Magnetic Moments of Iron Clusters with 25 to 700 Atoms and Their Dependence on Temperature

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Magnetic moments $\mu(N)$ of iron clusters in a molecular beam, with temperatures ranging from 100 to 1000 K, are investigated from their Stern-Gerlach deflections. We find that at a temperature of 120 K, μ ($25 \leq N \leq 130$) is $3\mu_B$ per atom, decreasing to about the bulk value ($2.2\mu_B$ per atom) near $N=500$. For all sizes, μ decreases with increasing temperature, and is approximately constant above a temperature $T_C(N)$. For example, $T_C(130)$ is about 700 K, and $T_C(550)$ is about 550 K (T_C bulk = 1043 K). Limitations of the superparamagnetic model due to rotational effects are discussed.

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Ferromagnetism is caused by the spontaneous mutual alignment of magnetic moments. This effect, caused by the exchange interaction mediated by the itinerant electrons, is well understood in the bulk. However, much less is known about ferromagnetism in small systems such as thin films and very small particles or clusters. A fascinating, still open question is how ferromagnetic properties evolve from the atom via clusters to the bulk. The molecular beam is ideally suited to study this problem [1], but since most experiments in this interesting size regime have concentrated on very small ferromagnetic particles embedded in a host matrix [2], we first briefly review some of their relevant properties.

In a magnetic field B, the magnetic moment μ of a monodomain particle tends to align with B. However, thermal motion counteracts the alignment, so that in equilibrium the magnetization M is related to the temperature and field by $M=\mu L(\mu B/kT)$, where L is the Langevin function [3]. By definition M is the average projection of μ along the magnetic field direction: $M=|\boldsymbol{\mu}\cdot\mathbf{B}|/B$. For small values of the argument this simplifies to

$$M=\mu^2 B/3kT. \quad (1)$$

In this model the particles are treated as if they were paramagnetic with large magnetic moments (and hence are called superparamagnetic [4]). The large moment in turn is caused by the ferromagnetic alignment of the atomic moments μ_0, so that (at low temperatures T) $\mu \approx N\mu_0$ [4], where N is the number of atoms in the particle. However, μ also depends on T and vanishes at a sufficiently high temperature.

In earlier work we found that very small iron clusters are ferromagnetic. Furthermore, we observed that spin relaxation occurs even when the clusters are isolated in the molecular beam [1]. This was in fact unexpected since it contradicted an earlier similar experiment [5]. Spin relaxation in turn suggests a thermodynamic treatment, leading to the superparamagnetic model (however, see Ref. [6] for an alternative). In contrast, our experiments show a reversed temperature dependence when the clusters are cooled in the supersonic expansion of the source [1,7]. We attributed these effects to the cluster rotations. Curiously, when they are not thus cooled, the superparamagnetic model does apply [7]. In this Letter, we first investigate the applicability of the superparamagnetic model. This requires some background in supersonic beam properties. Next we discuss the temperature dependence of the magnetic moments of iron clusters with 25 to 700 atoms.

In our experiments clusters are formed in a laser vaporization cluster source with He carrier gas (see Refs. [1,8] for detailed descriptions). In this source the nozzle temperature T_{noz} can be adjusted between 100 and 1000 K. The beam is collimated and the clusters are deflected in the field of a Stern-Gerlach magnet. Deflections of mass selected clusters are measured using a time-of-flight mass spectrometer by sweeping the collimated ionizing light from an excimer laser across the cluster beam and synchronously recording the selected cluster ion intensity. The magnetization of the cluster is related to its deflection by $d=K(dB/dz)M/Nm_0v^2$ where d is the deflection, v is the velocity, Nm_0 is the mass, K is a constant, and dB/dz is the field gradient in the Stern-Gerlach magnet. Cluster velocities and dwell times (see below) are determined using a beam chopper mounted in front of the source.

In the laser vaporization cluster source a pulse of He gas fills a 1 cm^3 cavity at time $t=0$, coincident with the laser pulse [8]. The clusters are formed and thermalize in the cavity within 1 μs [9,10], after which the gas/cluster mixture is ejected out of the nozzle. Hence the helium pressure in the cavity P_{He} is time dependent. In particular, from the He flow rates [9] we find that $P_{He}(t) \approx P_0 e-(t-t_0)/\tau$, where $P_0=100$–200 Torr, $t_0 \approx 100$ μs, and $\tau \approx 150$–200 μs. Clusters are selected depending on the time they exit the nozzle (i.e., their dwell time t). This is important because the clusters are cooled due to the adiabatic expansion of the helium into the vacuum [9]. In particular, when the P_{He} is high, the beam is supersonic and the cooling is effective. The cooling is less effective when the pressures are reduced and ultimately, for very low P_{He} the clusters are not cooled [9]. (For brevity we call this source condition quasief-

fusive.) In that case the cluster temperature is essentially equal to T_{noz}.

However, the cooling of the different degrees of freedom of the clusters occurs at different rates. Consequently $T_{noz} > T_{vib} > T_{rot} > T_{He}$, where T_{vib} is the vibrational, T_{rot} is the rotational temperature of the cluster, and T_{He} is the final temperature of the He beam itself [9,10]. We estimate T_{He} to be about 9 K (for $T_{noz}=300$ K) at the peak P_{He}, corresponding to a Mach 10 supersonic beam [10]. As a consequence, the temperatures of clusters selected with short dwell times are lower than T_{noz}, while for long dwell times the temperatures are essentially equal to T_{noz}. These temperature trends correspond with our earlier claims [1] which we later verified in independent experiments [11]. Using molecular dynamics, Ballone and Mareschal [10] recently calculated the cooling of the various degrees of freedom for iron clusters under both static and supersonic expansion conditions. Their results are consistent with the description given above.

With this background on cluster temperatures the predictions of the superparamagnetic model [i.e., Eq. (1)] can be tested. In fact, we showed that for supersonically cooled iron clusters the magnetization is reduced compared with quasieffusive clusters. This can be seen in Fig. 1(a). Note that M increases with increasing t and then becomes constant after sufficiently long t. This limit corresponds to quasieffusive conditions where the cluster temperature equals T_{noz}, and where we find that M depends inversely on the temperature consistent with Eq. (1). In contrast, for small t (i.e., in the supersonic limit), M becomes very small. In fact the magnetization for $T_{noz}=120$ K is smaller than for $T_{noz}=320$ K. (These observations have been confirmed by Persson [12], but refuted by Bucher and co-workers [13].)

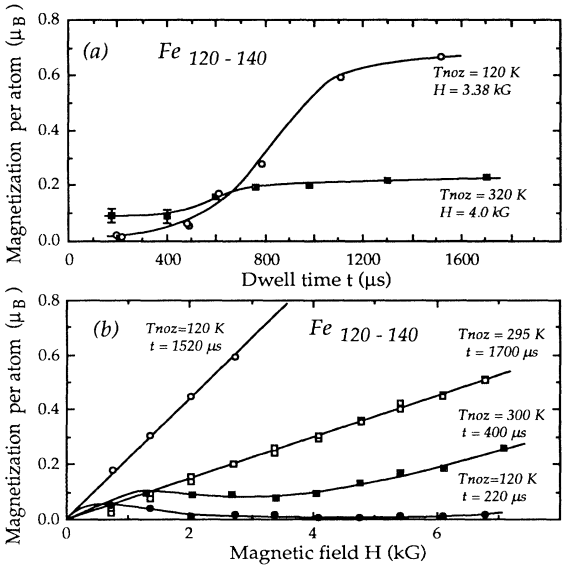

FIG. 1. Magnetization of $Fe_{120-140}$: (a) as a function of the dwell time in the source t; (b) as a function of H. For long dwell times, M saturates and depends linearly on B, and inversely on T_{vib} ($\approx T_{noz}$) consistent with the superparamagnetic model. For small t the rotations are cooled and the model no longer applies.

Figure 1(b) shows M as function of B for several source conditions giving deeper insight into the effect of the supersonic expansion. For the quasieffusive conditions (i.e., $T_{noz}=120$ K, $t=1520$ μs; $T_{noz}=295$ K, $t=1700$ μs) the magnetization is linear with B and depends inversely on T_{noz}. On the other hand, for the supersonic conditions (i.e., $T_{noz}=120$ K, $t=220$ μs; $T_{noz}=300$ K, $t=400$ μs), M is not linear with B and is greatly reduced compared with the quasieffusive conditions. Note in particular for $T_{noz}=120$ K, $t=220$ μs, and $B=2.70$ kG, M is about 100 times smaller than for $T_{noz}=120$ K, $t=1520$ μs at the same field. If we applied Eq. (1), we would find that the clusters had a temperature of more than 12000 K, showing how dramatically the superparamagnetic model fails for supersonically cooled clusters [14]. However, for quasieffusive clusters the model applies very well, judging from the temperature and field dependence of M.

These observations show that the magnetization must depend on more than B and T_{vib}. In fact there is compelling evidence that the observed anomalies are related to T_{rot} (which may become very low in the supersonic expansion [9,10]). Specifically, we find that the anomalies can be explained with a resonant spin-rotation coupling which strongly reduces the magnetization when the precession frequency of μ in the magnetic field B (i.e., the Larmor frequency) is near a multiple of the rotational frequency. When T_{rot} is sufficiently low, the fields required to reach the resonant condition are within the experimental range thereby explaining the dependence on the supersonic condition. Details of this fascinating effect are in Ref. [7]; see Ref. [15] for recent calculations.

We next concentrate on the quasieffusive conditions, where the temperatures are well defined, and the superparamagnetic model applies. The magnetic moments of clusters ranging from 30 to 600 atoms per cluster were determined from the magnetization data using Eq. (1). Figure 2 shows the average magnetic moment per atom $\bar{\mu}(N,T)=\mu(N,T)/N$ as a function of temperature for five cluster size ranges.

In general $\bar{\mu}$ decreases with increasing temperature. For Fe_{50-60}, $\bar{\mu}$ shows a gradual reduction from $3\mu_B$ at 120 K to $1.53\mu_B$ at 800 K. The $Fe_{120-140}$ data show more features: $\bar{\mu}$ is approximately constant ($\approx 3\mu_B$) below $T=400$ K and then decreases to about $0.7\mu_B$ at 700 K whereafter it levels off (and perhaps increases slightly). The size range Fe_{82-92} is intermediate between these two, resembling $Fe_{120-140}$ below and Fe_{50-60} above 400 K.

On the other hand, for the two larger size ranges ($Fe_{250-290}$; $Fe_{500-600}$) the low temperature $\bar{\mu}$ values are reduced and decrease with increasing temperature. In both cases $\bar{\mu}$ levels off at about $0.4\mu_B$. For $Fe_{250-290}$ this occurs at about $T=700$ K, whereas for $Fe_{500-600}$ the tran-

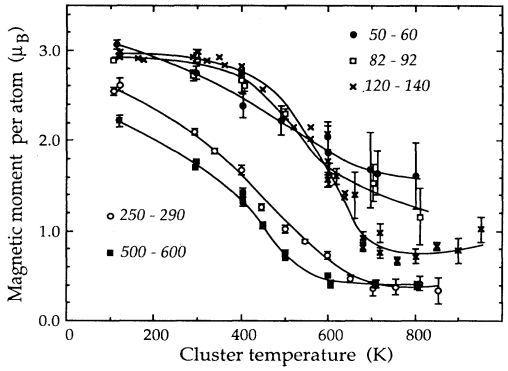

FIG. 2. Iron cluster magnetic moments per atom as a function of temperature for five size ranges. The uncertainty of the vertical scale is estimated to be 7%.

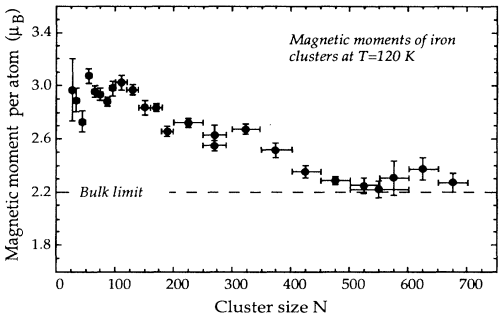

FIG. 3. Iron cluster magnetic moments per atom at $T=120$ K. Horizontal bars indicate cluster size ranges.

sition is between $T=500$ and 600 K. Overall it is seen that the limiting values for $\bar{\mu}$ are reached at lower temperatures the larger the cluster: i.e., for Fe_{50-60} and Fe_{82-92}, $T_C > 800$ K; for $Fe_{120-140}$ and $Fe_{250-290}$, $T_C \approx 700$ K; and for $Fe_{500-600}$, $T_C \approx 600$ K.

This behavior can be compared with the bulk $\bar{\mu}$ (i.e., from the saturation magnetization as a function of temperature), where $\bar{\mu}=2.2\mu_B$ at $T=0$ (and $d\bar{\mu}/dT=0$). With increasing temperature, $\bar{\mu}$ decreases, finally vanishing at the Curie temperature $T_C=1043$ K. The reduction of $\bar{\mu}$ is related to the thermally induced disorder in the mutual alignment of the spins [3,16]. At the Curie temperature $\bar{\mu}$ vanishes.

Theoretically, from Heisenberg model calculations applied to clusters [17], one finds a decrease of $\bar{\mu}$ with increasing temperature gradually leveling off to $\bar{\mu}(T=0)/\sqrt{N}$ for temperatures above the bulk Curie temperature. Although we qualitatively observe some resemblance with these predictions, there is no detailed agreement. For example, the reduction of T_C with increasing N (to about 0.5 of the bulk T_C for $N=500$–600) is inconsistent with the model. (Similar Curie temperature reductions are observed for thin films, however, T_C increases as the film thickness increases [18].) This is not surprising since the Heisenberg model, which does not take into account possible temperature dependence of the exchange interaction and neglects long range interactions, is not expected to be very predictive.

These considerations notwithstanding, it is puzzling that the high temperature values are significantly larger than predicted [i.e., $\bar{\mu}(T>T_C)\approx\bar{\mu}(T=0)/\sqrt{N}$]. This is important since this value simply represents the sum of N randomly oriented atomic magnetic moments (i.e., for $T>T_C$), hence should be model independent. Perhaps this indicates that the magnetic system has more than one component (for example, the surface and the interior) with different Curie temperatures.

We also measured the magnetic moments as a function of cluster size at 120 K and Fig. 3 shows the results for $N=25$–700. Up to about $N=120$, $\bar{\mu}$ is about $3\mu_B$ with relatively large oscillations and maxima near $N=55$ and 110. Next $\bar{\mu}$ gradually decreases from $3\mu_B$ at $N=240$ to $2.2\mu_B$ at $N=520$, and for larger sizes it is approximately constant. However, oscillations are seen with maxima near $N=325$ and 625 (and perhaps one near $N=225$).

Qualitatively several features can be understood from properties of iron [3,16]. Iron has 8 valence electrons per atom of which approximately 7 are in the $3d$ bands and 1 is in the $4s$ band. In the case that the $3d$ spin up (majority) band is fully polarized it is occupied with 5 electrons (since it is completely below the Fermi level) leaving 2 electrons in the $3d$ spin down (minority) band. Consequently, each atom contributes $\mu_0=(5-2)\mu_B=3\mu_B$ to the total moment. On the other hand, if both bands are only partly occupied (i.e., intersect the Fermi level), μ_0 is reduced to less than $3\mu_B$. This is the case for bulk iron where μ_0 is approximately $2.2\mu_B$ [3]. Applying this reasoning to Fig. 3, it appears that the fully polarized majority spin band case applies for small clusters ($N<140$). Between $N\approx140$ and $N\approx550$ there seems to be a gradual transition from the fully polarized band to a more bulklike situation, and for larger N the magnetic moment corresponds approximately with the bulk value. Note, however, that these measurements were made at $T=120$ K where the slope $d\bar{\mu}/dT$ is negative (see Fig. 2), so that in particular for the larger sizes these values are lower limits for $\bar{\mu}(T=0)$.

These trends are in qualitative agreement with tight binding calculations by Pastor, Dorantes-Davila, and Bennemann [19] (see also Ref. [20]), who find for small clusters that $\bar{\mu}(T=0)$ is about $3\mu_B$ whereas larger ones approach $2.2\mu_B$, however, they find that the transition occurs for smaller sizes than observed experimentally. Furthermore, the calculations reveal a strong structural dependence on $\bar{\mu}$. This latter effect could cause the observed oscillations. For example, icosahedra can be constructed with $N=13,55,147,309,561,923$ corresponding to respectively 1 to 6 layers of atoms. Experimentally, $N\approx55$ is found to give a maximum in μ. However, the other maxima (except the one at 309) do not correspond.

Nevertheless, we do see 5 oscillations between $N=25$ and $N=700$ while in this same interval 5 layers of atoms are added to the cluster.

In summary, these results provide considerable insight into the evolution of the magnetic properties of iron particles as their size increases. The decrease of $\bar{\mu}(T=120\ \mathrm{K})$ from $3\mu_B$ to $2.2\mu_B$ is in principle understood. However, even for the largest clusters investigated it is clear that the bulk limit has not been reached, since for these clusters the apparent Curie temperature is about a factor of 2 lower than the bulk value. Since for $N\approx 600$, T_C still seems to be decreasing with increasing size, it is not possible to extrapolate where this trend will change direction and converge to the bulk limit.

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