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Magnetic properties of CoO nanoparticles

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Abstract. The magnetic circular X-ray dichroism (MCXD) of CoO nanoparticles was measured at low temperatures and in high magnetic fields. The particles show a superparamagnetic behaviour at room temperature, and a large orbital contribution to the magnetic moment at low temperatures was observed. This enhancement of orbital magnetism is largely determined by the contribution of the surface atoms. The larger spin–orbit coupling of the electrons of the surface atoms of the particle can cause a change in magnetic ordering in the core of the particles.

PACS. 71.23.An Theories and models; localized states – 75.30.Pd Surface magnetism – 75.50.Ee Antiferromagnetics – 75.50.Tt Fine-particle systems

1 Introduction

Because of the unique magnetic properties of small particles, as well as their potential use for technological applications, small-particle magnetism has generated increasing interest recently [1]. Antiferromagnetic nanoparticles (AFN) have gained increased attention for exhibiting magnetization reversal by quantum tunneling [2, 3]. In 1961, Neel suggested that fine particles of an antiferromagnetic material should exhibit magnetic properties such as superparamagnetism and weak ferromagnetism [4]. He attributed the permanent magnetic moment to an uncompensated number of spins on two sublattices, and neglected all complicated surface effects resulting from the reduced coordination of the surface atoms. Large magnetic moments in AFN have been observed, but their origin is still not well understood. Recently, Kodama *et al.* [5] observed large magnetic moments for small NiO particles, which they have explained by a multisublattice spin configuration in which the reduced coordination of surface spins causes a fundamental change in the magnetic order throughout the particle. In this paper, we report an experimental investigation using the technique of magnetic circular X-ray dichroism (MCXD) to determine the orbital-to-spin relative magnetic moment ($\langle L_z\rangle/\langle S_z\rangle$) of CoO nanoparticles, in combination with an atomic multiplet calculation, which enables us to compare the surface and bulk $\langle L_z\rangle/\langle S_z\rangle$ contribution within the nanoparticle.

2 Experimental

The preparation of the nanoparticles have been described in more detail for CuO in [6]. In this case, we used Co acetate, which was solved in ethanol, as a starting material. The solution was spin-coated on an Si(100) substrate. This was performed in a glove box under inert N_2 conditions. Following deposition, the Co acetate particles were transformed to CoO by calcination in air at 750 K for 4 hours. X-ray photoelectron spectroscopy (XPS) characterization experiments showed that a small contribution of the starting material was still present in the particles. An atomic force microscopy (AFM) image (see Fig. 1; the range is 500 nm by 500 nm) reveals a narrow size distribution of well-separated nanoparticles 4 nm in diameter. The white colored dots in this 2-dimensional AFM picture represent the CoO particles; the z range varies between 0 and 4 nm (black–white).

The MCXD experiments were performed at the Dragon beamline 26 (ID12B) at the European Synchrotron Research Facility (ESRF) [7]. Circular polarized light, with an 88% degree of polarization and an energy resolution of 0.5 eV, has been used. The MCXD signal was detected by measuring the drain current from sample to ground. The photon-energy incident angle was fixed at 90 degrees, and the measurements were performed at different temperatures (2–300 K) at a magnetic field of 6 T. The magnetic field was applied along the Si(100) surface normal, and the MCXD data were taken by the al-

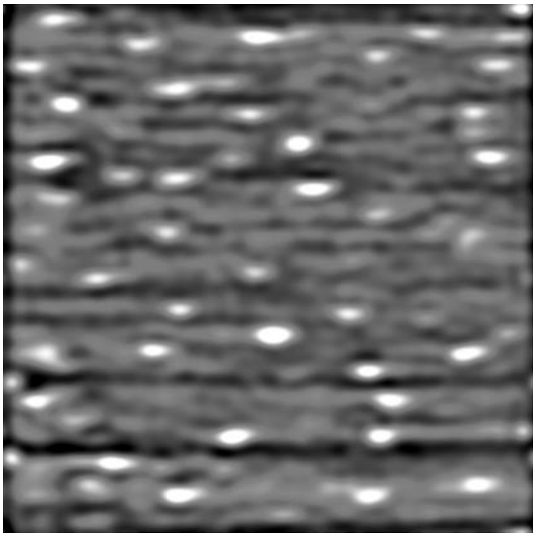

Fig. 1. A 2-dimensional 500 × 500 nm AFM topography picture of CoO particles deposited on Si(100); the z range is from 0 (black) to 4 nm (white).

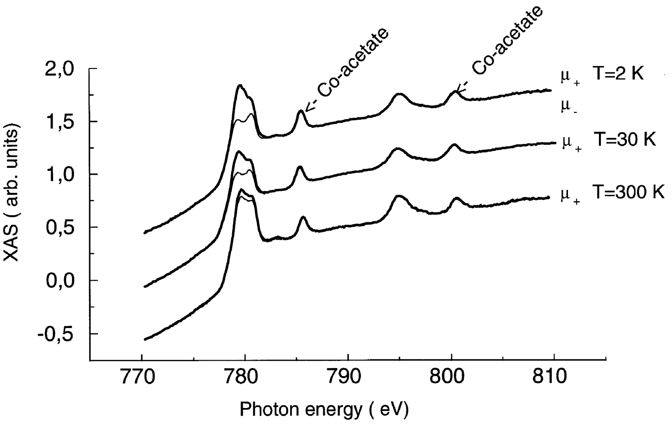

Fig. 2. $L_{2,3}$ MCXD spectra of Co at two opposite polarization directions (thick and thin black: μ_+ and μ_-, respectively) at $B = 6$ T (field-cooled).

ternation of the polarization of the light from right- to left-handed.

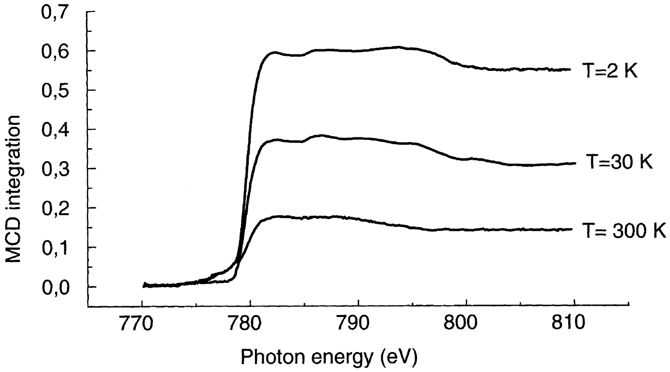

Fig. 3. The integration of the MCXD spectra corresponding to the spectra of Fig. 2.

Table 1. Measured orbital-to-spin relative magnetic moment as a function of temperature.

Temperature [K]	$\langle L_z\rangle/\langle S_z\rangle$
2	1.08
30	0.81
300	0.62

3 Results and discussion

In Fig. 2, we present the Co $L_{2,3}$-edge spectra of CoO nanoparticles deposited on Si(100) at the three given temperatures, field-cooled in a magnetic field of 6 T. The spectra shown are normalized to the incident photon flux and consist of two doublets, which can be assigned to CoO [8] and rests of the starting material Co acetate respectively. It is clear from the spectra that the difference between the opposite polarization directions (μ_+ and μ_-) for CoO increases when the temperature is reduced.

Since it is nearly impossible to rigorously determine the individual expectation value of the orbital- and spin-angular momentum with the derived sum rules [9,10] without a reliable $3d$ electron occupation number and an accurate knowledge of the X-ray absorption edge jump, we will compare the orbital-to-spin relative magnetic moment. To determine the $\langle L_z\rangle/\langle S_z\rangle$ ratio, we have used to the same method as described by Chen *et al.* [11]. Figure 3 shows the integration of the MCXD spectra from Fig. 1. The saturation behaviour near the end of the integrated spectra clearly illustrates that there is no observable MCXD signal at photon energies 15 eV above the L_2 white line. In Table 1, the $\langle L_z\rangle/\langle S_z\rangle$ of the CoO nanoparticles at 2, 30, and 300 K in a magnetic field of 6 T are compared with each other.

These results give experimental confirmation that, first, the CoO nanoparticles are magnetic, and second, the $\langle L_z\rangle/\langle S_z\rangle$ ratios are greatly enhanced, compared to Co bulk and even to Co/Pd multilayers [11,12].The value of the $\langle L_z\rangle/\langle S_z\rangle$ ratio at 2 K reveals that the orbital contribution to the magnetic moment is even of the same size as the spin part. The decrease of the $\langle L_z\rangle/\langle S_z\rangle$ ratio as the temperature is increased indicates that the ferromagnetic behaviour has a superparamagnetic origin. At temperatures higher than 2 K, the magnetic field is no longer large enough to fully align the spins of the particles in the magnetic field direction. The large contribution of the orbital part to the magnetic moment would also implicate a large spin–orbit coupling, which is directly related to the magnetocrystalline anisotropy.

To understand the large $\langle L_z\rangle/\langle S_z\rangle$ ratio for small CoO nanoparticles, we have carried out atomic multiplet calculations [9,13] for Co^{2+} in different O surroundings. The ground state $\langle L_z\rangle$, $\langle S_z\rangle$ and $\langle L_z\rangle/\langle S_z\rangle$ values of Co^{2+} ($3d^7$) in an exchange field of 0.01 eV [14] and Co−O distances of 2 A [15] are given in Table 2. Large differences are ob-

Table 2. Calculated $\langle L_z \rangle$ and $\langle S_z \rangle$ values of Co^{2+} for different coordination numbers.

Co coordination	$2\langle S_z \rangle$	$\langle L_z \rangle$	$\langle L_z \rangle / \langle S_z \rangle$
6 (bulk)	2.277	1.008	0.885
5 (interface)	−2.744	−1.092	0.796
4 (edge)	−2.924	−2.082	1.424
3 (corner)	−2.275	−1.144	1.006

Table 3. Calculated number of Co atoms with its corresponding number of nearest neighbours in a sphere-shaped CoO nanoparticle 4 nm in diameter.

Number of nearest neighbours	Number of Co atoms
6	251
5	54
4	36
3	96
2	0
1	0
0	0

tained, which are mainly ascribed to different symmetries of the ground state. What is remarkable is the relative large surface contribution. By assuming the bulk lattice parameter of 2 A and the face-centered cubic (fcc) NaCl structure for CoO, we can calculate the Co coordination number of the different Co−O configurations for a sphere-shaped CoO nanoparticle of 40 A diameter (see Table 3). Combining both calculation results, the average $\langle L_z \rangle / \langle S_z \rangle$ value for Co^{2+} can be calculated; the value is 0.92. This theoretically determined value is in reasonable agreement with the experimental value of 1.08. The relatively large value of $\langle L_z \rangle$ for atoms with a small coordination numbers (surface atoms) can possibly change the magnetic ordering throughout the particle, due to an enhanced spin–orbit coupling. This view is different from the explanation of Kodama *et al.* [5] for NiO particles, which is focused on a change in spin configuration only, without spin–orbit coupling taken into account, because of a weak coupling between the individual sublattices. However, even the orbital moment in bulk NiO contributes 17% to the total magnetization [16].

In conclusion, we have observed experimentally a large orbital contribution to the magnetic moment of small CoO nanoparticles. This enhancement of orbital magnetism is largely determined by the contribution of the surface atoms, as was calculated. The stronger spin–orbit coupling of the electrons at the surface of the particle can cause a change in magnetic ordering in the core of the particles.

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