$A(E) = \frac{N_{\uparrow}(E) - N_{\downarrow}(E)}{N_{\uparrow}(E) + N_{\downarrow}(E)} \quad (1)$$

where $N_{\uparrow,\downarrow}(E)$ is the yield of electrons at a kinetic energy E for parallel and anti-parallel spins.

III. RESULTS AND DISCUSSION

Fig. 1 (a) shows a TEM image of a group of nanoclusters from a typical deposition. Both cuboid and spheroid clusters are observed. The high resolution image of a cuboid nanocluster in Fig. 1 (b) shows a ~ 10 nm wide bcc Fe particle surrounded by an Fe oxide shell formed as a result of exposure to air. By comparing fast Fourier transforms of high-resolution Z-contrast images of the shell and core of the nanoparticles, the phase of the oxide was determined to be Fe_3O_4 . At the time of analysis, the average oxide layer thickness was measured to be 2.7 ± 0.1 nm. Taking the average post-oxidation cluster size of ~ 12 nm and assuming the presence of a single crystal fcc Fe_3O_4 oxide layer, the average deposited cluster size is ~ 10.5 nm. Vystavel *et al.* have shown that this oxide shell may be removed with a low temperature anneal (500°C) to leave a pure Fe particle [5]. Interestingly, the authors of that study did not observe any cuboid Fe clusters and found that the most probable cluster geometry was a truncated rhombic dodecahedron. This observation agrees with theoretical work that shows for clusters between 10 and 10,000 atoms, a bcc rhombic dodecahedron consisting of 12 pseudo-close-packed

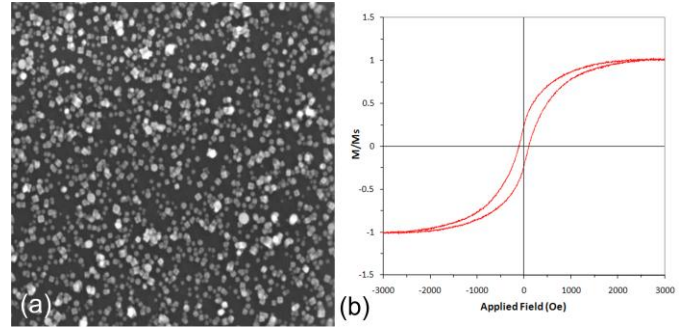


Fig. 2. (a) SEM image of an 8 \AA coverage of Fe clusters on Si(111). (b) The corresponding hysteresis loop of the sample shown in (a).

{110} faces is the most stable structure.

The shape of the clusters is determined by the kinetics of growth in the gas phase and for larger clusters faceting leads to thermodynamic stability. After nucleation, cluster growth occurs on individual crystal faces with the rate of growth on each face determining the final structure. Cuboids result when growth on the (100) face exceeds that on a (110) face. Larger clusters may be formed when smaller units self-assemble through collisions with a corresponding minimization of the surface energy.

Fig. 2 (a) shows an SEM image of an 8 \AA coverage of Fe clusters deposited onto a clean Si(111) 7×7 reconstructed surface. As with TEM, both spheroid and cuboid clusters are observed in a random configuration across the substrate. There is no evidence for diffusion across the surface or of clusters aligning along atomic step edges indicating a strong reaction with the substrate after landing. Having been exposed to air before insertion into the SEM the clusters are oxidized, as confirmed by EDS, and no shape deformation due to the impact with the surface is apparent, as expected for the low landing energies involved (< 0.5 eV/atom) [2].

Fig. 2 (b) shows the hysteresis loop, obtained using an alternating gradient force magnetometer, for the cluster coverage shown in Fig. 2 (a). The form of the loop reflects the distribution of particle sizes and shapes which are in a regime where the clusters are expected to be single domain and uniaxial with randomly oriented easy axes [6]. Such a system gives rise to a composite hysteresis loop with a remanent-to-saturation magnetization ratio lowered to 0.5 (the equivalent value for cubic anisotropy is 0.81) [2]. For a system also containing unblocked particles, this ratio decreases further and will reach zero when all particles are superparamagnetic (SPM). At larger fields beyond those needed to saturate the ferromagnetic clusters, the gradual increase in magnetization is due to smaller clusters on the surface that are SPM at room temperature.

Fig. 3 (a) shows the SPMDS spectra obtained from the sample shown in Fig. 2 along with the resulting asymmetry. At Fe and Si surfaces, metastable helium de-excites by resonance ionization (RI) followed by Auger neutralization (AN). Two electrons are involved in the AN process so that

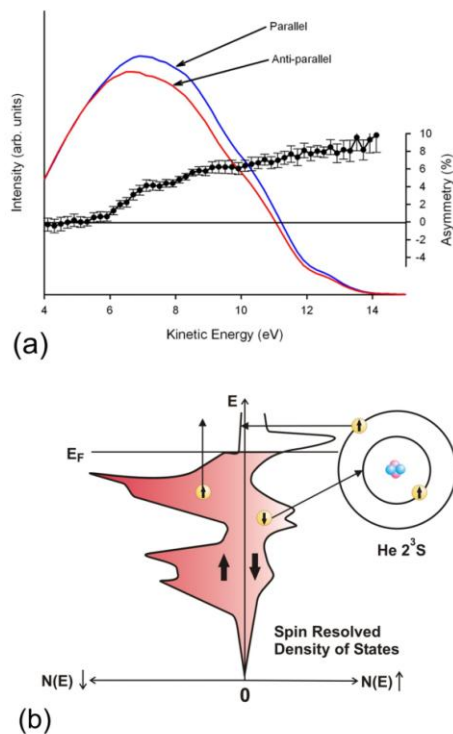


Fig. 3. (a) SPMDS data showing a high spin polarization at the surface of Fe nanoparticles deposited onto a clean Si(111) substrate. (b) Schematic of the de-excitation process that yields an asymmetry in electron emission for parallel and anti-parallel spins.

the resulting spectra generally display broad features reflecting a self-convolution of the surface DOS. The kinetic energy maximum in Fig. 3 (a) at ~ 14 eV is due to both electrons involved in the AN transition originating from the Fermi level, E_F . The shoulder just below E_F (corresponding to binding energies of a few eV) is due to emission from surface states of the Si(111) 7×7 reconstruction [4] and also Fe $3d$ electrons [7]. The shoulder at ~ 10.5 eV arises from emission of Si atomic $3p$ states found at the surface and in the bulk, and at low kinetic energies emission is dominated by true secondary electrons.

The asymmetry is due to the Fe $3d$ electron component of the spectra and increases with kinetic energy to a maximum of $\sim 10\%$ at E_F . A positive asymmetry indicates that minority electrons dominate in the surface vacuum region of the clusters, agreeing with SPMDS studies of thin Fe films [8]-[10]. High positive asymmetries have been reported before for thin Fe films on various substrates including GaAs (15%) [8], MgO(100) (9%) [9], Ag(100) (6%) [9], and W(110) (24%) [7]. However, these values are not directly comparable to the asymmetry reported here for a number of reasons. Firstly, all previous asymmetry measurements for Fe have been on thin films of 1 ML coverage or more whereas the coverage of clusters here is $< 100\%$. Also, due to the polydisperse nature of the nanoclusters studied, it is difficult to interpret the measured asymmetry in terms of the particle size distribution. Smaller clusters that are SPM do not contribute to the asymmetry, and the reduction in the remanent magnetization of the samples as a result of the magnetic texture of the easy-axis distribution also lowers its value. However, considering

these factors and the areal density of the nanoclusters, that the asymmetry measured is comparable to, and in some cases greater than, that obtained from thin Fe films suggests an enhanced value. Further work using a quadrupole mass-filter to size-select NPs will enable the exact nature of these relationships to be established.

For Fe growth on W(110) [7] it was previously found that the crystallographic quality and cleanliness of the Fe film formed drastically affected the maximum asymmetry obtained. By the nature of their formation and deposition, the surface of the Fe nanoclusters is inherently clean and this could also contribute to the apparent enhancement in asymmetry. It is worth noting here that using nanoclusters as a model surface circumvents many of the limitations associated with nucleation and growth techniques. These difficulties in sample preparation often lead to problems in interpreting results as has recently been discussed for spin-polarized photoemission measurements of Fe_3O_4 [11]. In fact, anomalous magnetic behavior in Fe_3O_4 films has been explained by the presence of anti-phase boundaries (APBs) that are inherent in nucleation and growth preparation methods [12]. The average distance between APBs was observed to be ~ 28 nm, much larger than the average size of nanoclusters used in this work.

In conclusion, a spin-polarized metastable helium beam has been used to study Fe nanoclusters and has shown a high positive asymmetry exists at E_F reflecting the dominance of minority electrons in the spin-split DOS at the surface vacuum level.

REFERENCES

- [1] S. Couet, K. Schlage, R. Ruffer, S. Stankov, Th. Diederich *et al.*, "Stabilization of antiferromagnetic order in FeO nanolayers," *Phys. Rev. Lett.*, 103, 097201, 2009.
- [2] C. Binns, "Magnetism in nanoclusters and cluster-assembled thin films," *J. Nanosci. Nanotechnol.*, 1, 243, 2001.
- [3] J. Bansmann, S. H. Baker, C. Binns, J. A. Blackman, J. -P. Bucher *et al.*, "Magnetic and structural properties of isolated and assembled clusters," *Surf. Sci. Rep.*, 56, 189, 2005.
- [4] A. Pratt and M. Jacka, "Scanning magneto-optical lens for surface analysis," *J. Phys. D: Appl. Phys.*, 42, 055308, 2009.
- [5] T. Vystavel, G. Palasantzas, S. A. Kock, and J. Th. M. De Hosson, "Nanosized iron clusters investigated with *in situ* transmission electron microscopy," *Appl. Phys. Lett.*, 82, 197, 2003.
- [6] T. Ibusuki, S. Kojima, O. Kitakami, and Y. Shimada, "Magnetic Anisotropy and Behaviors of Fe Nanoparticles," *IEEE Trans. Magn.*, 37, 2223, 2001.
- [7] S. Förster, G. Baum, M. Müller, and H. Steidl, "Oxygen adsorption on Fe/W(110) and Co/W(110) thin films: Surface magnetic properties," *Phys. Rev. B*, 66, 134427, 2002.
- [8] M. S. Hammond, F. B. Dunning, G. K. Walters, and G. A. Prinz, "Spin dependence in He (2^3S) metastable-atom de-excitation at magnetized Fe(110) and O/Fe(110) surfaces," *Phys. Rev. B*, 45, 3674, 1992.
- [9] R. Moroni, F. Bisio, M. Canepa, and L. Mettera, "Surface magnetism of iron films following the adsorption of oxygen: a comparison between Fe/Ag(100) and Fe/MgO(100)," *Surf. Sci.*, 433-435, 676, 1999.
- [10] M. Kurahashi, X. Sun, S. Entani, and Y. Yamauchi, "Observation of a high negative spin polarization at the Fe/MgO(100) surface oxidized at room temperature," *Appl. Phys. Lett.*, 93, 132505, 2008.
- [11] M. Fonin, Yu. S. Dedkov, R. Pentcheva, U. Rüdiger, and G. Güntherodt, "Spin-resolved photoelectron spectroscopy of Fe_3O_4 —revisited," *J. Phys.: Condens. Matter*, 20, 142201, 2008.
- [12] D. T. Margulies, F. T. Parker, M. L. Rudee, F. E. Spada, J. N. Chapman, P. R. Aitchison, and A. E. Berkowitz, "Origin of the anomalous magnetic behavior in single crystal Fe_3O_4 films," *Phys. Rev. Lett.*, 79, 5162, 1997.