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LETTER TO THE EDITOR

On the oscillation of the magnetic moment of free transition metal clusters

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Abstract

The results of Stern–Gerlach experiments on free clusters of Fe, Co, and Ni are usually interpreted in terms of magnetic moments that show oscillations as a function of cluster size. We demonstrate that the observed behaviour can be more convincingly explained in terms of magnetic anisotropy energies (MAEs) that oscillate with the size of the clusters. The magnitudes of the estimated MAEs are in reasonably good agreement with the experimental results for supported/embedded cluster assemblies. The oscillation of the MAE of a cluster with respect to its size may reveal the geometrical shell structures of free transition metal clusters.

A better understanding of magnetism in transition metal clusters is crucial not only for fundamental physics but also for potential applications in high density data storage devices. One of the central issues in this context is the evolution of magnetic anisotropy energies (MAEs) from single atoms via clusters to bulk metals [1–3]. The MAE, which represents the energy involved in rotating the magnetization from a low energy direction (easy axis) to a high energy direction (hard axis), determines the low temperature orientation of the magnetization with respect to the structure of the system. It has been found that the MAEs of clusters are enhanced compared to the bulk values because of a strong anisotropy induced at the surface of the clusters.

Most of the experimental studies on nanosized grains have been carried out on large assemblies of particles [1–4], where distributions of particle sizes, shapes, and defects render the interpretations quite difficult. Very recently, the MAE of a single cobalt nanoparticle embedded in niobium was investigated by using a micro-SQUID setup [5]. From a fundamental point of view, it is important to study the MAEs of isolated particles. However, in state-of-the-art experimental techniques, no direct measurement of the MAEs of isolated clusters is available.

Molecular beam deflection measurements [6–9] in a magnetic field gradient are widely used to extract the magnetic moments of free clusters from the Langevin function [8, 10]. The

experimentally determined saturated moments of Fe, Co, and Ni clusters oscillate with the cluster size, and the period is about one atomic layer [6]. This oscillation has stimulated strong interest in searching for magnetic shell structures. In the magnetic shell model developed by Jensen and Bennemann [11], the individual magnetic moments of atoms at different sites are determined by their local atomic coordinations. A pure electronic shell model [12] was also proposed to explain the moment oscillation. The oscillations experimentally observed are not in general reproduced in these magnetic shell models. Especially when the cluster size is large ($N > 200$), the predicted amplitudes of oscillations are too small. Electronic structure calculations [13–16] using tight-binding (TB) models have been performed to obtain the spin moments. For larger N (>200), contrary to the experimental observation, the predicted spin moments decrease smoothly with increasing cluster size, without any obvious oscillation.

It has been shown that, due to the presence of magnetic anisotropy, the effective moment of embedded/supported clusters deviates from classical Langevin behaviour [17, 18]. Recently, we have proposed a simple model to estimate the effective moment of free clusters in a magnetic field. Compared with a supported/embedded cluster assembly, the effect of magnetic anisotropy on free clusters is significantly enhanced [19]. The model can in principle be used to evaluate the MAE of a cluster, although it has been claimed that the MAEs of isolated superparamagnetic clusters cannot be measured by Stern–Gerlach experiments [20].

The purpose of this letter is to show that the apparent oscillations of the magnetic moments present in the experiment [6] can be properly analysed by taking the MAE into account. The MAEs of free Fe, Co, and Ni clusters are estimated under various reasonable experimental conditions and theoretical postulates. The estimated MAEs are in reasonably good agreement with the experimental results for supported/embedded cluster assemblies, which verifies the validity of our theoretical model.

The average magnetic moment μ of a single domain N-atom cluster is extracted in Stern–Gerlach experiments [6, 7] from $\mu_{\rm eff}$, which is the projection of μ along the axis of magnetic field $\mathbf{H}$. In the simplest picture, the cluster moments are subject to rapid orientational fluctuations. The moments can explore the full distribution of projections onto the field axis within the timescale of the experiment, and the effective moment $\mu_{\rm eff}$ is given by the Langevin function [8, 10]

$$\frac{\mu_{\rm eff}}{\mu} = \coth(\xi) - \frac{1}{\xi}, \tag{1}$$

where $\xi = N\mu H/k_{\rm B}T_{\rm vib}$ and $T_{\rm vib}$ is the internal vibrational temperature of the cluster.

Equation (1) is valid only when $k_{\rm B}T_{\rm vib} \gg E_{\rm a}$, where $E_{\rm a}$ is the MAE of a cluster. The energy of a single ferromagnetic particle with uniaxial anisotropy in an external field $\mathbf{H}$ is composed of Zeeman energy $-N\mu H[\mathbf{e}\cdot\mathbf{h}]$ and anisotropy energy $-E_{\rm a}[\mathbf{e}\cdot\mathbf{k}]^2$, where $\mathbf{e}$, $\mathbf{h}$, and $\mathbf{k}$ are the unit vectors along the directions of $\boldsymbol{\mu}$, $\mathbf{H}$, and magnetic easy axis, respectively. The magnetization m in thermal equilibrium can be obtained readily as a function of θ_h [18, 19], which is the angle between $\mathbf{h}$ and $\mathbf{k}$. In obtaining a generalization of the Langevin expression in the presence of MAE, an average over all easy axis orientations has to be performed,

$$\langle m\rangle = \int_0^{\pi/2} {\rm d}\theta_h\, \rho(\theta_h)\sin\theta_h m(\theta_h), \tag{2}$$

where $\rho(\theta_h)$ is the probability of the easy axis making an angle θ_h with $\mathbf{H}$. The magnetization $m(\theta_h)$ oscillates about the Langevin value, with a maximum at $\theta_h = 0$ and a minimum at $\theta_h = \pi/2$. The amplitude of oscillations increases with increasing $\sigma = E_{\rm a}/k_{\rm B}T_{\rm vib}$ [19].

For a randomly oriented system like the embedded cluster assembly, $\rho(\theta_h) \equiv 1$. The deviation of $\mu_{\rm eff}$ from classical Langevin behaviour only becomes obvious when $\xi > 1$ and

$\sigma > 2$ [17, 18]. The quenched effect of anisotropy results from cancellations that occur when averages are taken over different alignment angles.

The free clusters arrive from the cluster generation process rotating rapidly [8, 21]. For a free rotating cluster, the probability ρ will depend on θ_h [19]. Generally, the cluster stays for a longer time at $\theta_h = \pi/2$ than at 0. When averaging over the time taken for the cluster to pass through the magnetic field, the magnetization is effectively reduced because it reaches its minimum value at $\theta_h = \pi/2$ [19]. For well determined vibrational and rotational temperatures, the MAEs can be evaluated from the available magnetization curves of the Stern–Gerlach experiments.

Both the magnetic shell models [11, 12] and electronic structure calculations [13–16] predicted that the average magnetic moment $\mu(N)$ of a cluster is insensitive to the cluster size for $N > 200$. The magnetic moment of a surface atom is larger than that of a bulk atom because of reduced atomic coordinations [22]. From simple physical considerations, the average moment per atom is given by [11]

$$\mu(N) = \mu_{\text{bulk}} + \Delta\mu N^{-1/3}, \tag{3}$$

where $\Delta\mu$ is proportional to the difference between the moment of a surface atom μ_{surf} and that of a bulk atom μ_{bulk}, with a prefactor of 6.0 for a cube and 4.8 for a sphere. Obviously, we do not expect that the simple postulate can describe the variation of the magnetic moment with cluster size precisely. However, the general trend of the variation must be well captured, particularly when the cluster size is relatively large.

Using the assumed magnetic moment values as described in equation (3), we can calculate from equation (2) the effective moment of a cluster under different experimental conditions and for various values of MAE. Using equation (1), the effective moments measured experimentally can be deduced from the extracted moments [6]. The MAE of a cluster is determined by varying its value in equation (2) until the effective moments obtained by both procedures are equal.

The experimental magnetic moments [6] of Fe, Co, and Ni clusters, which are shown as open squares in figure 1, are extracted from equation (1) for small values of ξ (say $\xi \leqslant 1$) without taking the MAEs into account [7]. For non-aligned particles like the embedded cluster assembly, the theoretical magnetization curves are superimposed for $\xi \leqslant 1$ independently of the anisotropy strength σ [18]. However, for free clusters, the deviation from Langevin behaviour appears at much smaller values of ξ (<0.5) [19]. Extracting μ from a Stern–Gerlach experimental μ_{eff} of a cluster ignoring the MAE *underestimates* the magnetic moment. As shown in figure 1, the experimental extracted moments can even be below the bulk values, namely 2.2 μ_{B} for Fe, 1.72 μ_{B} for Co, and 0.606 μ_{B} for Ni [23] (see, in particular, the plots for Co and Ni). The moments of clusters predicted by the magnetic shell model [11] or electronic structure calculations [13–16] are always larger than the bulk values. Including the anisotropy in calculating the effective moments will certainly push the extracted moments above the bulk values, and thus yield the physically expected behaviour.

Assuming the magnetic moments of clusters as described in equation (3), we can calculate the effective moments μ_{eff} of clusters under different values of ξ and σ. In order to compare with the experimental extracted magnetic moments, we have calculated the corresponding moments μ from equation (1) with $\xi = 1$. The magnetic field used in experiment is $0 \leqslant H \leqslant 7$ kG [6]. Correspondingly, the maximum field used in our calculations is 7 kG, i.e. ξ may be smaller than 1 for small cluster sizes N. As shown in figure 1, by adjusting the values of E_{a}, our theoretical curves can be brought into excellent agreement with the experimental data. The evaluated MAEs are depicted in figure 2.

Obviously, the evaluated MAEs depend on the values of $\Delta\mu$ in equation (3). The evaluated MAEs for large clusters ($N > 300$) are insensitive to the reasonable choice of values of $\Delta\mu$.

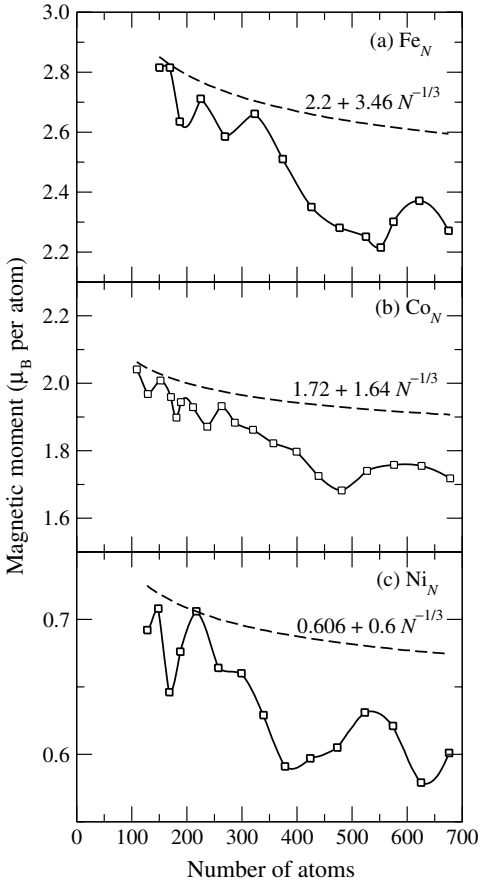

Figure 1. Average magnetic moment per atom for (a) Fe clusters at 120 K, (b) Co clusters at 78 K, and (c) Ni clusters at 78 K, as a function of the number of atoms in the clusters. The open squares are experimental results [6] extracted from the Langevin function while the continuous curves are extracted from the Langevin function using $\mu_{\rm eff}$ calculated for free rotating clusters with uniaxial anisotropy and $\mu(N)$ given by equation (3).

We have chosen the values of $\Delta\mu$ as shown in figure 1. Different choices of $\Delta\mu$ do not affect the general trend and order of magnitude of the MAEs.

The cluster temperature strongly depends on the dwell time inside the source nozzle with temperature $T_{\rm noz}$, during which the clusters are cooled by the carrier gas He with temperature $T_{\rm He}$. The cooling of $T_{\rm rot}$ is much more efficient than that of $T_{\rm vib}$, which makes $T_{\rm noz} > T_{\rm vib} > T_{\rm rot} > T_{\rm He}$ [7, 21]. In the case of long dwell times and therefore $T_{\rm vib} = T_{\rm noz}$, the so-called superparamagnetic model was used to extract the magnetic moments [7]. As shown in figure 2, for each experimental temperature $T_{\rm noz}$, three rotational temperatures are considered. It was proved previously that [19], for a particular value of $T_{\rm vib}$, the effect of anisotropy increases with decreasing rotational temperature. Roughly the MAEs evaluated at $T_{\rm rot} = 1.0$ and 0.2 correspond to the upper and lower bounds.

The magnitude of the evaluated MAEs of free clusters is one or two orders of magnitude larger than the corresponding bulk values, which are 1.4, 1.3, and 2.7 μ eV/atom respectively for bcc Fe, fcc Co, and fcc Ni [24]. The evaluated MAEs of free Fe clusters are in reasonable agreement with the experimentally determined value ($\sim$0.1 meV/atom) from

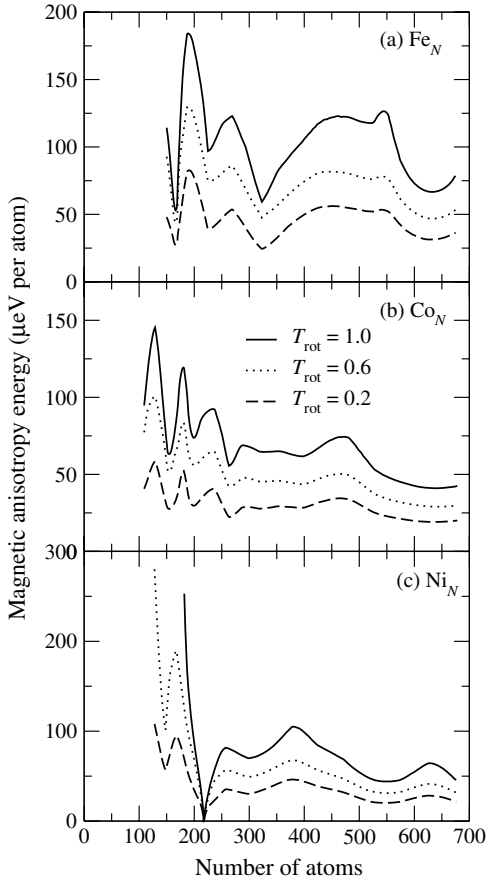

Figure 2. Size dependence of the effective anisotropy constants for (a) Fe, (b) Co, and (c) Ni clusters. Three different rotational temperatures (1.0, 0.6, and 0.2 in units of vibrational temperature) are considered.

magnetization measurements on granular alloys of Fe in matrices [25]. As shown in figure 2, the effective anisotropy constants $K_{\rm eff}$ (MAEs per atom in the uniaxial anisotropy) decrease slowly with increasing cluster size, which is in good agreement with the experimental results for supported/embedded cluster assemblies [1–3]. The MAEs of nanoparticles of metallic iron on carbon supports has been determined by use of Mössbauer spectroscopy [1]. $K_{\rm eff}$ increases from 7.5 to 22 μeV/atom with decreasing particle diameter from 6 nm ($\sim$10 000 atoms) to 2 nm ($\sim$350 atoms). A recent study of the magnetic properties of spherical Co clusters with diameters between 0.8 nm and 5.2 nm (25–7000 atoms) embedded in Al_2O_3 show that $K_{\rm eff}$ is enhanced with respect to the bulk value and that it is dominated by a strong anisotropy induced at the surface of the clusters [3]. $K_{\rm eff}$ decreases from 160 to 25 μeV/atom with increasing cluster size N from 25 to 7000 atoms. Our evaluated MAE for a Co cluster with $N \approx 700$ is in good agreement with that ($\sim$20 μeV/atom) of a single 1000-atom Co cluster embedded in a niobium matrix [5]. We believe the evaluated values of MAEs of free clusters are reasonable and realistic.

By ignoring the effect of magnetic anisotropy, the size dependence of experimentally extracted magnetic moments presents some obvious oscillations [6]. As shown in figures 1

and 2, the spurious moment oscillations can be well captured by the oscillations of the MAEs. The experimentally observed peaks of moments actually correspond to the dips of MAEs. The oscillation of the MAE can be seen from the experimental size dependence of the effective MAE constants of supported/embedded clusters [1–3], although it was supposed to be proportional to the inverse particle diameter [1]. Because the effect of magnetic anisotropy on free clusters is significantly enhanced compared with that on supported clusters [19], it is possible to demonstrate the oscillation of MAE more clearly by careful Stern–Gerlach measurements on free clusters.

The systems that are close packed in bulk have a structure that is more clearly defined than the bcc ones such as Fe. Small clusters of Co or Ni adopt an icosahedral structure, with a characteristic filling clearly evident in experiments [27]. For larger sizes, cobalt nanoparticles form mainly truncated octahedra [5]. The cuboctahedron, an octahedron truncated by a cube, can have two forms [28], one with triangular (111) facets (T-*cubo*), the other with hexagonal (111) facets (H-*cubo*). The T-*cubo* has the same closed shell sequence as the icosahedron, 13, 55, 147, 309, 561, while the H-*cubo* has the closed shell sequence of 38, 201, 586. From simple symmetry considerations, the MAEs of perfect polyhedra with high symmetry, for which the second order terms are forbidden, are very small [26]. From experimental observation [5, 28], after a closed shell configuration, the clusters grow by the filling of successive facets. Clusters with a size between two perfect polyhedra will generally have a lower symmetry. Consequently, the MAEs are much larger than those of clusters with perfect polyhedral configurations. We expect that the magnitude of MAE will oscillate with the cluster size N with minima at close shells, which let the experimental extracted moments [6] exhibit oscillation, with maxima at N corresponding to close shells. As shown in figure 1, there is a peak around 561–586 for Co and Ni clusters and a dip around 480 for Co clusters (400 for Ni clusters) in the experimentally extracted magnetic moments [6], which correspond perfectly to the MAE minimum and maximum if the cluster grows via facet filling. Other possible moment maxima are around $N = 147, 201, 309$. All maxima correspond to the complete icosahedral or cuboctahedral structures. For Fe clusters, the moments oscillate with maxima near $N = 325$ and 625. All these maxima presented in magnetic moments correspond to the minima of MAEs of the clusters, which can be seen from figure 2. Although some of the minima in the MAE can be associated with closed shell structures, it must be remembered that experimentally there is a width to the cluster size distribution, and making an unambiguous assignment for the smaller clusters ($N < 200$) would be very tentative.

To show how the MAEs of clusters change with symmetry, we have calculated the MAEs of Co_{201} and Co_{209} clusters using a TB model [16]. We only consider the contribution from spin–orbital coupling. The contribution to MAE from magnetic dipole interactions is very small in the clusters considered. As shown in figure 3, Co_{201} is a perfect truncated octahedron while Co_{209} is constructed from Co_{201} by adding one layer on the top and bottom squares. The average magnetic moments (sum of spin and orbital moments) of the two clusters are almost equal. However, the MAE of Co_{209} is one order of magnitude larger than that of Co_{201}, which has an O_h symmetry. The additional layers lower the symmetry of Co_{209} to D_{4h}. We can see very clearly that the MAE is very sensitive to the symmetry of the clusters. The calculated MAE of Co_{209} is within the range of the evaluated ones. The details of the calculations will be presented elsewhere.

In summary, the magnetic moment oscillation presented in the Stern–Gerlach experimental results of free Fe, Co, and Ni clusters can be well captured by the oscillation of the MAEs, which can be well explained by the cluster growth pattern of successive filling of the polyhedral facets. The failure of previous magnetic shell models or electronic structure calculations to account for the oscillation of the magnetic moment for larger clusters is due to ignoring the effect of

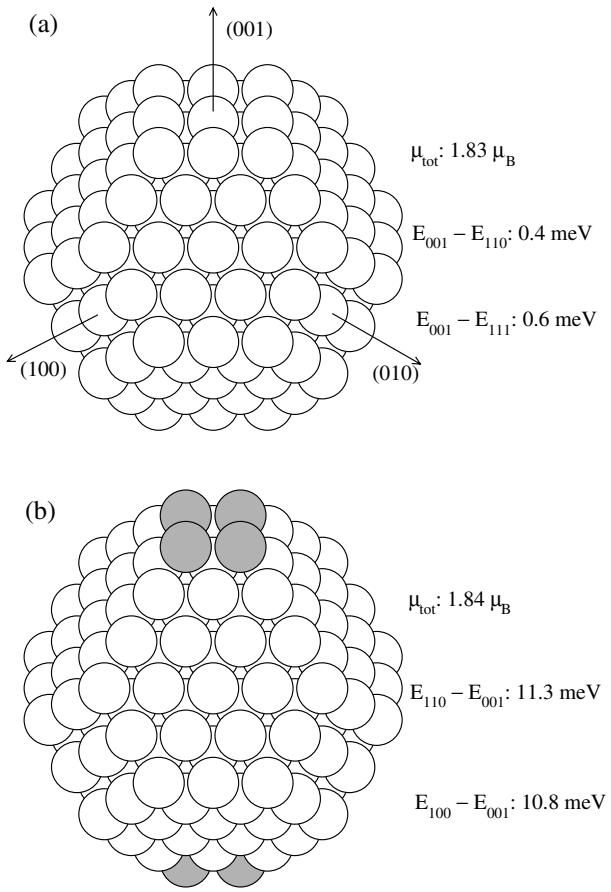

Figure 3. Total average magnetic moments μ_{tot} and MAEs calculated from TB models for (a) Co_{201} and (b) Co_{209}. Co_{209} is constructed from Co_{201} by adding one layer (shadowed atoms) to the top and bottom squares.

magnetic anisotropy. Importantly, the inclusion of MAE into the analysis avoids extracted cluster moments with values lower than those of the bulk. The values of the evaluated MAEs are reasonable and realistic, comparable to the values determined for the supported/embedded cluster assemblies. The effective anisotropy energy constants decrease slowly with increasing cluster sizes.

The effect of magnetic anisotropy on free clusters is significantly enhanced. Further experiments on free clusters are needed to confirm the prediction of MAE oscillation with cluster size. The fascinating oscillation of MAE with cluster size can be used to control the magnetic properties of cluster assembly based materials, such as hard or soft magnets.

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