Journal of Optoelectronics and Advanced Materials Vol. 6, No. 4, December 2004, p. 1275 - 1285

STRUCTURAL AND MAGNETIC INVESTIGATIONS OF NICKEL CLUSTERS IN C₆₀ MATRICES

C. M. Teodorescu^{*}, D. Macovei, A. Lungu

National Institute R&D of Materials Physics, Bucharest-Magurele P.O. Box MG 07, Atomistilor 105b, 77125 Romania

Nanostructured Ni/C₆₀ thin films, produced by co-evaporation of Ni and fullerene, have been investigated by both X-ray diffraction (XRD) and X-ray magnetic circular dichroism (XMCD). X-ray diffraction has shown the co-existence of diffraction specific peaks for the fullerene face-centered cubic crystal structure and diffraction peaks of Ni nanoparticles in the face-centered cubic structure, which are broadened by nanoparticule finite dimensions. Analysis of peak widths shows that the Ni nanocrystallite size ranges from 4.7 to 19.2 nm. The XMCD signals for a sample series, preparated on relatively low-temperature substrates during the co-evaporation, can be interpreted as having distinct contributions due to both bulk and surface Ni atoms. These two kind of atoms are antiferromagnetic coupled. The Ni atoms which are at the interface with the fullerite matrix show an enhanced orbital magnetic moment, while the orbital magnetic moment of Ni atoms in the bulk has very low values, as it can be expected for a crystalline field with a cubic symmetry.

(Received September 3, 2004; accepted after revision November 29, 2004)

Keywords: Nanostructured Ni/C₆₀, X-ray diffraction, X-ray magnetic circular dichroism

1. Introduction

Magnetism of low-dimensional systems represents a new and deeply subject over the last years. Amongst scientific aspects which are today of highest attention to the scientific community, one may consider: (i) enhanced magnetic moments in two-dimensional (2D, surfaces and interfaces), one-dimensional (1D, metalic wires) or zero-dimensional (0D, nanoparticles) systems [1]; (ii) enhanced orbital magnetic moments up to three times their "bulk" value for low-dimensional systems, especially for surfaces and interfaces [2]; (iii) superparamagnetic properties of metal nanoparticles, deposited on several substrates [3], with applications in fabrication of magnetic field sensors; (iv) special magnetic anisotropy properties for the magnetic nanoparticles, resulting from their specific (columnar) shape [4]; for the perpendicular magnetic anisotropy, this properties can lead to obtaining of strongly enhanced storage densities [5]; (v) the temperature dependency of magnetization, and especially at low temperatures, where low-dimensionality manifests through low dimensional magnon dispersion law in the temperature exponent [6].

Some of the above specified properties can also be found for transition metal nanoparticles, embedded in fullerite (C_{60}). In a recent study about systems produced by co-evaporation of metal and fullerene [7], the existence of several synthesis regimes of nanoparticles was shown, depending on the metal/fullerene relative concentration: (i) for small concentrations of metal (lower than 10%), metal nanoparticles with dimensions of approximately 3 nm are formed, embedded in the facecentered cubic fullerite matrix; (ii) for larger concentrations of metal (30-70 %), a "self-assembled columnar growth" of metal nanoparticles has been observed (Fig. 1). Each C_{60} molecule attaches to the fullerenes located around the metallic columns, while metal atoms attach to the metallic columns which have a diameter of the order of 7 nm. These columns exhibit some remarkable magnetic

^{*} Corresponding author: teodorescu@infim.ro

anisotropy properties, with easy magnetization axis oriented along the columns, i.e. perpendicular to the thin film surface. Simple calculations show that, in this manner, the dimension of one information bit can be as low as 10 nm \times 10 nm, which means an information storage density on magnetic support with up to 1000 times that of current values in last generation hard-disks. Another very important aspect resulting from this new synthesis technique is the role of the fullerite matrix in protecting metal nanoparticles against oxidation, hence preserving their magnetic properties.



Fig. 1. The "self-assembly growth" mechanism of metallic columns surounded by fullerene molecules. The evaporated metal atoms attach to the metallic columns, while fullerene molecules (C_{60}) attach to the fullerene edge, favouring the synthesis of metallic columns, through its surfactant role.

The aim of the present study is focused on investigation of the magnetic properties of Ni nanoparticles, embedded in fullerite matrix, connected to the physical parameters of the deposition process (presure, source temperature, and metal/fullerene concentration ratio), correlated with structural determinations by X-ray diffraction. For the investigation of magnetic properties, the recent technique of X-ray magnetic circular dichroism (XMCD) was used. In addition to usual techniques for magnetic properties investigation, this technique allows:

- a quantitative evaluation of atomic magnetic moments for each species of atom carrying magnetic moment in the sample;

- a quantitative evaluation of orbital and spin magnetic moments in the sample;

- as we will prove in this paper, a quantitative evaluation of both orbital and spin atomic magnetic moments for atoms in different chemical states (different oxidation states, surface or bulk atoms, etc.).

This new analysis technique and the most important stages of the experimental data analysis, are described in Section 2 of this paper. The XMCD spectra obtained for Ni nanoparticles in fullerite matrix, correlated with structural determinations by X-ray diffraction, and also considerations about the XMCD satelite intensity, related to the $3d^8$ configuration, are described in Section 3. The application of XMCD sum rules for determination of the magnetic moments of Ni nanoparticles is described in Section 4, with emphasis on the effect of co-existence of two distinct components in the X-ray absorption spectra for Ni, due to the bulk and surface Ni atoms. Section 5 presents more comments on a completely new result of this study, i.e. the antiferromagnetic coupling between bulk and interface Ni atoms, and Section 6 presents the conclusions.

2. The X-ray magnetic circular dichroism: theoretical aspects, sum rules, separation of orbital and spin magnetic moments

The X-ray magnetic dichroism was first observed by Schütz and coworkers in 1987 [8]. This new kind of measurements consist in recording X-ray absorption spectra (XAS) near absorption edges which imply transitions towards final one-electron states responsible for the total magnetic moment of the absorbing atoms (3*d* orbitals for transition metals, 4*f* orbitals for rare earths, etc.), by varying the polarisation state of the incident radiation. Thus, two techniques emerged:

1) The X-ray magnetic circular dichroism (XMCD), consisting in recording XAS when the incident radiation is left- or right-hand polarized. This technique allows the determination of the total atomic magnetic momentum, but also, additionally, of the separate spin and orbital magnetic moment contribution for each species of absorbing atoms.

2) The X-ray magnetic linear dichroism (XMLD), consisting in recording the XAS in linearly polarized incident radiation, parallel or perpendicular to the magnetic (ferromagnetic or antiferromagnetic) ordering direction. This effect is, in fact, a second order effect in perturbation theory, in a series development over the atomic magnetic moment (M), thus it is proportional to M^2 . This implies that the XMLD, although generally with an order of magnitude lower than the circular dichroism, is one of the rare techniques which can be used for probing antiferromagnetic materials. Also, the recently derived sum rules for XMLD [11] allow the direct determination of the atomic magnetic anisotropy energy, for both ferromagnetic and antiferromagnetic materials [12].

X-ray dichroism methods could be fully developed only by using synchrotron radiation facilities, the only source of continuous radiation source ranging from microwave to hard X-rays; especially with the construction of the so-called "third generation synchrotron radiation facilities", where the polarization state of the radiation can be controlled by using various methods (adjusting of wigglers or undulators, use of X-ray optics, etc.)

In the following, we will discuss in more detail the sum rules and the procedure of exploitation of XMCD data. These principles were applied in a software package fully developped by the authors. This software package is highly versatile, allowing the orbital and spin moment extraction in a few seconds once the X-ray absorption spectra are recorded. This allowed an almost simultaneous analysis of the experimental spectra, which is highly important when working at synchrotron radiation facilities.

The XMCD signal is defined as the difference between X-ray absorption spectra (as a function of the energy of incident radiation, E) obtained when the circular polarization vector of the incident radiation is parallel (a situation denoted by "+") and antiparallel ("-") with the orientation of atomic magnetic moments in the sample. Thus:

$$\mu(E) = \sigma_+(E) - \sigma_-(E), \qquad (1)$$

The sum rules are applied as following: from the "isotropic" absorption spectrum, i.e. from the average $\frac{1}{2}[\sigma_+(E) + \sigma_-(E)]$, one has to separate the component representing the dipole allowed transition with participation of the magnetic orbitals (3*d* or 4*f*) as final absorption one-electron states, i.e. transitions such as $2p_{1/2, 3/2} \rightarrow 3d$, $3d_{3/2, 5/2} \rightarrow 4f$, etc. This is usually done by subtracting from the total spectrum of transitions on one-electron orbitals not participating in atomic magnetic momenta, by simulating globally these transitions as unstructured absorption edges. In practice, in order to take into account the finite core hole lifetime of the excited state [13], this unstructured absorption is simulated by an arctangent function:

$$A\sigma_0(E;E_0) = \frac{A}{\pi} \left[\tan^{-1} \left(\frac{E - E_0}{\Gamma} \right) + \frac{\pi}{2} \right], \tag{2}$$

where the fitting parameter A represents the amplitude of the unstructured absorption. In fact, the absorption spectra are represented by spin-orbit splitted doublets (corresponding to $2p_{1/2} \rightarrow 3d$ to $2p_{3/2} \rightarrow 3d$ transitions for $L_{2,3}$ edges or to $3d_{3/2} \rightarrow 4f$ to $3d_{5/2} \rightarrow 4f$ transitions for $M_{4,5}$ edges).

Therefore, one has to subtract from the total isotropic absorption spectrum the sum of two unstructured arctangent absorptions, i.e., for instance, for $L_{2,3}$ edges, of a function $\sigma_0(E, E_{L3}) + \sigma_0(E, E_{L2})$, where the corresponding amplitudes are weighed by the branching ratio of the corresponding atomic transitions (2 for the ratio of amplitudes of L_3 / L_2 edges, and 3/2 for the ratio of M_5 / M_4). This procedure is schematized in Fig. 2.

For $L_{2,3}$ edges the unstructured absorption will be given by:

$$\sigma_{unstr.}(E) = \frac{A}{3} \left(2\sigma_0(E; E_{L3}) + \sigma_0(E; E_{L2}) \right) + B + CE , \qquad (3)$$

where: *A* is the total amplitude of unstructured absorption cross section, *B* is the continuous absorption background, and *C* is the a linear absorption variation parameter as a function of the photon energy, introduced in order to take into account possible non-linearities of the detection system. *A*, *B*, and *C* are fitting parameters for the double arctangent unstructured absorption function. In the fitting procedure, the following parameters are held constant: the energies of the two absorption edges $E_{L2,3}$, and the intrinsic core hole width values computed, tabulated and experimentally verified [13,14].

Hence, one computes the isotropic absorption spectrum corrected for the unstructured absorption:

$$\widetilde{\sigma}(E) = \frac{1}{2} \left(\sigma_+(E) + \sigma_-(E) \right) - \sigma_{unstr.}(E) , \qquad (4)$$

This corrected isotropic spectrum will be used, in the following, for the application of XMCD sum rules.

First (orbital moment) XMCD sum rule [9]:

The integral of the XMCD spectrum over a spin-orbit split doublet $(L_{2,3} \text{ or } M_{4,5})$ is proportional to the orbital magnetic moment of an absorbing atom:

$$\langle L_z \rangle \frac{c(c+1) - l(l+1) - 2}{2l(l+1)(4l+2-n)} = \frac{\int \mu(E)dE}{3\int \widetilde{\sigma}(E)dE} , \qquad (5)$$

Here *c* represents the angular momentum of the initial core state for the transition (c = 1 for *p* states, c = 2 for *d* states, etc.), *l* represents the angular momentum of the final one-electron state (l = 2 for *d* states, l = 3 for *f* states, etc.), *n* represents the number of electrons occupying the final state (the value $n_h = 4l + 2 - n$ denotes in the following as the "number of holes" on the corresponding valence shell). $j = c \pm \frac{1}{2}$ are the values of the total (orbital and spin) moment on the core shell (e.g. for L_3 edges j = 3/2, and for L_2 edges j = 1/2). The integrals are performed over the whole energy range corresponding to the spin-orbit split doublet of absorption edges $j = c \pm \frac{1}{2}$.

For $L_{2,3}$ edges of transition metals (transitions $2p \rightarrow 3d$), this implies:

$$\frac{\langle L_z \rangle}{n_h} = -\frac{2q}{3rP} \quad , \tag{6}$$

where the significance of parameters q and r is schematized in Fig. 2. The parameter q represents the value of the integrated dichroism spectrum over both $L_3 + L_2$ edges, whereas r is the integral over both absorption edges of the isotropic corrected spectrum $\tilde{\sigma}(E)$. P represents the circular polarization rate of the incident radiation, P = 0.75 in the present study.

Second (spin momentum) sum rule [9]:

The weighed difference between integrals of the XMCD spectrum over each of the two absorption edges corresponding to a spin-orbit split doublet is proportional to the average value of the spin magnetic moment plus a contribution due to the dipole magnetic operator:

$$\frac{l(l+1)-c(c+1)-2}{c(4l+2-n)}\langle S_z\rangle + \frac{l(l+1)[l(l+1)+2c(c+1)+4]-3(c-1)^2(c+2)^2}{2cl(l+1)(4l+2-n)}\langle T_z\rangle = \frac{\int\limits_{c+1/2} \mu(E)dE - \frac{c+1}{c} \int\limits_{c-1/2} \mu(E)dE}{\int\limits_{c-1/2} \widetilde{\sigma}(E)dE},$$
 (7)

In most applications, for local cubic symmetry the average value of the magnetic dipole operator $\langle T_z \rangle$ is considered zero [15] ($\mathbf{T} = \sum_i \mathbf{s}_i - 3\mathbf{r}_i (\mathbf{r}_i \cdot \mathbf{s}_i)/r_i^2$). In fact, a nonzero value of $\langle T_z \rangle$ can be obtained only by considering the spin-orbit splitting on the valence shell. Also, of 3*d* transition metals, Ni has the lowest value of $\langle T_z \rangle$ [9].

For $L_{2,3}$ edges of transition metals and within 10% accuracy, the above formula yields:



Fig. 2. (a) X-ray magnetic circular dichroism spectra at the Fe $L_{2,3}$ edges, obtained for an Fe thin film (4 nm) deposited on GaAs, together with the unstructured absorption signals (i.e. the double arctangent fit) used for obtaining the $2p \rightarrow 3d$ absorption $\tilde{\sigma}(E)$. (b) integrals of the $2p \rightarrow 3d$ absorption signal (thick line) and of XMCD spectrum (thin line), used for obtaining parameters p, q and r.

(8)

where the significance of q and r is the same as for the first sum rule. The parameter p is the integral of the XMCD signal only on the L_3 edge, as represented in Fig. 2.

Fig. 2 presents the procedure of XMCD data analysis for $L_{2,3}$ edges: (i) subtraction of the double arctangent unstructured absorption spectrum; (ii) computing the XMCD spectrum and, finally, subtraction of a linear background from it in order to compensate detection non-linearities; (iii) computation of integrals of absorption and dichroism spectra, and extraction of parameters p, q, and r for evaluating of orbital and spin magnetic momenta.

3. XMCD spectra for Ni nanoparticles in C_{60} matrix. General considerations, correlations with X-ray diffraction data. XMCD sattelite structure attributed to the $3d^8$ configuration

Ni/C₆₀ thin films were synthesized by nickel and fullerene co-deposition, using a high vacuum deposition chamber. Nickel was evaporated by using an electron bombardment source (4 kV, 200 mA), and C₆₀ was deposited by sublimation from a Knudsen cell at temperatures of 420-490°C. The deposition rates, of about 1-2 nm per minute, were calibrated by using a quartz thickness monitor. The total Ni content in the fullerite matrix was checked by electron dispersive spectroscopy (EDS) as varying between 0.2 and 75 atomic percent. The pressure during deposition was 2-3 x 10⁻⁵ Torr.



Fig. 3. X-ray diffraction spectra ($\theta - 2\theta$ scans) obtained for Ni nanoparticles embedded in C₆₀ matrix. These spectra show the combined contribution of Ni nanoparticles of crystallised Ni nanoparticles and of the fullerite fcc matrix. Insert: simulation of a region of the diffraction spectrum of sample P4 [Ni(220), Ni(311), and Ni(222) diffraction maxima] using Voigt profiles (convolutions between lorentzian and gaussian curves), to deduce the average crystallite size and the lattice strain.

X-ray diffraction spectra were measured on DW22 beamline of the DCI storage ring at the LURE synchrotron radiation facility in Orsay, France. Fig. 3 presents $\theta - 2\theta$ scans of several samples with the fixed incident radiation wavelength $\lambda = 1.0736$ Å. Sample P1, with the highest Ni content (75 *at.* %), does not show any contribution of the fullerite *fcc* matrix, while the other samples show broadened (111), (200), and (220) diffraction maxima of *fcc* Ni, together with fullerite characteristic diffraction maxima on (111), (220), (311), (420), (422), and (511) planes in the angular range $2\theta = 7 - 25$ deg. This result is different from the one recently reported on Ni/C₆₀ samples obtained by magnetron sputtering [16], where the C₆₀ deposition resulted in the formation of a completely amorphous carbon matrix. The Ni diffraction maxima were simulated using Voigt profiles (convolutions of lorentzian and gaussian lines [17]), for the separation of the lorentzian contribution to the line broadening, from the gaussian broadening, which is due to the monochromator bandwidth and to the lattice strain. According to the limited coherence length model, the lorentzian broadening, β (in radians), is connected to the nanoparticle average size *D* by Scherrer's formula:

$$D \approx \frac{0.9\lambda}{\beta \cos \theta} , \qquad (9)$$

The values obtained for the average crystallite dimension are given in Table 1. It should be noted that this value ranges from 19.2 nm (for sample P1) to 4.7 nm (samples P4 and P6). In the following, these data will be correlated with the measured magnetic properties of Ni nanoparticles in C_{60} matrices.

The X-ray magnetic circular dichroism of Ni/C₆₀ thin films was measured using an alternating magnetic field of \pm 0.6 T in the "flipper" chamber installed on the 1.1 beamline (75% of circular polarization) at the SRS storage ring in Daresbury, UK. Fig. 4 shows the X-ray absorption (XAS) spectra for P1 and P6 samples, obtained with the applied magnetic field parallel, respectively antiparallel, with the helicity of the circular polarized X-rays, and also the difference between the two XAS spectra, i.e. the XMCD signal.

Sample P1 shows an XMCD signal very close to that of the metallic Ni, negative at the L_3 edge and positive at the L_2 edge. The origin of the satellite **A** occuring at 3.3 eV higher photon energy with respect to the principal absorption maximum at L_3 is attributed to the core-valence exchange-field split state $2p^53d^9$ [19,20]. Anderson ionized impurity calculations showed that the relative intensity (with respect to the main XMCD structure at the L_3 edge) of this satellite corresponds to a ground state with mixed configuration of 18% d^8 , 49% d^9 , and 33% d^{10} . This relative amplitude, in Fig. 1a, is about 12%, a value which has to be compared with the value of 9.5% in bulk Ni [21], 10% for a 20 monolayers (ML) Ni film grown on Co/Cu(100) [22], whereas this relative amplitude is 14% for 0.1 ML Ni/Cu(100) [23]. Scanning tunneling microscopy (STM) images for 0.1 ML Ni/Cu(100) have shown [23] the presence of a considerable amount of Ni clusters of approximately 3 nm diameter. Therefore, an increased value of the intensity of the satellite **A** can be attributed to the presence of reduced dimension of Ni nanoparticles, with an increased ratio between the surface and bulk atoms. Owing to the charge transfer from the Ni surface atoms to the neighbouring matrix, these atoms will have an increased $3d^8$ contribution in the overall electronic configuration of the valence shell.

4. Application of XMCD sum rules. Effect of the co-existence of two distinct components in the X-ray absorption spectra of Ni and correlations with structural determinations by X-ray diffraction

The XMCD spectra are represented in Fig. 5. The samples P6, P8 and P9 which, altogether, will be denoted hereafter as "Series 2", present completely different dichroism spectra with respect to the "normal" XMCD, discussed previously, for instance, for sample P1. The L_3 XMCD spectrum as function of photon energy is first negative, then positive, as if it were a sum of a positive and a negative XMCD signal, shifted in energy. The L_2 XMCD signal does not present this aspect; it is

positive over the whole L_2 energy range. The L_3 XMCD signal cannot be explained by a single contribution, but can be attributed to the presence of at least two components of the XMCD signal, resulting from different positions occupied by the Ni atoms, however, signature in XAS and XMCD spectra appear at different photon energy, as a relative "chemical shift". The simplest interpretation of the presence of the two distinct Ni species is that one contribution is due to Ni atoms located at the surface of nanoparticles, whereas the second is due to bulk Ni atoms.



Fig. 4. X-ray absorption spectra obtained with 75 % circularly-polarized x-rays at the Ni $L_{2,3}$ edges, with the sample magnetisation parallel (dashed line), respectively antiparallel (full line) with the circular polarization vector of the X-rays. Separately, the XMCD spectrum (multiplied by 5) is shown, as well as the unstructured absorption which will be subtracted from the total spectra in order to determine the r parameter by integrating the $2p \rightarrow 3d$ absorption. (a) represents the spectra obtained for sample P1, (b) for sample P6. The amplitude of the satellite A is extensively discussed in text.

The XMCD sum rules, as described in Section 2, were used to derive the values of orbital and spin magnetic moments. Following the procedure described above, the first step was the subtraction of the "unstructured absorption" (see Figs. 2 and 3) for computing the $2p \rightarrow 3d$ XAS spectra. After that, the XAS spectra in absence of dichroism $\tilde{\sigma}(E)$ and the XMCD spectra $\mu(E)$ were integrated for calculating the values for p, q and r parameters. The orbital and spin magnetic moments are obtained from eqs. (6) and (8). We neglected the contribution of the dipole magnetic operator [15]. The polarisation degree P = 0.75 of the incident X-rays was experimentally obtained. The number of Ni 3d holes used in (6) and (8) was the theoretically computed value of $n_h = 1.45$ [20], a value confirmed in several XMCD studies at the Ni $L_{2,3}$ edges. The results of these computations are also listed in Table 1. In the same table, we have summarized the substrate temperature during the sample preparation.

5. Antiferromagnetic coupling between surface and bulk Ni atoms. Increased orbital magnetic moments for Ni atoms localized at the nanoparticle surface

The individual spin and orbital magnetic moments for the two kind of atoms whose XAS spectra are chemically shifted are obtained on the assumption that the number of 3d holes and the $2p \rightarrow 3d$ absorption cross section have similar values for Ni bulk and surface atoms. It should be noted here that the chemical shift between the two kind of atoms is about 0.86 - 0.98 eV, which represents a charge transfer of about 0.3 elementary charges, if one compares the above chemical shift with chemical shifts reported for nickel in different ionization states in the literature [24]. However, one

cannot precisely state about the orbital character (predominantly *s* or *d*) of the charge which is transferred outside the Ni nanoparticle. Therefore, in the following we will use the simplifying hypothesis that the 3*d* occupancy is the same for Ni bulk and surface atoms. On the other hand, the atomic absorption cross section $2p \rightarrow 3d$ increases when the absorbing atom is in a relatively positive ionization state, because the 3*d* wavefunction collapsing towards the nucleus leads to a more important superposition with the one-electron initial core state, 2p. Thus, the *r* parameter should increase in this case and this implies an underestimation of the orbital and spin magnetic moments for surface atoms. These two effects (increase of n_h , discussed previously, and increase of the *r* parameter) act in opposite senses. Therefore, it is a reasonable approximation to state that these two parameters are the same for bulk and surface atoms.

In the presence of two kind of atoms, the value measured for orbital (m_l) and spin (m_s) moments will be given by a weighed average value as follows:

$$m_{l(s)} = m_{l(s),surface} \frac{N_{surface}}{N} + m_{l(s),bulk} \left(1 - \frac{N_{surface}}{N} \right), \tag{10}$$

where $N = N_{surface} + N_{bulk}$. The interface contribution will be estimated from XRD data: by approximating a spherical shape of nanoparticles, as derived by previous investigations using electron microscopy, $N_{surface} / N = 6d / D$, where D is the average nanoparticle size, listed in Table 1, and d is the *fcc* Ni nearest-neighbour distance, d = 0.250 nm.

The experimental XMCD data were fited by (10), and the results are plotted in Fig. 5 (b) and (c). The resulting values for the magnetic moments are $m_{s, surface} = -0.567 \ \mu_B, m_{l, surface} = -0.045 \ \mu_B, m_{s, bulk} = 0.303 \ \mu_B$, and $m_{l, bulk} = 0.003 \ \mu_B$ (errors: $\pm 20\%$). In conclusion, as shown for the "Series 2" of samples (P6, P8, and P9), the orbital and spin magnetic moments for the bulk and surface atoms are antiparallel, which implies an *antiferromagnetic coupling* between the two kind of atoms. The bulk Ni atoms show also a drastic decrease of the orbital magnetic moment, as compared with the bulk *fcc* Ni, where this moment is about 0.06 μ_B [20]. In contrast, the orbital magnetic moment for the interface atoms is highly increased with respect to the bulk atoms, a result similar with that reported recently for iron nanoparticles in pyrolitic graphite [25] (0.23 μ_B , compared with 0.08 μ_B for bulk *bcc* Fe). Also, previous studies have shown increased orbital magnetic moments for the surface atoms in Ni(111) [26] and for Co nanoparticles [27]. Thus, the present study is in line with practically all studies which reported an increased orbital magnetism for surface and interface atoms. This is mainly due to the breaking of the cubic symmetry at interface, which is responsible for the orbital momentum quenching [28]. The completely new feature observed in the present work is the antiferromagnetic coupling between bulk and interface Ni atoms.

An additionnal comment should be made regarding the sample classification according to their magnetic properties in "series 1" (samples P1, P4, P5 and P7) and "series 2" (samples P6, P8, and P9). As can be seen from Fig. 5, samples belonging to "series 1" shows "usual" XMCD spectra, which are negative at the L3 edge and positive at the L_2 edge, whereas for samples from "series 2" the simultaneous presence of two contributions of opposite signs is more evident. The main difference between the two series of samples is the substrate temperature during deposition. It seems that for higher substrate temperatures (over 130°C) the antiferromagnetic ordering between substrate and interface atoms is less evident than for samples obtained on lower temperature substrates. Most probably, at higher temperatures interface Ni and surrounding carbon form an alloy, resulting in a magnetically inert interface layer, while at lower temperatures the antiferromagnetic ordering is preserved as if this behaviour is an intrinsic property of free Ni nanoparticles.

6. Conclusions

Summarising, nanostructured Ni clusters in C_{60} matrices produced by metal and fullerene co-evaporation in vacuum were for the first time studied by the novel method of X-ray magnetic circular dichroism, correlated with nanoparticle structural measurements by X-ray diffraction. We have shown Ni nano-particle formation dispersed in a relatively ordered *fcc* C_{60} matrix.



Fig. 5. XMCD spectra obtained for Ni/C₆₀. (a) represent XMCD spectra for all samples which have shown a measurable XMCD signal. (b) and (c) represent fitting of the orbital and spin moments dependence with a model which takes into account the presence of two kind of Ni atoms, for the nanoparticle surface (or interface with the C₆₀ matrix), and for the atoms located inside the nanoparticles, as explained in text.

The Ni clusters show the unique feature of atiferromagnetic coupling between bulk Ni atoms and surface Ni atoms, which are localized at the interface with the fullerite matrix. Also, the orbital magnetic moment for interface Ni atoms is strongly increased with respect to the bulk Ni atoms. We hope that these results will stimulate theoretical effort in nanoparticle magnetism.

Sample	Substrate	Average diameter D (nm)	N _{surface} /N (%)	XMCD-derived magnetic moments*	
	$T(^{\circ}C)$			$m_l(\mu_B)$	$m_{s}(\mu_{B})$
P1	195 ± 5	19.202 ± 1.341	7.8 ± 0.5	0.014	0.493
P4	140 ± 17	4.709 ± 0.794	31.9 ± 5.4	0.014	0.223
P5	126 ± 2	6.124 ± 1.842	24.5 ± 7.4	0.000	0.038
P7	135 ± 15	10.942 ± 2.867	13.7 ± 3.6	0.000	0.025
P8	105 ± 25	10.730 ± 3.178	14.0 ± 4.1	- 0.025	0.052
P9	112 ± 8	6.113 ± 0.249	24.5 ± 1.0	- 0.027	0.011
P6	129 ± 19	4.727 ± 1.550	31.7 ± 10.4	- 0.029	- 0.004

Table 1. Properties of the different samples measured by XMCD, listed in decreasing order of orbital magnetic moments.

*errors of about ± 20 %.

References

- [1] I. M. L. Billas, A. Châtelain, W. A. de Heer, Science 265, 1682 (1994).
- [2] Y. B. Xu, D. J. Freeland, M. Tselepi, J. A. C. Bland, J. Appl. Phys. 87, 6110 (2000); Y.B. Xu, M. Tselepi, C. M. Guertler, C. A. F. Vaz, G. Wastlbauer, J. A. C. Bland, E. Dudzik, G. van der Laan, J. Appl. Phys. 89, 7156 (2001).
- [3] Y. B. Xu, E. T. M. Kernohan, D. J. Freeland, A. Ercole, M. Tselepi, J. A. C. Bland, Phys. Rev. B 58, 890 (1998).
- [4] V. I. Nikitenko, V. S. Gornakov, L. M. Dedukh, Y. P. Kabanov, A. F. Khapikov, A. J. Shapiro, R. D. Shull, A. Chaiken, R. P. Michel, J. Appl. Phys. 83, 6828 (1998); R. A. Fry, L. H. Bennett, E. Della Torre, R. D. Shull, W. F. Egelhoff Jr., R. F. C. Farrow, C.H. Lee, J. Magn. Magn. Mat. 193, 162 (1999); M. D. Upward, P. Moriarty, P. H. Beton, S. H. Baker, C. Binns, K. H. Edmonds, Appl. Phys. Lett. 70, 2114 (1997).
- [5] N. Grobert, W. K. Hsu, Y. Q. Zhu, J. P. Hare, H. W. Kroto, D. R. M. Walton, M. Terrones, H. Terrones, P. Redlich, M. Rühle, R. Escudero, F. Morales, Appl. Phys. Lett. 75, 3363 (1999).
- [6] M. Tischer, D. Arvanitis, T. Yokoyama, T. Lederer, L. Tröger, K. Baberschke, Surf. Sci. 307-309, 1096 (1994); J. Hunter Dunn, D. Arvanitis, N. Mårtensson, Phys. Rev. B 54, R11157 (1996); F. May, M. Tischer, D. Arvanitis, J. Hunter Dunn, H. Henneken, H. Wende, R. Chauvistré, K. Baberschke, J. de Physique IV C2-389 (1997).
- [7] L. A. Zheng, B. M. Lairson, E. V. Barrera, R. D. Shull, Appl. Phys. Lett. 77, 3242 (2000).
- [8] G. Schütz, W. Wagner, W. Wilhelm, P. Kienle, R. Zeller, R. Frahm, G. Materlik, Phys. Rev. Lett. 58, 737 (1987); C. T. Chen, F. Sette, Y. Ma, S. Modesti, Phys. Rev. B 42, 7262 (1990).
- [9] B. T. Thole, P. Carra, F. Sette, G. van der Laan, Phys. Rev. Lett. 68, 1943 (1992); P. Carra,
 B. T. Thole, M. Altarelli, X. Wang, Phys. Rev. Lett. 70, 694 (1993).
- [10] C. T. Chen, Y. U. Idzerda, H.-J. Lin, N. V. Smith, G. Meigs, E. Chaban, G. H. Ho, E. Pellegrin, F. Sette, Phys. Rev. Lett. 75, 152 (1995).
- [11] G. van der Laan, Phys. Rev. Lett. 82, 640 (1999); ibid., J. Phys. Condens. Matter 13, 11149 (2001).
- [12] S. S. Dhesi, G. van der Laan, E. Dudzik, A. B. Shick, Phys. Rev. Lett. 87, 067201 (2001);
 S. S. Dhesi, G. van der Laan, E. Dudzik, Appl. Phys. Lett. 80, 1613 (2002).
- [13] C. M. Teodorescu, R. Karnatak, J. M. Esteva, A. El Afif, J. Phys. B: At. Mol. Opt. Phys. 26, 4019 (1993).
- [14] M. O. Krause, J. H. Oliver, J. Phys. Chem. Ref. Data 8, 2689 (1979).
- [15] C. M. Teodorescu, F. Chevrier, R. Brochier, V. Ilakovac, O. Heckmann, L. Lechevalier, K. Hricovini, Eur. Phys. J. B 28, 305 (2002).
- [16] Z. Zhao, H. Wang, B. Wang, J. G. Hou, G. L. Liu, X. F. Jin, Phys. Rev. B 65, 235413 (2002).
- [17] C. M. Teodorescu, J. M. Esteva, R. C. Karnatak, A. El Afif, Nucl. Meth. Phys. Res. A 345, 141 (1994).
- [18] R. Popescu, D. Macovei, A. Devenyi, R. Manaila, P. B. Barna, A. Kovacs, J. L. Lábár, Eur. Phys. J. B 13, 737 (2000).
- [19] G. van der Laan, B. T. Thole, J. Phys. Condens. Matter 4, 4181 (1992).
- [20] S. S. Dhesi, H. A. Dürr, G. van der Laan, E. Dudzik, N. B. Brookes, Phys. Rev. B 60, 12852 (1999).
- [21] E. Dudzik, G. van der Laan, S. M. Thompson, Synchrotron Radiation News 13, 18 (2000).
- [22] A. Ney, A. Scherz, P. Poulopoulos, K. Lenz, H. Wende, K. Baberschke, F. Wilhelm, N. B. Brookes, Phys. Rev. B 65, 024411 (2001).
- [23] J. Lindner, P. Poulopoulos, F. Wilhelm, M. Farle, K. Baberschke, Phys. Rev. B 62, 10431 (2000).
- [24] Handbook of x-ray photoelectron spectroscopy (XPS), Perkin-Elmer, 1984.
- [25] K. W. Edmonds, C. Binns, S. H. Baker, S. C. Thornton, C. Norris, J. B. Goedkoop, M. Finazzi, N. B. Brookes, Phys. Rev. B 60, 472 (1999).
- [26] M. A. Hoyland, M. Surman, C. F. J. Flipse, B. T. Thole, Phys. Rev. Lett. 69, 3827 (1992).
- [27] H. A. Dürr, G. van der Laan, J. Vogel, G. Panaccione, N. B. Brookes, E. Dudzik,
 R. McGrath, Phys. Rev. B 58, R11853 (1998); H. A. Dürr, S. S. Dhesi, E. Dudzik, D. Knabben,
 G. van der Laan, J. B. Goedkoop, F. U. Hillebrecht Phys. Rev. B, 59, R701 (1999).
- [28] A. Aharoni, Introduction to the Theory of Ferromagnetism, Oxford University Press, Oxford (1998).