Simple Simulation of Magnetic Structure for Nanoclusters

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Abstract: A simple discrete model for magnetic structures of chromium nanoclusters, found with the help of local-spin DFT by Kohl and Bertsch, still confirms their conclusion that in most of the clusters the magnetic moments are not collinear; instead, in most of the cases they are oriented within one plane. We also simulate the destruction of the anti-ferromagnetic ordering by thermal fluctuations.

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Nanosized materials possess unique properties, which are intermediate between the molecular ones and the properties of the corresponding bulk materials. The magnetic behaviour of nanostructured systems is generally governed by both the intrinsic properties of the magnetic nanoclusters (grains) and the interactions between the grains. The present study is related to the clusters themselves, specifically the size dependence of the magnetic ordering in chromium and mixed chromium-iron clusters.

This work is based on a simple discrete model of the problem known as non-collinear magnetic ordering [1], and studied by Kohl and Bertsch [2] in the frame of a general rotationally invariant form of local spin-density theory.

The revived interest in very small magnetic nanoparticles is mainly caused by recent advances in synthesis techniques of nanometer-size magnetic particles and their application in magneto-optics [3, 4, 5]. For a technological process, it is necessary to know the size-evolution of the cluster magnetization in order to design materials with a long-lasting property, e.g. high (low) magnetic moments, stable structures of particles with specific shapes. It worth mentioning that the surface effects of small particles introduce two different relaxation times in the system [6] and thus, a dynamical metastability [7], which further increases the interest in having a fast and simple tool to compute the property needed.
Bulk chromium crystallizes in body-centered cubic bcc structures \cite{8} with anti-ferromagnetic ordering of the spins which are collinear along a fixed quantization axis. However, in clusters their finite sizes lead to a different magnetic behaviour from the bulk: enhanced moments \cite{9,10}, an altered temperature dependence of the magnetization \cite{11}, and non-collinear effects \cite{1,2,12,13}.

Non-collinear arrangements in anti-ferromagnetic clusters are now obtained with the help of a discrete model of classical spins and Monte Carlo simulations \cite{14}.

We simplified the computation of Kohl and Bertsch by giving each atom a classical Heisenberg spin $S$ of fixed magnitude $2\mu_B$ and restricted us to an interaction "Hamiltonian" $H = \beta \sum_{i<j} S_i \cdot S_j$ with positive (anti-ferromagnetic) exchange coupling $\beta$. A Monte Carlo simulation slightly changed every spin's orientation, randomly and independently of other spins. The new configuration was accepted if it lowered the configuration energy. We started from ten independent random spin configurations to check if several different energy minima could be found.

Most of the cluster configurations are shown in Figs. 1 and 3 of Kohl and Bertsch and are defined in our table caption. Most of the configurations investigated did not use all three directions for the spins, and the final spin orientations pointed all in a plane (taken as the $x$-$y$-plane by fixing (1,0,0) for the first spins and zero for the z component of the second spin). Some of the configurations can be solved exactly and serve to check the simulation: A single pair has two anti-parallel spins and an energy $-\beta$. Configuration 3 has its three spins pointing at angles zero, 120 degrees and 240 degrees from the positive $x$-axis; 4c has its four spins collinear: right, left, right, left; the two triangles of 6 are oriented opposite to each other, with every triangle as configuration 3; configuration 12b has the top spin right, the four spins in the plane below all point left, the two in the next lower plane both point right, the four in the next lower plane again all point left, and the lowest spin points right. For 13 spins, each triangle of neighbours has spins as in configuration 3, as if the other bonds did not exist. For configuration 4c, which could also be visualized as a tetrahedron, the frustration leads to different orientations in every simulation, but with the same final energy: Two pairs of anti-parallel spins, with an arbitrary orientation of one pair to the other, give the minimum energy of $-2\beta$ coming from the two unbroken bonds; the energies of the other bonds add up to zero. Configuration 4b
| configuration | $-E_H$ | $-E_I$ | Diff | $m_H$ | $m_I$ | planar? |
|---------------|--------|--------|------|-------|-------|---------|
| 2             | 1      | 1      | 0    | 0     | 0     | linear  |
| 3             | 1      | 1      | 1/2  | 0     | 1/3   | yes     |
| 4a            | 4      | 4      | 0    | 0     | 0     | linear  |
| 4b            | 3      | 3      | 0    | 0     | 0     | linear  |
| 4c            | 2      | 2      | 0    | 0     | 0     | no      |
| 5             | 3.86   | 3      | 0.86 | .114  | 1/5   | yes     |
| 6             | 6      | 5      | 1    | 0     | 0     | yes     |
| 12a           | 16.39  | 12     | 4.39 | .057  | 1/6   | yes     |
| 12b           | 20     | 20     | 0    | .333  | 1/3   | linear  |
| 13            | 18.00  | 12     | 6    | .076  | 1/13  | yes     |
| 51            | 128.00 | 128    | 0    | .2549 | 13/51 | linear  |

Table 1: Cluster properties (H = Heisenberg, I = Ising) for the following topologies numbered by their number of spins: 2 = single pair, 3 = triangle, 4a = square without diagonals, 4b = square with one diagonal, 4c = square with both diagonals, 5 = three triangles in one line, 6 = two triangles on top of each other, 12a = one bcc cube with center site plus 3 adjacent cube centers with all 12 bonds of the basic cube plus all nearest-neighbour bonds, 12b = 12a with only nearest-neighbour bonds, 13 = symmetrized 12a with fourth adjacent cube center. Diff is the energy gain by moving away from collinearity. 51 is a "magic" spherical cluster of four shells, containing 8, 6, 12, and 24 chromium atoms respectively, mimicking a bcc structure [16]. Energies $E$ are measured in units of exchange coupling $\beta$, absolute value of magnetic moment per atom, $m$, in units of $2\mu_B$; each atom has a classical spin of length $2\mu_B$. Diff is the energy difference between Ising and Heisenberg case. The last column indicates if for the Heisenberg case all spins point into the $x$-$y$-plane ("planar") or even only along the $x$-axis ("linear").
converged very slowly to its linear ground state when the two spins with only two bonds point right, and the two diagonal ones with three bonds point left.

To simulate mixtures like iron-chromium clusters, we assumed in configuration 12b four of the twelve atoms, forming one horizontal plaque of the bcc lattice, to be connected with their neighbours through ferromagnetic instead of anti-ferromagnetic bonds; thus $\beta$ switched sign for them. Now the two of the modified spins which have only two neighbours are completely frustrated and show in various direction for different simulations. The magnetization is no longer unique, while the energy is always $-11|\beta|$.

In four of the above cases collinearity resulted by itself, in the other six cases, mostly the larger clusters, it is energetically less favorable. The largest
cluster of 51 atoms is a "magic" one and because of its special symmetry it
has collinear spins; omitting a suitable spin destroys both collinearity and
planarity. 'Suitable' is a spin located not on a symmetry axes.

For collinearity we allow in a separate simulation the spins to show only to
the right or left which defines an Ising magnet. The results are also given in
the table. We see that for the larger clusters it may become bad even though
for an infinite bcc lattice it becomes exact. Cheng and Wang [15] seem to
allow zero spins, which we do not allow. (For 51 atoms energy minimization
did not always find the absolute minimum.)

At any finite temperature \( T \), bonds can be broken with a Boltzmann
probability \( \propto \exp(-E/k_B T) \) where \( E \) is the energy and \( k_B \) is the Boltz-
mann’s constant. The highest binding energy of the above configuration is
obtained for 12b where all bonds are satisfied. We define an order parameter
("staggered magnetization") \( \Psi \) through the similarity of the spin configu-
ration \( S_i \) at finite \( T \) with the ground state configuration \( S^0_i \), averaged over
many equilibrium configurations:

\[
\Psi = \langle | \sum_i S_i \cdot S^0_i | \rangle
\]

Standard Metropolis Monte Carlo simulation was applied to this nanocluster
12b. Fig.1 shows the gradual destruction of magnetic order (Heisenberg
model) with increasing temperature; of course, no sharp Neél point can be
expected in such nanoclusters. Since \([15]\) the exchange energy \( \beta \) is about 2
eV or \( \sim 10^4 \) Kelvin, the room temperature corresponds nearly to the ground
state. We averaged over 100 samples of 100,000 Monte Carlo steps per spin,
ignoring the first 90 percent of each sample. We see that the unfrustrated
cluster is more resistant against thermal fluctuations. The magnetization at
high temperatures comes from the random spin orientations which do not
exactly cancel each other.

Our computer simulations, which usually took only seconds, cannot give
the geometrical structure or the magnitude of the magnetic moments; these
were taken from the much more time consuming calculations of [2]. No
quantitative agreement with [2] could be obtained because of our simplifi-
cation, mentioned already in [2], of only one bond strength. Despite this
simplification, we confirmed the trend of Kohl and Bertsch that clusters of
\( \sim 10 \) atoms in general have no collinear spins even though both the smallest
cluster (pair) and the infinite bcc lattice have collinear spins, see the Table.
Moreover, a surprisingly large fraction of the clusters investigated here have
all the spins pointing in the $x$-$y$-plane. Finally, we complemented previous works \cite{15, 2} by looking at the thermal destruction of the anti-ferromagnetic order in configuration 12b where the ground state satisfies all bonds.

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[16] A. Proykova, R. Radev, F.-Y. Li and R. Stephen Berry, J. Chem. Phys. 110, 3887 (1999), in particular Fig. 5.