



# Surface anisotropy of iron oxide nanoparticles and slabs from first principles: Influence of coatings and ligands as a test of the Heisenberg model



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## ABSTRACT

We performed *ab initio* computations of the magnetic properties of simple iron oxide clusters and slabs. We considered an iron oxide cluster functionalized by a molecule or glued to a gold cluster of the same size. We also considered a magnetite slab coated by cobalt oxide or a mixture of iron oxide and cobalt oxide. The changes in magnetic behavior were explored using constrained magnetic calculations. A possible value for the surface anisotropy was estimated from the fit of a classical Heisenberg model on *ab initio* results. The value was found to be compatible with estimations obtained by other means, or inferred from experimental results. The addition of a ligand, coating, or of a metallic nanoparticle to the systems degraded the quality of the description by the Heisenberg Hamiltonian. Proposing a change in the anisotropies allowing for the proportion of each transition atom we could get a much better description of the magnetism of series of hybrid cobalt and iron oxide systems.

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## 1. Introduction

Numerous experimental and theoretical studies have been performed in the last decades to provide an understanding of the properties of magnetic nanoparticles, such as superparamagnetism or surface-enhanced anisotropy [1,2].

It has been proven possible to create nanoparticles built with alternating layers of various materials exhibiting different magnetic behaviors, which will influence the magnetic moment structure at the surface or interface [3]. An induced magnetic anisotropy (exchange bias) can appear in such systems, corresponding to a shifted hysteresis loop and a ferrimagnetic alignment of the moments near the center of the nanoparticle as well as a pinning of the magnetic moments on the surface.

It has been demonstrated that surface modification by organic ligands have a strong influence on the magnetic structure of the nanoparticles (as described in the pioneering work of [4]) and also cause spin pinning near the surface [5].

Surface effects alone can change the magnetic structure, as it was demonstrated for instance in the case of cobalt [6], cobalt oxide [7], magnetite powders [8], and maghemite nanoparticles [9]. Those effects have been reviewed in the case of iron oxide in [10].

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From the theoretical point of view, those effects and the related phenomena have been considered mainly from the phenomenological side. Typically, Monte-Carlo calculations on the classical Heisenberg model were performed [11], and results were compared to experimental data obtained on CO-functionalized NiPt clusters, as well as to DFT calculations where magnetic moments were computed in the collinear local density functional approach.

The Monte-Carlo-Metropolis approach was also used in the case of magnetite nanoparticles in [12]. In this work, the authors have demonstrated that the surface anisotropy constant can heavily influence the exchange-bias behavior. But this value remains a parameter and cannot even be precisely inferred from experimental data; only a range of possible values is estimated from the resulting magnetic behavior and the comparison to experiment.

The problem of the *ab initio* computing of the magnetic anisotropy at the surface of a nanoparticle will be the focus of this paper. In literature, this parameter is a phenomenological input in large scale classical calculations based on modified Heisenberg models. In the present work, on the example of a small cluster, namely  $\text{Fe}_{13}\text{O}_8$  we linked various magnetically constrained calculations to a Heisenberg model in order to estimate magnetic properties of the nanoparticle from first principles. We studied the change in magnetic properties due the presence of a ligand (dopamine) or of a nearby gold cluster. We also considered a magnetite surface, with an eventual cobalt oxide layer. We discussed the resulting pertinence of the description by a Heisenberg Hamiltonian. We

then adjusted the same Hamiltonian on an ensemble of results obtained on mixed cobalt oxide and iron oxide clusters.

## 2. Theory/calculation

### 2.1. Structure of the chosen systems

The first objective was to obtain an optimized structure of  $\text{Fe}_{13}\text{O}_8$ , which according to mass spectrometry shows a higher abundance than other iron oxide clusters with different compositions [13]. We chose this system because it is small enough to be easily modelled by repetitive first-principle calculations and yet provide interesting surface effects, and was already structurally studied [18]. We used an *ab initio* ultrasoft pseudopotential scheme with a plane-wave basis as implemented in the Quantum Espresso (QE) suite [15]. The plane wave basis set was defined by an energy cutoff of 30 Ry (408 eV), confirmed to be sufficient by the test of convergence of the total energy. A mixing factor of 0.17 was employed on the densities in between each self-

consistent field iteration. Integration in the first Brillouin zone was performed using  $1 \times 1 \times 1$  points sampling, since the system is an isolated cluster in a large computational cubic box of the size of 30 Å. The GGA density functional from PBE [16] was used with the corresponding pseudopotentials computed by A.dal Corso with the “rrkj3” code [17] and taken from the Quantum ESPRESSO pseudopotential data base. The optimization procedure was conducted without any symmetry. The structural results are close to the one previously reported in the literature [18].

We also considered two cases of infinite surfaces: first, a 001 oriented slab of magnetite with atomic positions taken from [20]. This system provides an interesting approach to magnetic nanoparticles of medical interest. The small surface to volume ratio of those nanoparticles of a diameter close to 10 nm makes possible the study of the grafting of ligands by considering a locally flat surface in order to reduce computational cost [19]. Another interest of such surfaces lies in their catalytic properties.

In a second step, we coated this surface in a close to epitaxial condition with 5 crystallographic units of a 012 surface of cobalt oxide, using periodic boundary conditions, and a vacuum of 12 atomic units on top, generated thanks to the ASE package [21], with the same computational conditions as previously described for the isolated cluster. The atomic positions, represented on Fig. 3, changed by less than 2% in comparison to the input values after optimization, and the cell parameters changed by less than 1%. A potential application of such a system might be found in the pinning of magnetic moments, and hence a change in hysteresis curves, from the coupling to antiferromagnetic materials [26,27].

From discussions with experimental teams [19] developing ferrites made of hybrid oxide nanoparticles we then tried a combined

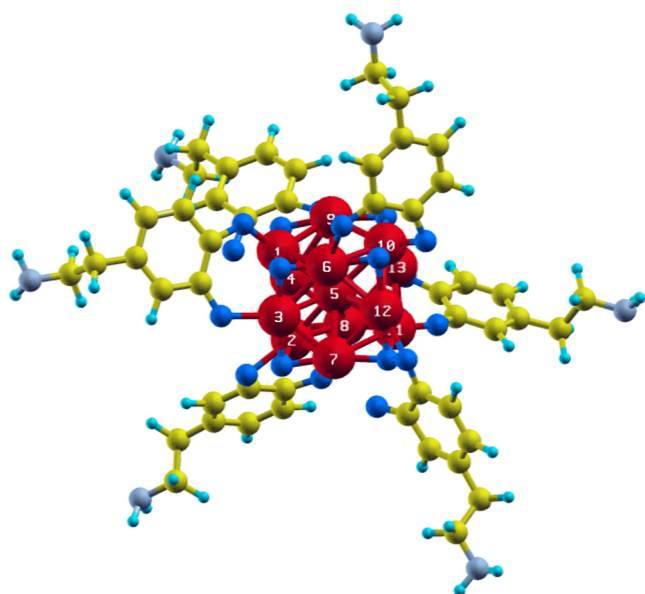


Fig. 1.  $\text{Fe}_{13}\text{O}_8$  cluster with six dopamine molecules.

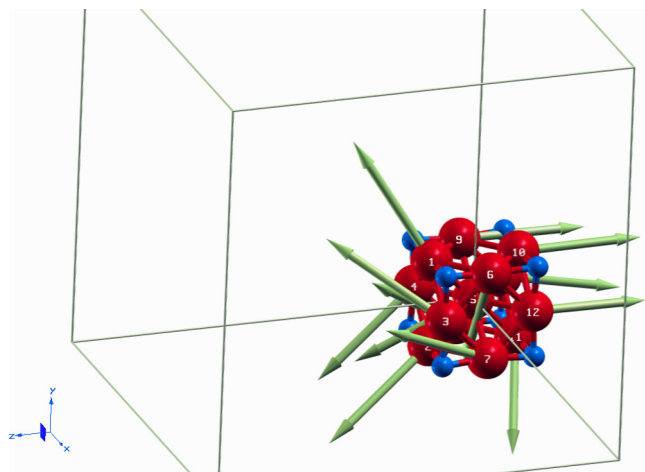


Fig. 2. Result of a typical non-collinear constrained calculation of the iron oxide cluster; here we imposed magnetic moments of 5, 1 and  $45 \mu_B$  on each axis.

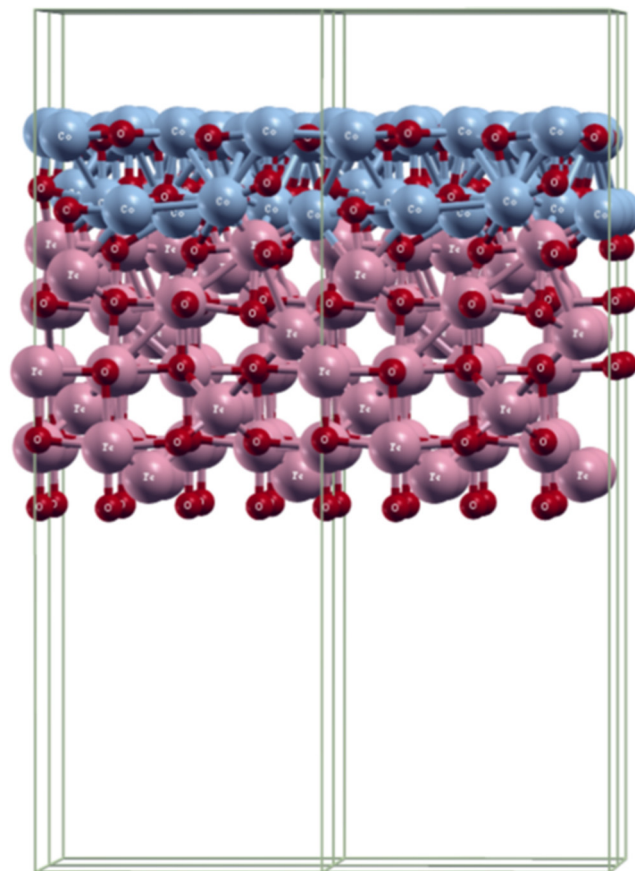
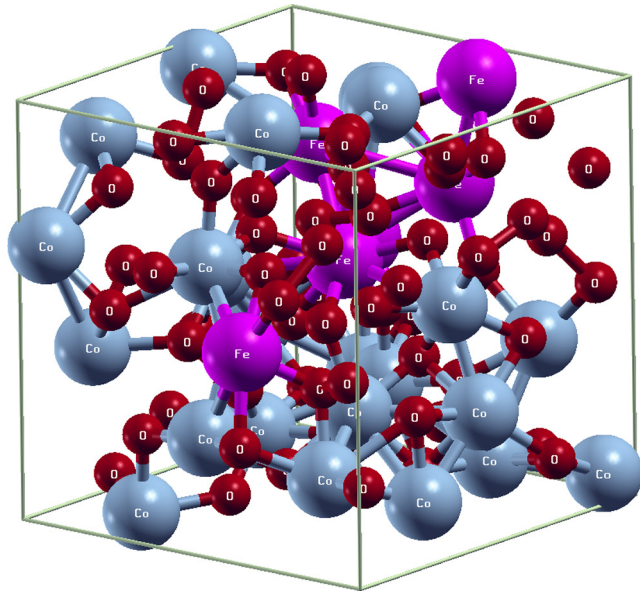


Fig. 3. Atomic positions in a magnetite slab coated with cobalt oxide.



**Fig. 4.** A typical hybrid cobalt oxide and iron oxide configuration after structural optimization.

approach, generating a simple molecular dynamics simulation of a maghemite cluster coated with cobalt oxide, at 1000 K, based on simple, Buckingham-like ionic potentials [26] and extracting several representative clusters of increasing size around a random atom. The atomic positions in these clusters were then optimized using the BFGS procedure within the Quantum Espresso suite with the same conditions discussed above, using periodic boundary conditions with a cubic cell of 32 atomic units. With the largest clusters discussed the systems are close to the bulk, the smaller ones being close to isolated systems. We think that these clusters, even though the crystallography or the stoichiometry deviate from pure allotropic forms, reflect what can be found in a typical molecular dynamics run. One should note however that before optimization of the atomic positions, the magnetic moments around each iron or cobalt atom were found close to zero. A typical cluster is given on Fig. 4.

## 2.2. Ab initio magnetic computation

The change in local magnetic moments was computed using the Quantum Espresso (PWSCF) code. We would like to note that such magnetic moments are sometimes referred to in the literature as “spins”, when they are actually expectations on the values of spin components integrated over a sphere of reasonable but arbitrary radius centered on each atom. For the purpose of this calculations, we used non-collinear density functional theory [22].

We first considered four cases,  $\text{Fe}_{13}\text{O}_8$  alone, with one dopamine molecule added, with six dopamine molecules (Fig. 1), and with a structurally optimized 20 atoms gold cluster in the framework of non-collinear magnetism calculations. We then considered a magnetite surface coated or not by cobalt oxide, and finally, a series of hybrid iron oxide/cobalt oxide clusters trending towards the bulk thanks to periodic boundaries conditions. In the case of magnetic computations we found that a reduction of the cutoff energy by half ensured consistency of the results (a convergence test showed that a cutoff energy of 30 Ry is a sufficient value to compute structural properties), and a 0.17 mixing factor of densities for self-consistency was employed. A smearing factor of 0.02 Ry was used. We performed calculations assuming the systems to be isolated (in

the case of the cluster) with a Martyna-Tuckerman correction [23]. We checked the results by performing calculations with relativistic pseudopotentials and spin-orbit coupling which we generated from the values suggested in the QE distribution for cutoff (1.4 and 1.6 a.u. for Oxygen with 6 active electrons and a projector on empty 3d states), and the ultrasoft pseudopotentials without spin-orbit as described previously. It is to be noted that the *ab initio* package we used (QE) does not compute orbital moments.

We enforced a set of arbitrary magnetization states by imposing total moments different from the ground-state result but close to it within  $2 \mu_B$  in each direction, and extracted the corresponding magnetic field from the converged values, using the constrained magnetic calculation option from the latest version of the Quantum Espresso code, which gives the magnetic field as a function of the distribution of magnetic moments. We used a penalty factor of 0.001 for this purpose in order to speed up convergence under this external constraint. When the magnetic moments from the ground state result are used as a constraint, the magnetic field found is equal to zero.

In the case of the isolated clusters, we found a magnetic structure rather hard to describe in simple terms. In the case of the magnetite surface, we found, as known from the literature, a slightly ferrimagnetic state with a resulting magnetization of zero along the  $x$  and  $y$  axes and of  $0.17 \mu_B$  in the  $z$  direction, orthogonal to the surface, with an absolute magnetization of  $2.48 \mu_B$ . In the case of the magnetite surface coated by cobalt oxide, we found an enhancement of total magnetization, to  $9.89 \mu_B$  in the  $z$  direction, as expected experimentally. In the case of mixed iron oxide/cobalt oxide clusters, the magnetic structure is hard to describe, depending on the chosen configuration and on the stoichiometry. We kept for the calculations structures where the average magnetization was above  $0.75 \mu_B$  per magnetic atom, the cobalt atoms inducing a reduction of total magnetization.

## 2.3. Magnetic model

The previous procedure gives a distribution of local magnetic moments ( $\vec{S}_i$ ), magnetic fields ( $\vec{H}$ ), and total energies ( $H$ ). We collected these values from various QE runs under different constraints, varying the total magnetization in either direction by a few  $\mu_B$ , and fitted the parameters from the Heisenberg Hamiltonian [12], given as:

$$H = -2 \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j - K_V \sum_i \left( S_{x,i}^2 S_{y,i}^2 + S_{y,i}^2 S_{z,i}^2 + S_{x,i}^2 S_{z,i}^2 \right) - K_S \sum_k \left( \vec{S}_k \cdot \vec{e}_k \right)^2 - g \mu_B \vec{H} \cdot \sum_i \vec{S}_i \quad (1)$$

It is to be noted here that the Zeeman energy (last term) is absent from total energy QE results; the magnetic field is output separately.

The first sum involves nearest neighbors interactions between iron atoms. In reference [12] these were computed as from coordination numbers. In the bulk three different coordination numbers appear:  $Z_{AA} = 4$ ,  $Z_{BB} = Z_{BA} = 6$ , and  $Z_{AB} = 12$ . These numbers apply for the core of the nanoparticle. In our case, these numbers were computed from the coordinates of the iron atoms, enforcing a cut-off radius of 3.2 Å such that no atom had more than 12 neighbors. This is to be compared to experimental results obtained on cobalt ferrites for instance [14] where similar values are found (at room temperature compared to the present, zero temperature study), with a maximum interatomic distance of 3.56 Å to ensure a coordination of 12.



The second term in the Hamiltonian is the core cubic magneto-crystalline anisotropy and reference [12] chose a value of  $K_V = 0.002$  meV/spin.

The third term accounts for the single-ion site surface anisotropy where the unitary vector reads

$$\vec{e}_k = \frac{\sum_j \vec{P}_k - \vec{P}_j}{|\sum_j \vec{P}_k - \vec{P}_j|} \quad (2)$$

with  $\vec{P}_i$  the position vector of each iron atom on the surface and the sum runs over iron neighbors of  $j$ .

In reference [12] the exchange parameters were set at a value of  $J_{AA} = -0.11$  meV,  $J_{BB} = +0.63$  meV, and  $J_{AB} = -2.92$  meV corresponding to a mix of ferromagnetic and anti-ferromagnetic interactions. Those values were taken from [24] where they were fitted on *ab initio* results using a method similar in principle to the one we presently discussed: bulk spin waves were fitted to non-collinear spin calculations.

#### 2.4. Fitting procedure

The results of the *ab initio* calculations (energies) were fitted using the Monte-Carlo Metropolis result method, based on random configurations of the parameters.

We used a basic, proven quasi-random recurrence generator [25] and a Metropolis algorithm where we accept configuration changes (in our case, a change of the Heisenberg parameters) ( $q'_i = q_i + \Delta q_i$ ) corresponding to a  $\Delta E = E'(q'_i) - E(q_i)$  change in the virtual energy of the system. The virtual energy  $E$  is here a penalty function representing the distance in between the set of energies found with *ab initio* calculations and these found with the Heisenberg model applied to the distribution of moments. The change is accepted if a random number  $y$  uniformly drawn in between 0 and 1 is lower than  $P(\Delta E, T)$ .

To fit the *ab initio* results using the Metropolis simulated annealing method we choose the following parameters: a reference energy  $H_0$  (fit parameter), the set of  $J_{<ij>}$  (enforcing  $J_{<ij>} = J_{<ji>}$ ),  $K_V$ ,  $K_S$  and  $g$ . We first used a small set of  $J_{<ij>}$  corresponding to a small cutoff in neighborhood search, then increased the number of neighbors to increase the quality of the fit. In order for the results to keep a physical meaning we kept the total number of fitted parameters (maximum of 40) well under the number  $N$  of samples used to define the virtual energy or penalty function from the energies in Rydbergs:

$$E = \frac{1}{N} \sum_i^N |H_{\text{abinitio}} - H_{\text{Heisenberg}}|$$

In the case of the isolated cluster, since the set of  $J_{<ij>}$  is not too large, we allowed those to take any value, but in the case of the surfaces, the large number of  $J_{<ij>}$  gave an excellent fit anytime, whatever the conditions, and the distribution of values obtained was hard to read. Therefore, in this latter case, we used the same model already used in [26], namely two parameters for each kind of super-exchange (iron-iron, iron-cobalt or cobalt-cobalt) related to the super-exchange angle  $\theta$  in between atoms separated by an oxygen atom, using the relation

$$J_\theta = J_{180^\circ} \cos^2 \theta + J_{90^\circ} \sin^2 \theta \quad (3)$$

which can be written in the form

$$J_\theta = J_{90^\circ} + (J_{180^\circ} - J_{90^\circ}) \cos^2 \theta \quad (4)$$

where  $J_{90^\circ}$  and  $J_{180^\circ}$  are the coupling constant corresponding to the super-exchange angle of  $90^\circ$  and  $180^\circ$ , respectively. Those two

parameters per couple of atoms (therefore six in total) are the only ones fitted in the model with the volume and surface anisotropies.

In the case of the isolated cluster we also modified the Heisenberg Hamiltonian in the model to allow for a local change in surface anisotropy ending up with:

$$\begin{aligned} H = H_0 - 2 \sum_{<ij>} \vec{J}_{<ij>} \cdot \vec{S}_i \cdot \vec{S}_j \\ - K_V \sum_i (S_{x,i}^2 S_{y,i}^2 + S_{y,i}^2 S_{z,i}^2 + S_{x,i}^2 S_{z,i}^2) \\ - \sum_k K_{Sk} (\vec{S}_k \cdot \vec{e}_k)^2 - g \mu_B \vec{H} \cdot \sum_i \vec{S}_i \end{aligned} \quad (5)$$

We also had to chose several parameters of the simulated annealing procedure such as the fictitious temperature, the annealing law, and the dependence of random changes to the temperature.

All the software used is archived on

[http://perso.univ-lemans.fr/fcalvay/surf\\_anis\\_code](http://perso.univ-lemans.fr/fcalvay/surf_anis_code)

### 3. Results and discussion

#### 3.1. Iron oxide clusters

We generated sets of  $N = 101$  configurations randomly drawn from *ab initio* results corresponding to a total enforced magnetization running from  $l$  to  $5 \mu_B$  along the  $x$  axis, 1–5 along the  $y$  axis, and 37 to  $41 \mu_B$  along the  $z$  axis.

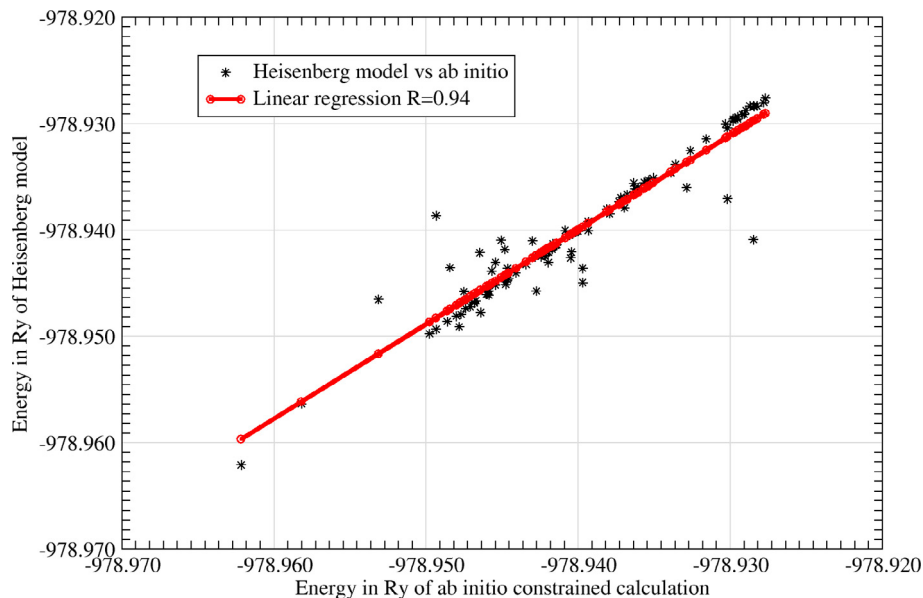
The best result (penalty function as defined above less than  $10^{-4}$  Ry) was, as could be expected from the increased number of degrees of freedom in the model, found using the largest number of fitting parameters (full set of  $J_{<ij>}$  and set of surface anisotropy constants  $K_{Sk}$ ). A typical fit of *ab initio* values versus Heisenberg model is given on Fig. 5; in this case it can be seen that the Heisenberg model seems to model correctly the *ab initio* results. A further confirmation is found in the fact that the  $g$  factor is obtained with a value lower than  $10^{-2}$  confirming that the absence of Zeeman energy in the QE code results is found by the fitting procedure.

A histogram of the obtained parameters for the  $J_{<ij>}$  is illustrated on Fig. 7. It can be seen that those values are close to the ones of reference [24], with an alternation of ferromagnetic and anti-ferromagnetic couplings.

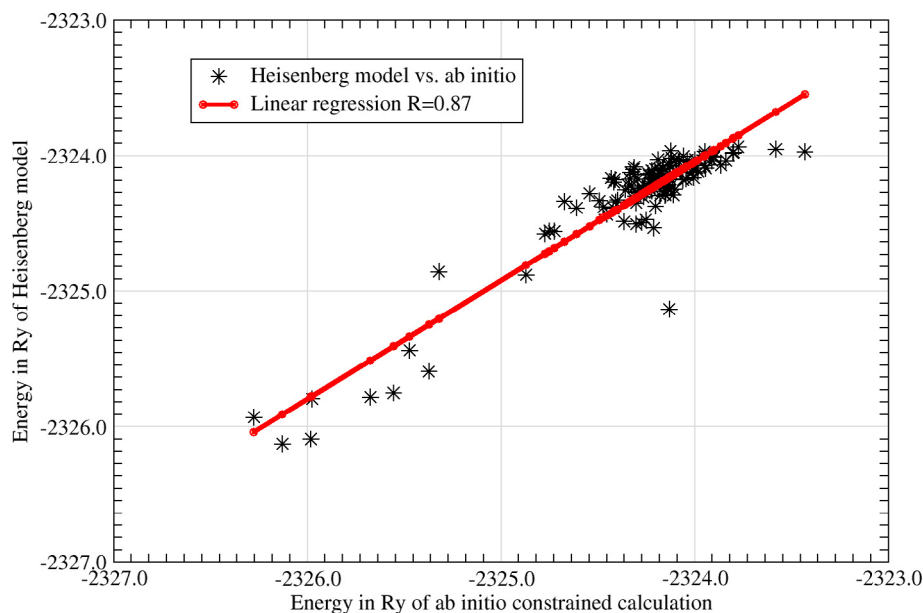
The volume anisotropy was found to have a value of  $-2 \times 10^{-5}$  a.u, coherent with the one used in [12]. The values for the local surface anisotropy constants are given in Table 1. It can be seen that the best fit corresponds to an alternation of positive and negative values for those constants. This fact raises the question of the validity of the Hamiltonian used in [12] in which a constant surface anisotropy was used.

Indeed, we found that the model does not adjust as well when we use a constant surface anisotropy. The best penalty was found at a value of  $1.13 \times 10^{-3}$  Ry. This corresponds to a value of the surface anisotropy of  $1.753$  a.u and a volume anisotropy of  $6.31 \times 10^{-5}$  a.u. The latter value is now positive, but the authors of [12] found that the  $K_S/K_V$  ratio is the more important parameter to predict the magnetic structure of a nanoparticle of intermediate size. Here, the value of  $27780$  we find for this ratio hints at a hedgehog type magnetic structure (Fig. 2). It might be that the large surface contribution of such a small system as the one we study is responsible for this fact, but at least the value we find is not a free, almost unknown parameter as in the literature. Physically, such a result would correspond to jumps during magnetization reversal, and exchange bias properties. Such results have been experimentally observed and are also reviewed in [12].

When we tried the same method with full spin-orbit coupling and relativistic pseudopotentials, the increased disorder in the



**Fig. 5.** Results of the total energy *ab initio* calculations fitted using the Monte-Carlo Metropolis (without spin-orbit) in the case of the isolated  $\text{Fe}_{13}\text{O}_8$  cluster.



**Fig. 6.** Results of the total energy *ab initio* calculations fitted using the Monte-Carlo Metropolis in the case of the magnetite surface.

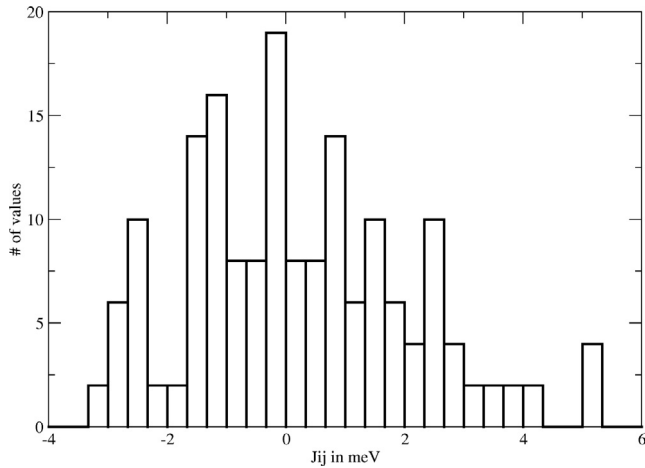
magnetic moments resulted in a penalty function of  $2 \times 10^{-3}$  Ry, with essentially similar results for the fitting parameters.

### 3.2. Iron oxide clusters and dopamine

Linking to previous work [19] on the coating of magnetic nanoparticles by various ligands in order to make them more biocompatible or to link to antibodies in order to better target tumors, we then added a dopamine molecule next to the cluster from the previous section and, after optimizing the atomic positions, tried the same fitting procedure with a Heisenberg model. It turned out that we could not achieve a fit with a penalty function better than  $5 \times 10^{-3}$  Ry, which more or less corresponds to the distribution of energies in the *ab initio* results, and unrealistic coupling

constants as well as a strongly unstable distribution of surface anisotropy constants. We concluded that a Heisenberg model might be too simple to describe such a system, where electrons donated by the dopamine molecule can lead to some itinerant magnetism, or at least to some symmetry breaking. The accuracy of *ab initio* results could also maybe be improved to the expense of computational time, but since the fitting procedure works in isolated cases the origin of the lack of fit seems to come more from the model than from the quality of the results on which it is fitted.

In order to address the question of the symmetry breaking, we added 6 dopamine molecules (Fig. 1) symmetrically distributed around the cluster. The simulation time was found to be too large to compute as many constrained points as in the previous section, but, by plotting the magnetization as a function of the magnetic



**Fig. 7.** Histogram of exchange constants found by the fitting procedure on the iron oxide cluster.

**Table 1**  
Local surface anisotropy constants.

Fe atom	Surface anisotropy in a.u.
1	$0.5592594 \times 10^{-01}$
2	$-0.5450376 \times 10^{-01}$
3	$0.4755301 \times 10^{-01}$
4	$-0.2952414 \times 10^{-01}$
5	$0.4511738 \times 10^{-01}$
6	$0.5525300 \times 10^{-01}$
7	$-0.4852317 \times 10^{-01}$
8	$-0.2241407 \times 10^{-01}$
9	$0.8430323 \times 10^{-01}$
10	$-0.7067873 \times 10^{-02}$
11	$0.7141519 \times 10^{-01}$
12	$0.7437612 \times 10^{-01}$
13	$0.8089262 \times 10^{-01}$

field, as can be seen in Fig. 8, we could check that the response of the system seems to be unchanged from this functionalization.

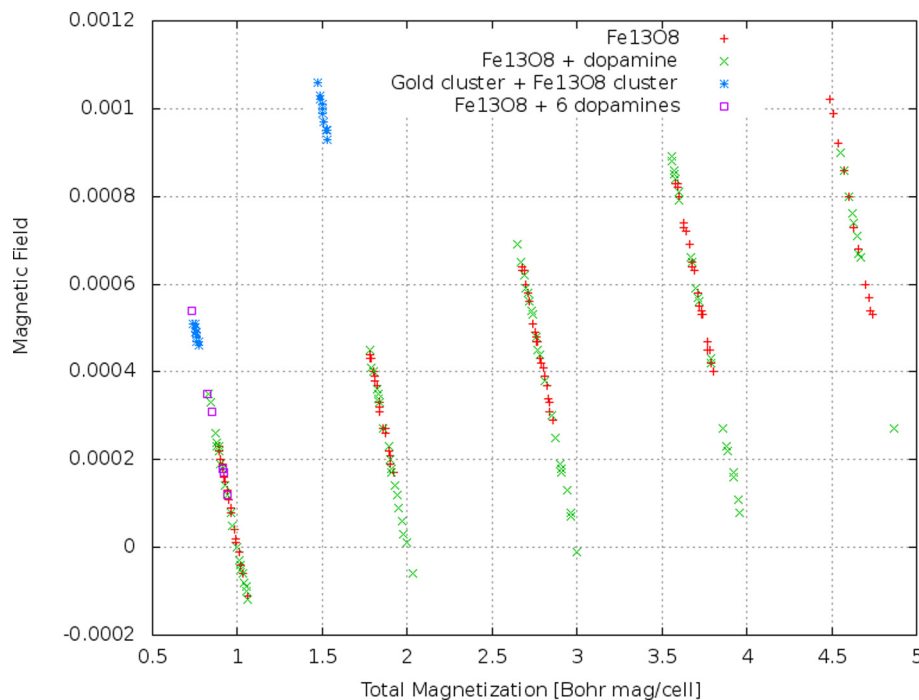
### 3.3. Iron oxide clusters and gold cluster

We also introduced in the system a small gold cluster (which could act as a nano-antenna in plasmonics) which was found after structural optimization to adhere to the iron oxide cluster. In this case, the Heisenberg model did not fit very well either the computed *ab initio* values of energies, probably because the metallic character of the system makes the Heisenberg model inappropriate. However, as can be seen on Fig. 8, although the absolute values of external magnetic field to achieve the same total magnetization along the x axis are strongly different from the previous cases (with or without dopamine), the slope of the curve does not change by more than a few percent, meaning that the response of the system is unchanged by the presence of a metallic gold cluster.

### 3.4. Magnetite surface and magnetite coated with cobalt oxide

In the case of the magnetite surface, generating 124 samples for 6 parameters, we found the best fit, with a correlation coefficient of 0.87 in between the *ab initio* results and the fit for a surface anisotropy of 784.00 meV, a volume anisotropy of  $6.96 \times 10^{-3}$  meV, a Landé *g* factor close to zero (which we see as a proof of correctness of our model), and coupling constants used to generate the  $J_{<ij>}$  of 1.102 meV and 2.076 meV respectively. The results of the fit are shown on Fig. 6 and, in this case also, we conclude that the Heisenberg model corrected with a surface anisotropy term gives a good description of the magnetism of the system. The values we find for volume anisotropy is in good agreement with the literature, and the ratio of surface to volume anisotropy is in the range expected by experimentalists.

In the case of the magnetite surface coated by iron oxide, in which we could only generate 55 samples due to the much higher numerical cost, we found that the model was much harder to fit (with a correlation coefficient of only 0.54 between the *ab initio* values and the fitted values). The best fit was obtained with a sur-



**Fig. 8.** Magnetic moments in a.u. vs. magnetic field in a.u., the latter extracted from the constrained calculation for the studied clusters.

face anisotropy of 546.77 meV, volume anisotropy of  $2.63 \times 10^{-3}$  meV, and coupling constants of 0.98 meV and 2.11 meV in the case of iron-iron, 0.77 meV and 2.09 meV in the case of iron-cobalt, and 0.97 meV and 2.37 meV in the case of cobalt-cobalt pairs. In this case, either a better *ab initio* calculation would have been needed (using for instance the LDA + U method in order to better describe the insulating behavior of cobalt oxide), or the magnetic model has to be improved, including for instance interface anisotropy terms.

### 3.5. Mixed iron oxide and cobalt oxide clusters

We then addressed the case of clusters of iron, cobalt and oxygen atoms of increasing size, going close to the bulk, which we submitted to a global magnetic constraint, in this case, rather than enforcing total moments like in the previous sections we found that the quantum calculations converged faster when imposing a global angle of respectively 530.45 and 75° with respect to the z axis, cases to which we will refer as numbers 0–3 in the figures. This constraint allows to get a value of the magnetic field from the *ab initio* calculations. In this case we adjusted the difference in between the total *ab initio* energy taking into account the spin components in the wavefunctions and the *ab initio* energy without magnetism. Here, surface atoms (for the surface anisotropy term) are defined by the criterion that the number of neighbors is inferior to the values found in the bulk.

In order to estimate the change in the anisotropy term from the cobalt/iron mixing, after various functional tries, we found that the

best fit was obtained when we allowed a change in the volume and surface anisotropy term depending on the number of iron and cobalt atoms present in the cluster. The additional term was multiplied by adjustable parameters  $a_i$  (where  $i$  represents iron and cobalt atoms), so if there are  $N$  different species in the system with  $n_i$  atoms of each kind per cell for the volume term or per surface site in the case of surfaces, the volume and surface anisotropies read

$$K_{S,V,i} = K_{S,V}^0 a_i^{n_i} \quad (6)$$

so that the final Hamiltonian we used reads

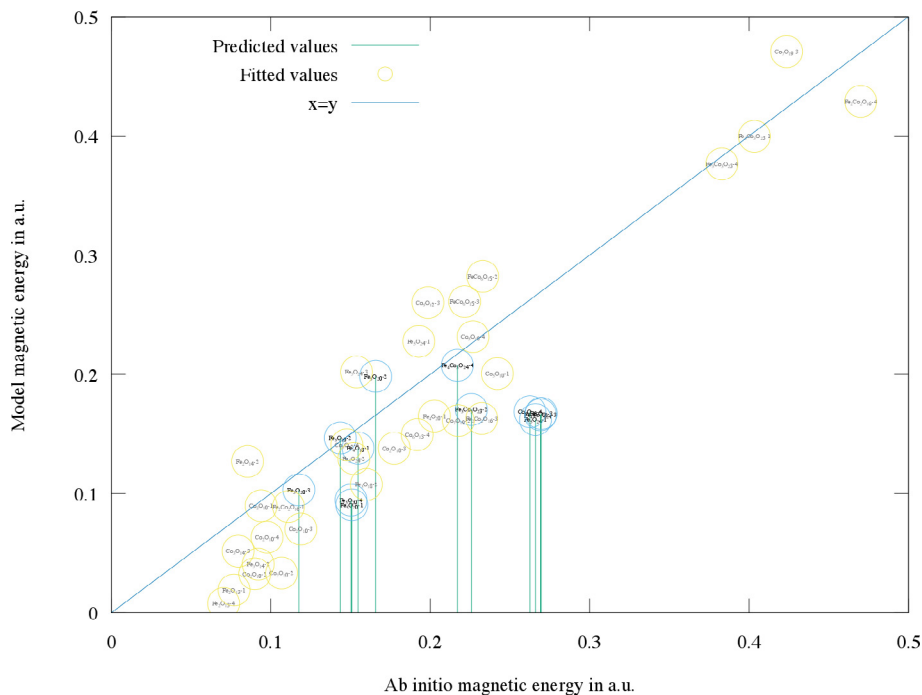
$$H = -2 \sum_{\langle i,j \rangle} J_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j - \sum_i K_{V,i} (S_{x,i}^2 S_{y,i}^2 + S_{y,i}^2 S_{z,i}^2 + S_{x,i}^2 S_{z,i}^2) - \sum_k K_{S,k} (\vec{S}_k \cdot \vec{e}_k)^2 - g \mu_B \vec{H} \cdot \sum_i \vec{S}_i \quad (7)$$

The advantage of the modification of the volume and surface anisotropies we used in Eq. 6 is that such a term allows simply to take into account the changes in anisotropy due to a varying ratio of cobalt to iron atoms.

We tried to include a factor in the Hamiltonian in order to model the effect of the various oxygen stoichiometries of the clusters on the energy but for the functional form we tried (multiplying each anisotropy term by the ratio of magnetic to oxygen atoms) we found that the corresponding parameter was converging to zero.

**Table 2**  
Parameters obtained for mixed iron oxide/cobalt oxide clusters.

System	Parameter	Value	Parameter	Value
Whole	$K_S^0$	749.15 meV	$K_V^0$	4.43 meV
Whole	$a_S$	2.20	$a_V$	1.66
Fe	$J_{Fe,90^\circ}$	0.77 meV	$J_{Fe,180^\circ}$	1.39 meV
Co	$J_{Co,90^\circ}$	−1.25 meV	$J_{Co,180^\circ}$	−1.35 meV
FeCo	$J_{FeCo,90^\circ}$	0.70 meV	$J_{FeCo,180^\circ}$	1.17 meV



**Fig. 9.** Results of fitting the Heisenberg model on mixed iron oxide and cobalt clusters under varying magnetic constraints.

The values of the parameters converged to values presented in Table 2.

As can be seen on Fig. 9 the fitting procedure of the Hamiltonian converged to a satisfying level, with a correlation coefficient close to 1 in between *ab initio* values of the magnetic energy and energies given by the model. We then added, after the fitting procedure several configurations chosen at random, in order to check the predictive capabilities of the model (points labeled with an impulse), which can be seen as satisfying, despite obviously less good than the ones given by the model when reusing the input configurations used for fitting as in the previous case. The model can nevertheless be seen as adequate, since it uses only 12 fit parameters for 30 couples of input values, and has some predictive power.

From the physical results one can see that the values of the exchange constants kept the same order of magnitude as in the previous case of pure surfaces, although the values changed, with an interesting information for Fe/Co pairs. The same goes for the surface and volume anisotropies, with an enhancement in the case of iron oxide in comparison to cobalt oxide, the mixed situations being intermediate. The negative sign found in the case of cobalt oxide reflects the different magnetic order in the material, and the values at the interface reflecting the particular magnetic properties of the interface, as has been studied experimentally in the case of flat surfaces [28]. One should note that in the total energies, the main contribution comes from the surface term, followed respectively by the volume and exchange contributions. It is then no wonder that the latter term is particularly difficult to adjust.

Nevertheless, we can now display values of the surface anisotropy of iron oxide, and the changes induced by the presence of cobalt oxide.

A problem remaining to be solved is that for the time being, we do not have at our disposal a clear physical way to predict the magnetic moments emerging from a given configuration of atoms. A machine learning approach based on physically relevant data such as relative angles and distances can be envisaged; nevertheless the present study gives surface anisotropy values from an adjustment over *ab initio* results, and if values of magnetic moments are set to physically reasonable values as found in the bulk, can give a phenomenological description of magnetic nanoparticles of large size if the geometric configurations of atoms do not diverge too much from the bulk.

#### 4. Conclusions

In this work, we adjusted a classical Heisenberg model of magnetism using the Metropolis simulated annealing method including surface anisotropy effects on magnetically constrained, non collinear *ab initio* results obtained a small iron oxide cluster functionalized or not by one or several dopamine molecules or a nearby gold cluster. We conclude that the Heisenberg model seems to apply well to the simpler systems (namely, a free iron oxide cluster or a magnetite surface), allowing us to give some absolute values of the surface anisotropy constant, although a locally varying surface anisotropy alternating positive and negative values seem to provide a better description.

This could allow us to describe the magnetic behavior of a nanoparticle of size 1 to 10 nm, which *ab initio* calculations can hardly tackle for the time being because of computing power limitations, hoping that the large surface proportion of iron atoms in the small cluster we have studied does not influence the results.

In the case of functionalized cluster by one or several molecules of dopamine, or by a nearby gold cluster, the Heisenberg picture does not apply as well as for the simpler system, but we could nevertheless observe that the linear relation in between magnetic field

and magnetization was unchanged in all those cases even if absolute values changed.

In the case of clusters of varying sizes and compositions, with periodic boundaries conditions, we were able to give a model describing hybrid ferromagnetic and antiferromagnetic systems, describing functionally the enhancement in surface anisotropy due to the juxtaposition and mixing of the systems and giving estimations of the corresponding values.

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#### References

- [1] R.H. Kodama, Magnetic nanoparticles, *J. Magn. Magn. Mater.* 200 (13) (1999) 359–372.
- [2] A.-H. Lu, E. Salabas, F. Schüth, Magnetic nanoparticles: Synthesis, protection, functionalization, and application, *Angewandte Chemie Int. Ed.* 46 (8) (2007) 1222–1244.
- [3] E. Tronc, D. Fiorani, M. Nogus, A. Testa, F. Lucari, F. Dorazio, J.-M. Grenèche, W. Wernsdorfer, N. Galvez, C. Chanac, D. Mailly, J. Jolivet, Surface effects in noninteracting and interacting gamma-Fe<sub>2</sub>O<sub>3</sub> nanoparticles, *J. Magn. Magn. Mater.* 262 (1) (2003) 6–14.
- [4] A.E. Berkowitz, J.A. Lahut, I.S. Jacobs, L.M. Levinson, D.W. Forester, Spin pinning at ferrite-organic interfaces, *Phys. Rev. Lett.* 34 (10) (1975) 594–597.
- [5] Y. Kseolu, Effect of surfactant coating on magnetic properties of Fe<sub>3</sub>O<sub>4</sub> nanoparticles: {ESR} study, *J. Magn. Magn. Mater.* 300 (1) (2006) e327–e330.
- [6] F. Luis, J. Torres, L. Garcia, J. Bartolomé, J. Stankiewicz, F. Petroff, F. Fetta, J.-L. Maurice, A. Vauras, Enhancement of the magnetic anisotropy of nanometer-sized Co clusters: Influence of the surface and of interparticle interactions, *Phys. Rev. B* 65 (9) (2002).
- [7] P. Hajra, P. Brahma, S. Dutta, S. Banerjee, D. Chakravorty, Enhancement of magnetic anisotropy in mechanically attrited Cr<sub>2</sub>O<sub>3</sub> nanoparticles, *J. Magn. Magn. Mater.* 324 (7) (2012) 1425–1430.
- [8] A. Kihal, G. Fillion, B. Bouzabata, B. Barbara, High field surface magnetic study of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, *Physica Status Solidi (b)* 249 (3) (2012) 604–614.
- [9] K. Nadeem, H. Krenn, T. Traussnig, R. Wurschum, D.V. Szabo, I. Letofsky-Papst, Spin-glass freezing of maghemite nanoparticles prepared by microwave plasma synthesis, *J. Appl. Phys.* 111 (11) (2012) 113911.
- [10] E. Tronc, A. Ezzir, R. Cherkaoui, C. Chanéac, M. Nogues, H. Kachkachi, D. Fiorani, A.M. Testa, J.M. Grenèche, J.P. Jolivet, Surface-related properties of -Fe<sub>2</sub>O<sub>3</sub> nanoparticles, *J. Magn. Magn. Mater.* 221 (1) (2000) 63–79.
- [11] D.A. van Leeuwen, J.M. Van Ruitenbeek, L.J. De Jongh, A. Ceriotti, G. Pacchioni, O.D. Haberen, N. Resch, Quenching of magnetic moments by ligand-metal interactions in nanosized magnetic metal clusters, *Phys. Rev. Lett.* 73 (10) (1994) 1432–1435.
- [12] J. Mazo-Zuluaga, J. Restrepo, F. Munoz, J. Mejia-Lopez, Surface anisotropy, hysteretic, and magnetic properties of magnetite nanoparticles: A simulation study, *J. Appl. Phys.* 105 (12) (2009) 123907.
- [13] Q. Sun, B.V., M. Marquez, P. Jena, C. Gonzalez, Q. Wang, Theoretical study on gold-coated iron oxide nanostructure: magnetism and bioselectivity for amino acids, *J. Phys. Chem. C* 111 (2007) 4159–4163.
- [14] D. Carta, M.F. Casula, A. Falqui, J.Z. Yu, B.L. Gu, K. Mountjoy, C. Sangregorio, A. Corrias, A structural and magnetic investigation of the inversion degree in ferrite nanocrystals MFe<sub>2</sub>O<sub>4</sub> (M = Mn Co, Ni), *J. Phys. Chem. C* 113 (2009) 860.
- [15] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougousis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, R.M. Wentzcovitch, Quantum espresso: a modular and open-source software project for quantum simulations of materials, *J. Phys.: Condens. Matter* 21 (39) (2009) 395502.
- [16] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (1996) 3865–3868.
- [17] A.D. Corso, A.M. Conte, Spin-orbit coupling with ultrasoft pseudopotentials: application to Au and Pt, *Phys. Rev. B* 71 (2005) 115106.
- [18] Q. Sun, M. Sakurai, J.Z. Yu, B.L. Gu, K. Sumiyama, Y. Kawazoe, Geometry and electronic structure of magic iron oxide clusters, *Phys. Rev. B* 59 (1999) 12672–12677.
- [19] J. Fouineau, K. Brymora, L. Ourry, F. Mammeri, N. Yaacoub, F. Calvayrac, S. Ammar-Merah, J.-M. Grenèche, Synthesis, Mössbauer Characterization, and Ab Initio Modeling of Iron Oxide Nanoparticles of Medical Interest Functionalized by Dopamine, *J. Phys. Chem. C* 117 (2013) 14295–14302.
- [20] S. Grazulis, A. Daskevicius, A. Merkys, D. Chateigner, L. Lutterotti, M. Quaresima, N.R. Serebryanaya, P. Moeck, R.T. Downs, A. Le Bail, Crystallography Open Database



- (COD): an open-access collection of crystal structures and platform for world-wide collaboration, *Nucl. Acids Res.* 40 (D1) (2012) D420–D427.
- [21] S.R. Bahn, K.W. Jacobsen, An object-oriented scripting interface to a legacy electronic structure code, *Comput. Sci. Eng.* 4 (3) (2002) 56–66.
- [22] U.V. Barth, L. Hedin, A local exchange-correlation potential for the spin polarized case: I, *Solid State Phys.* 5 (1972) 1629.
- [23] G.J. Martyna, M.E. Tuckerman, A reciprocal space based method for treating long range interactions in ab initio and force-field-based calculations in clusters, *J. Chem. Phys.* 110 (6) (1999) 2810–2821.
- [24] M. Uhl, B. Siberchicot, A first-principles study of exchange integrals in magnetite, *J. Phys.: Condens. Matter* 7 (22) (1995) 4227.
- [25] W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, *Numerical Recipes in Fortran 77: The Art of Scientific Computing*, Cambridge University Press, NY, 1992.
- [26] B. Fongang, Y. Labaye, F. Calvayrac, S. Zekeng, J.-M. Grenèche, Coupled structural and magnetic properties of ferric fluoride nanostructures: Part II, a Monte Carlo-Heisenberg study, *J. Magn. Magn. Mater.* 324 (22) (2012) 3646–3651.
- [27] M. Vasilakaki, E. Eftaxias, K.N. Trohidou, A Monte Carlo study of the exchange bias and the training effect in nanoparticles with core/shell morphology, *Physica Status Solidi (a)* 205 (8) (2008) 1865–1871.
- [28] M. Gruyters, Cobalt oxide/ferromagnet bilayers: exchange coupling and dominance of the antiferromagnet, *EPL (Europhysics Letters)*. 64 (2003) 803.