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On the anomalous temperature dependence of the magnetic moment of cobalt clusters

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Abstract

Cluster beam experiments using Stern–Gerlach type measurements yield information about the magnetic properties of transition metal clusters. One of the intriguing results to have come out of such measurements is the observation of a magnetic moment in cobalt clusters that increases with temperature up to about 500 K, before decreasing as the bulk Curie temperature is approached. We argue in this paper that this behaviour can be understood as an artifact of the method of extracting results from raw experimental data, and that the origin of the anomalous behaviour lies in the neglect of the magnetic anisotropy in the analysis.

1. Introduction

Transition metal clusters are important model systems to study the evolution of magnetic properties from single atoms to bulk metals [1]. A better understanding of magnetism in these low dimensional systems is crucial not only for fundamental physics but also for potential application in high density data storage devices.

The magnetization of free particles has been studied by means of cluster beam experiments using Stern–Gerlach type apparatus [1–3]. The average magnetic moment μ of a single domain N atom cluster is extracted from an effective moment, μ_{eff}, which is the projection of μ along the axis of a magnetic field **B**. Under the assumption that the magnetic properties in clusters follow conventional thermodynamics [4, 5], μ_{eff} will take the value of the assembly average at a temperature T, given by the classical Langevin function [6]

$$\frac{\mu_{\mathrm{eff}}}{\mu} = \coth\left[\frac{N\mu B}{k_{\mathrm{B}}T}\right] - \frac{k_{\mathrm{B}}T}{N\mu B}. \tag{1}$$

The experimentally [1] determined μ reveals some striking properties:

(a) μ is close to that of an isolated atom in the small size region and decreases to bulk value with increasing cluster size;

(b) the moment oscillates with the cluster size, and the period for Ni and Co is about one atomic layer;
(c) for some Co clusters, μ increases by about 7–8% with increasing T from 80 to 500 K.

The first point is simply related to the larger proportion of surface atoms in small clusters.

The moment oscillations have stimulated strong interest and there has been a search for the source of this behaviour in magnetic shell structures [1, 7–12]. In the shell model developed by Jensen and Bennemann [7], the individual magnetic moments of atoms at different sites are determined by their local atomic coordinations. Therefore, $\mu(N)$ is expected to vary with cluster size and structure and, in particular, go through a minimum when N corresponds to closed atomic shells. By assuming bulk-like structures (bcc, fcc) and different global cluster shapes, these authors found that the bcc cube for Fe, fcc octahedron for Co and fcc cube for Ni are the most possible cluster geometries in a concentric layer growth mode. However, all these structures, with large surface atom ratio and sharp edges or vertices, are unstable in energetics [13]. A pure electronic shell model [9] was also proposed to explain the moment oscillation. Realistic and reliable electronic structure calculations [11, 12, 14] using tight-binding (TB) models have been performed to obtain the spin moments. However, the experimentally observed oscillations of $\mu(N)$ are not in general reproduced in the magnetic shell models or in the spin moment calculations.

We have shown recently [15] that a resolution of this issue may be obtained if the effect of the magnetic anisotropy energy (MAE) is included in the analysis of the experimental data. It was shown [15] that an oscillation in the MAE with cluster size is to be expected, and it is the effect of this rather than an intrinsic oscillation in the moment itself that is likely to produce the behaviour observed experimentally.

With regard to the third observation, the increase in moment with temperature, it was suggested [1] initially that this might relate to a smaller ($\approx$1.5%) increase observed in the bulk at 650 K, where it is caused by a phase transition from hexagonal closed-packed to face-centred cubic. However the issue still remains open because the observed continuous increase is unlikely to be related to a phase transition.

In this paper we re-examine this anomalous increase in moment with temperature observed in some cobalt clusters. As in our earlier work [15], we again show that the behaviour can be ascribed to the MAE. We begin this paper by summarizing the behaviour of the magnetization at zero temperature, and then discuss our interpretation of the experimental observations of this anomalous increase in moment.

2. Zero temperature magnetization

We employ in our calculations a tight-binding methodology introduced for nonmagnetic materials [16], in which a minimal orthogonal basis set containing s, p and d orbitals was used. With an additional energy related to charge transfer and spin-polarization, we have extended the TB formalism to spin-polarized systems [14, 17], where the magnetic spin moments are determined from self-consistent calculations. The orbital moment and magnetic anisotropy originate from spin–orbital coupling, which is treated in the single-site approximation [18]. All the TB and electron–electron interaction parameters are the same as [17].

Co_N adopts an icosahedral structure for small N. It has been suggested that icosahedral structures becomes unfavourable for cobalt clusters at about $N = 120$, due to the loss of icosahedral signature [19]. For larger sizes, cobalt nanoparticles form mainly truncated octahedra [20]. The cuboctahedron, an octahedron truncated by a cube, can have two forms [13], one with triangular (111) facets (T-*cubo*), the other with hexagonal (111) facets

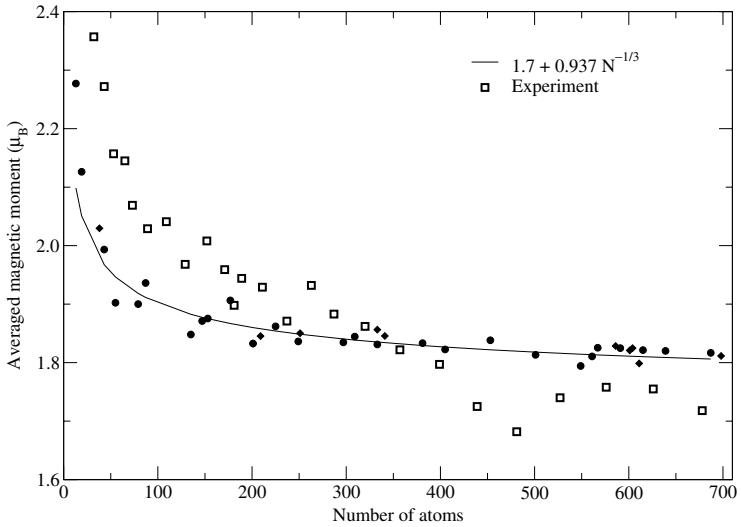

Figure 1. Average magnetic moment as a function of cluster size N. The open squares are the experiment results, while full circles denote the results of the clusters generated in a T-*cubo* shape as described in the text, the full diamonds are the results of other cluster shapes.

(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. Here, we consider only the fcc cuboctahedral cluster structures.

We first focus on the T-*cubo*. The clusters are constructed around a central site and follow the fcc structure with the experimental lattice constant. The clusters are constructed layer by layer along the (100) and (111) directions of the fcc structure. Main shell filling maintains T-*cubo* shape. In order to use symmetry adapted basis functions to simplify our calculation, sub-shells are filled with successive O_h symmetry occupation of free sites with the largest number of first nearest neighbours (FNN) or those with smallest distance from cluster centre if the numbers of FNNs of several available sets are equal. The calculation of the magnetic moment is performed in two steps. First, without the spin–orbital coupling, the spin moment and the charge density are calculated self-consistently, then we include the spin–orbital interaction and solve the one-electron problem using exact numerical diagonalization. Due to the presence of magnetization, the O_h symmetry is lowered to D_{4h}, D_{2h} and D_{3d}, corresponding, respectively, to the magnetization directions (001), (110) and (111). We also use the symmetry adapted basis of the double point group in the calculation of the orbital moment and the MAE. It allows us to reach a size of several hundred atoms with relative ease. The introduction of the spin–orbit interaction changes the local spin moment by only a small amount (of the order of 10^{-3} μ_B/atom), and the orbital moment remains almost unchanged with self-consistency [17]. Some of the orbital moments are obtained from non-self-consistent calculations. The calculated *total* magnetic moments are depicted in figure 1 as full circles.

It can be argued [7] from simple physical considerations that $\mu(N)$ should take the form

$$\mu(N) = \mu_{\text{bulk}} + \Delta\mu N^{-1/3}, \tag{2}$$

where $\Delta\mu$ is proportional to the difference between the moment of a surface atom and that of a bulk atom. The calculated $\mu(N)$ is described rather well by equation (2), and converges to $\mu_{\text{bulk}} = 1.7\mu_B$ at large N in good agreement with the experimental value of 1.72 μ_B.

The experimental results extrapolated to low temperature [1] are shown as open squares. For small values of N they lie above our calculated data. As stated earlier, for small N, cobalt clusters adopt an icosahedral structure. Calculations [21] indicate that the moments of small icosahedral clusters can be about 0.2 μ_B higher than those for an fcc cluster of the same size, which may account for the difference between the calculated and experimental results in figure 1. The calculated magnetic moments of relatively large clusters are insensitive to the detailed morphology and there is essentially no oscillation with respect to the cluster size for $N > 200$. However, even for N above about 400, there are strong oscillations in the moment extracted from the raw experimental data. It is this discrepancy that has been resolved in our earlier work [15] by introducing the anisotropy into the analysis. We consider now the source of anomalous temperature dependence of the magnetic moment.

3. Anomalous temperature dependent magnetic moment

The magnetic moments extracted from the experimental data show very different behaviour for the three ferromagnetic transition metals (see figure 3 of [1]). For clusters larger than about 100 atoms, the moment of Ni remains virtually constant to a temperature of about 300 K, and then decreases following fairly closely the bulk behaviour. A rather rapid decrease in moment is seen in Fe clusters, but it is claimed that this is related to a crystal phase transition that is well-established in the bulk. Co, on the other hand, is quite anomalous in showing an increase in magnetization with temperature for clusters larger than about 100 atoms, and only begins to display a decrease from around 500 K.

We need to consider how the MAE can affect the value of the moments extracted from experiment. To discuss this let us assume the simplest possible scenario, namely that the clusters display uniaxial anisotropy, and that the freedoms of cluster rotation and of magnetization can be considered separately [26]. We assume that, for any easy axis orientation with respect to the magnetic field **B**, the fluctuations in the direction of the axis of magnetization are quick enough to reach thermal equilibrium (as in the Langevin expression). In obtaining a generalization of the Langevin expression in the presence of MAE, an average over easy axis orientations has to be performed [26]. In the high field limit, an analytic expression can be obtained,

$$\frac{\mu_{\mathrm{eff}}}{\mu} = 1 - \frac{1}{\xi} - \alpha\left(\frac{\sigma}{\xi}\right)^2, \tag{3}$$

where $\xi = N\mu B/k_B T$ and $\sigma = E_a/k_B T$. E_a is the anisotropy energy, and α is a positive constant given by

$$\alpha = \tfrac{1}{2}\int_0^{\pi/2} \mathrm{d}\theta_b\, \rho(\theta_b) \sin\theta_b \sin^2(2\theta_b), \tag{4}$$

where $\rho(\theta_b)$ is the probability of the easy axis making an angle θ_b with **B**.

For a randomly oriented system like an embedded/supported cluster assembly, $\rho(\theta_b) \equiv 1$ and $\alpha = 4/15$ [23]. For freely rotating clusters $\rho(\theta_b)$ will depend on θ_b, and will be determined by factors such as the rotational energy of the cluster, as discussed in [26]. The effect is a larger value of α than that for embedded clusters.

Clearly, for a particular set of parameters, equation (1) gives a larger value of μ_{eff}/μ than equation (3) and so, if anisotropy is playing a role, the use of equation (1) to extract μ from experimental data will give an underestimate of its value [15]. We need to examine the likely size of the MAE before considering in detail the consequences for the Co clusters.

We calculate the MAE by using the full TB Hamiltonian with the spin–orbit term and solve self-consistently with a very high accuracy thus ensuring a reliable determination of the

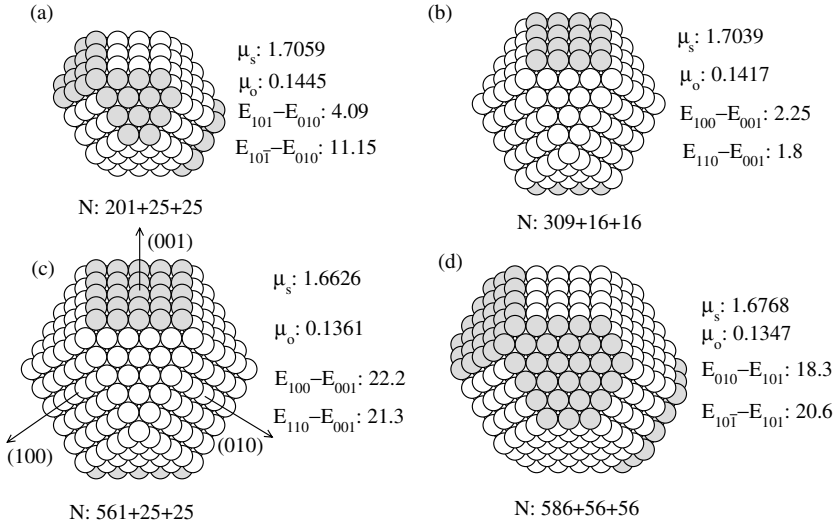

Figure 2. MAEs (in meV) of H-*cubo* Co_{201}, T-*cubo* Co_{309}, T-*cubo* Co_{561}, H-*cubo* Co_{586} with additional layer on some facets, with the shadowed atoms belonging to added facets. The average spin moment μ_s and orbital moment μ_l are also included (in μ_B/atom).

MAE from the total energy difference of various spin orientations. The spin–orbit coupling constant is taken from [22]. We consider first closed shell structures. From simple symmetry considerations, the MAEs of cubic systems, for which the second order terms are forbidden, are very small [22]. The calculated MAEs of the closed shell structures Co_{201}, Co_{309}, Co_{561} and Co_{586} are determined to be 2.9, 0.26, 0.13 and 0.25 μeV/atom, respectively, with the easy axis along (111) direction. It is noteworthy that most of the MAEs for these high symmetry clusters are smaller than the bulk value. The reason for this has been discussed elsewhere [24]. The experimental temperature used in the Stern–Gerlach studies [1] was 78 K (6.7 meV), so that $k_BT \gg E_a$ and the use of the Langevin expression in analysing data for high symmetry clusters is justified.

However, from experimental observation [13], the clusters grow, after a closed shell configuration, by the filling of successive facets. Clusters with a size between two perfect polyhedra will generally have a lower symmetry. To facilitate the calculations on the large clusters by maintaining some symmetry, we choose to fill the top and bottom squares or to fill four triangular/hexagonal facets as shown in figure 2. Although these structures are different from those obtained by successive facet-filling, we believe that the MAEs are of the same order. The calculated MAEs, as well as the magnetic moments along the easy axis, are given in figure 2. The difference of magnetization along different directions is negligible. For the lower symmetry clusters, the magnetic moments, as shown in figure 1, are very close to those of O_h symmetry clusters with similar sizes, and it can be seen very clearly that the calculated $\mu(N)$ is insensitive to the cluster growth pattern and details of the morphology of the fcc structure. However, the MAEs are about two orders of magnitude larger than in the high symmetry clusters. Interestingly, our calculated MAEs are comparable to the second order terms deduced in experiments on single cobalt clusters embedded in niobium ($\sim$16 μeV/atom) [25]. For these low symmetry clusters, the MAEs are of the same order as the temperature $\sim$100 K and the external magnetic field (in $N\mu B$) used in the experiments [1–3].

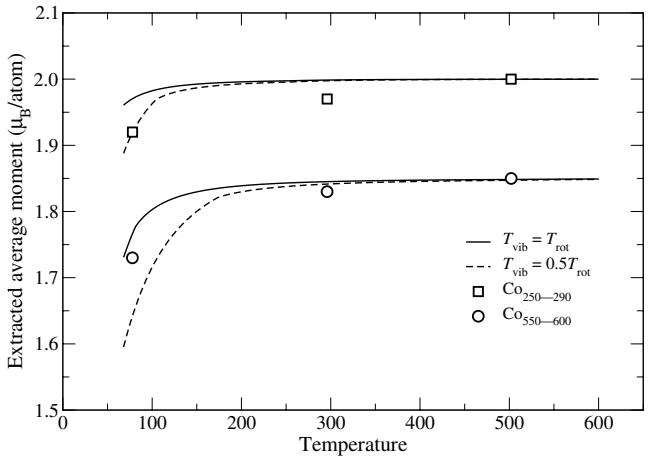

Figure 3. The extracted average magnetic moment of Co_{270} and Co_{575} as a function of the vibrational temperature using the Langevin relation. In calculating $\mu_{\rm eff}$, we have used $\mu = 2.05$ and $E_{\rm a} = 12$ meV for Co_{270}, $\mu = 1.85$ and $E_{\rm a} = 20$ meV for Co_{575}. The experimental data [1] are presented as open squares and circles.

We now return to consider in more detail the anomalous increase in magnetic moment with temperature derived from experiment. We make the assumption that the true saturated moment of a cluster is a constant at temperatures well below the bulk Curie temperature (1388 K for bulk Co [6]), and that the anomalous behaviour is in fact an artifact of the method of analysing the data. To investigate this assertion, we start with the assumed constant moment, and use equation (3) to obtain $\mu_{\rm eff}$ for a few typical clusters in a magnetic field ($\xi = 1$). This quantity provides a simulation of raw experimental data. The experimental magnetic moments [1] are extracted from the measured $\mu_{\rm eff}$ at small values of ξ (say $\xi \leqslant 1$) by using equation (1) without taking the MAE into account. Actually equation (3) itself represents the relation between $\mu_{\rm eff}$ and μ in certain limiting conditions (high field regime). In our analysis we have used a more general form valid for arbitrary fields, which cannot be reduced to a simple analytic expression. The details are given elsewhere [26] in a study of other features of the cluster beam experiments.

We then use the $\mu_{\rm eff}$ obtained as above to extract values for μ using the simple Langevin expression equation (1). This procedure provides a parallel to the experimental analysis. Our results are shown in figure 3 for two clusters. The calculated results for Co_{270} and Co_{575} are compared with the corresponding experimental data in figure 3. Note that we have ignored the cluster size distribution in the calculations. This should not affect the qualitative conclusion. The increase with temperature of the derived moment is remarkably similar to behaviour observed in the moments extracted from the experimental data.

In the calculations we have assigned values of 12 and 20 meV, respectively, to the $E_{\rm a}$ for Co_{270} and Co_{575}, guided by our calculated MAEs (see figure 2). Reasonable variations of the values of $E_{\rm a}$ and μ do not significantly affect the qualitative results. The cluster temperature depends on the dwell time inside the source nozzle, during which the clusters are cooled by the carrier gas He. The cooling of the rotational temperature $T_{\rm rot}$ is more efficient than that of the vibrational temperature $T_{\rm vib}$, which makes $T_{\rm vib} \geqslant T_{\rm rot}$ [2]. We have considered two possible values for the rotational temperature in figure 3. Either case shows a similar trend of an increasing moment. As a delicate property, the value of the MAE depends on the temperature.

It is generally believed that the MAE decreases with increasing temperature [22], which makes the effect of the MAE at low temperature even stronger. Generally, the qualitative features of the experimental results can be well captured by our idealized simple scenario.

The presence of MAE couples the freedoms of rotation, vibration and magnetization, which makes the relaxation process quite complicated. The uncertainty of T_{rot} makes it even harder to draw a quantitative conclusion [27]. Under the condition $k_{\mathrm{B}}T \ll E_{\mathrm{a}}$, the magnetic moment is fixed in the intrinsic frame of the cluster. This behaviour has been observed experimentally for gadolinium clusters [28]. In the locked moment scenario, the predicted effective magnetization as a function of the ratio of the magnetic energy $N\mu B$ to the rotational thermal energy $k_{\mathrm{B}}T_{\mathrm{rot}}$ is *smaller* than that of equation (1) and $2/3$ of the Langevin function in the low field [29]. Using the Langevin relation to extract the saturated moment will underestimate it at low temperature. For transition metal clusters like Co_N, E_{a} and $k_{\mathrm{B}}T$ are in the same order of magnitude. Our theoretical model, which considered both freedoms of the vibration and rotation, is a reasonable approach.

4. Conclusions

We have demonstrated the important role that the MAE can play in interpreting cluster beam experiments and in deducing magnetic moments from them. In particular we have shown that the anomalous increase in moment deduced from work on cobalt clusters can be convincingly explained by this effect. Clearly the precise results depend on the size of the anisotropy energies and the experimental temperatures. However, using values similar to those calculated for the MAE, it would appear that the experimental results can be convincingly interpreted as indicative of a constant rather than an increasing moment at temperatures below about 500 K.

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