Magnetic Behavior of Clusters of Ferromagnetic Transition Metals

S. N. Khanna
Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000

S. Linderoth
Laboratory of Applied Physics, Technical University of Denmark, DK-2800, Lyngby, Denmark
(Received 22 January 1991)

The effective magnetic moments of small iron and cobalt clusters have been calculated by assuming that the clusters undergo superparamagnetic relaxation. The effective moments per atom are found to be much below the bulk values, even at low temperatures (100 K). They increase with particle size and the applied magnetic field, and are in good agreement with recent beam experiments on Fe_N and Co_N clusters. We also provide the first realistic estimates of the true magnetic moments in small Co_N clusters. The present studies cast doubt on the recent theoretical interpretation of the observed reduced magnetic moments in small clusters compared to bulk as being due to melting of surface spins.

PACS numbers: 75.60.Jp, 36.40.+d, 73.20.Dx

Recent developments in experimental techniques have permitted researchers to generate, characterize, and study size-selected clusters in beams [1]. One of the areas currently being pursued is the magnetic behavior of clusters of ferromagnetic elements [2,3] such as Fe and Co. There are several reasons for such an interest. It is well known [4] that the magnetic moment of a ferromagnetic solid can be enhanced by reducing the dimensionality. For example, chains of ferromagnetic atoms are more magnetic than the planes and the planes are more magnetic than the bulk. Since a large fraction of atoms in a cluster are surface atoms, one expects clusters of these elements to exhibit large magnetic moments. Studies on clusters are also important for understanding how the magnetic behavior evolves as one reduces the size to clusters smaller than single domains and to answer whether the finite-size effects are observable due to the small dimension of the clusters.

In a recent experiment [2], de Heer, Milani, and Châtelain investigated the magnetic behavior of Fe clusters containing between 50 and 500 atoms. They generated size-selected clusters in a molecular beam and used the Stern-Gerlach profiles to determine the average effective moment μ_{eff} per atom. Surprisingly, they found that the μ_{eff} of clusters are far below the bulk moments of Fe. The experiment also showed three interesting features. (1) μ_{eff} was found to increase with the magnetic field H. The increase was linear for small fields. (2) μ_{eff} also increased with particle size N. (3) For small relaxation times, μ_{eff} apparently increased with temperature. Bucher *et al.* [3] have recently measured the μ_{eff} for Co_N clusters having 20–200 atoms. They also find that μ_{eff} increases with magnetic field and particle size. The increase with particle size is linear for clusters containing 20–110 atoms, indicating that μ_{eff} varies linearly at small sizes. The experimental setup used by Bucher *et al.* differs from that of de Heer, Milani, and Châtelain in that one can control the residency and the flight time of the clusters. By increasing the residency time, the cluster temperatures T can be made closer to source temperatures, and hence one can estimate the real temperatures of the clusters. These measurements, together with the theoretical model in this paper, provide, for the first time, a means for determining the actual cluster moments. The experimental findings of de Heer, Milani, and Châtelain and of Bucher *et al.* are in apparent disagreement with earlier Stern-Gerlach experiments on Fe_N clusters by Cox *et al.* [5] who found that Fe_N clusters containing 2–17 atoms have higher moments than in bulk.

In an attempt to resolve the above confusion Merikoski *et al.* [6] have recently proposed that the reduced magnetic moment for Fe_N clusters observed by de Heer, Milani, and Châtelain is due to thermal disorder of the surface spins. These authors suggest that the clusters have high spin temperatures and the surface spins which are weakly coupled compared to the bulk spins are disordered at cluster temperatures. The only magnetization is then due to the interior bulk spins. They have carried out Monte Carlo simulations by modeling the clusters as Ising spins with nearest-neighbor interaction on a fcc lattice. Their results for certain cluster temperatures do predict an increase of magnetization with size and magnetic field. A linear increase for small magnetic fields is obtained when the temperatures are above the Curie temperature, i.e., $k_BT/J=9.0$, where J is the exchange integral [6]. Taking $J=11.9$ meV for Fe [7], this corresponds to a temperature of about 1200 K. This temperature is much higher than the experimental cluster temperatures [2] that range between 75 and 225 K. One also notices that the magnetic fields needed to obtain the experimentally observed magnetization in such a model are extremely high. For example, the smallest field needed to observe $\mu_{\text{eff}}=0.2\mu_B$ for 225-atom clusters is $\sim 0.1(J/g)/\mu_B \approx 10$ T, which should be compared to the experimental fields of 0.2 T for similar sizes (we have used $g=2$). For Co_N clusters where the temperatures are ex-

perimentally known, this model would lead to μ_{eff} orders of magnitude smaller than the observed values at the experimental fields.

In this Letter we propose that the small ferromagnetic clusters possess superparamagnetic relaxation. We assume that the clusters are smaller than critical sizes for single domains, that the atomic moments in a cluster are ferromagnetically aligned, and that the magnetic anisotropy energy is much smaller than the thermal energy. This makes the clusters behave like paramagnetic atoms [8]. In the absence of an external magnetic field, the net magnetization in any given direction is zero. As the magnetic field is applied, the clusters develop a magnetic moment on time scales depending on the relaxation time. Using such a picture, we calculate μ_{eff} as a function of the magnetic field and the cluster size. The calculated μ_{eff} not only explain the experimental trends, but are in quantitative agreement with experiment. Using our model in conjunction with the recent results on Co_N clusters where the cluster temperatures are known, we provide, for the first time, realistic estimates of μ for small clusters. We show that μ in small Co_N clusters is indeed larger than the bulk value.

We start by considering an estimate of the relaxation time. The superparamagnetic relaxation can be described by the Arrhenius law with a relaxation time τ given by [9]

$$\tau = \tau_0 e^{CV/k_B T}. \tag{1}$$

In this expression C is the magnetic anisotropy energy per unit volume, T is the temperature, and V is the volume of the cluster. The value of τ_0 depends on the gyromagnetic precession time and is usually $\sim 10^{-10}$–10^{-13} s [9]. Since the clusters in beams are fairly isolated, one can ignore the cluster-cluster interactions. The value of C then depends on the electronic structure, shape, stress, and size of the cluster, and this can make it very different from its bulk value. Xia *et al.* [10] have carried out magnetization measurements on granular alloys of Fe in matrices and have determined $C \approx 2\times 10^7$ ergs/cm^3 for 20–40-Å Fe particles, which is much larger than the bulk value of 1×10^5 ergs/cm^3. The substantially larger anisotropy constant for small particles suggests that the contributions due to stress and surface anisotropies become most important. The value of C therefore increases with decreasing particle size. For free clusters, the stress-induced anisotropy is probably negligible, but the large fraction of surface atoms can increase C. However, in the absence of any knowledge about C in small clusters, we have used $C = 2\times 10^7$ ergs/cm^3. For Fe clusters containing 120–140 atoms, the relaxation time at 100 K is then about 1–1000 ps, which is substantially smaller than the passage time (~ 100 μs) for the clusters. Hence the clusters can be assumed to perform superparamagnetic relaxation.

We now consider the effective magnetic moment per atom, μ_{eff}, in the direction of the field H for an assembly of clusters at a temperature T. If μ is the moment of each atom and the cluster has N atoms, the total cluster moment will be $N\mu$. In reality the cluster moment $N\mu$ will be determined by the geometry of the clusters. Unfortunately, cluster calculations are not available for all cluster sizes and μ in clusters is not known. We have, therefore, assumed that μ in Fe clusters has the same value as in bulk Fe [4], namely, $2.2\mu_B$. For small magnetic anisotropy, the cluster moments $N\mu$ will exhibit a Boltzmann distribution of orientations with respect to H at thermal equilibrium. The μ_{eff} is then given by the classical expression

$$\mu_{\text{eff}} = \mu\left[\coth\left(\frac{N\mu H}{k_B T}\right) - \frac{k_B T}{N\mu H}\right]. \tag{2}$$

In Fig. 1 we show the μ_{eff} calculated using Eq. (2) for clusters containing 64, 130, and 240 atoms. These cluster sizes correspond to the average sizes for which de Heer, Milani, and Châtelain have measured μ_{eff} experimentally. We also show in Fig. 1 their measured μ_{eff} corresponding to clusters having 56–72, 120–140, and 225–256 atoms. Since the temperatures of the clusters are not known we determined μ_{eff} for various T values and found that the theoretical curves better represent the experimental data at $T = 135$ K for 64-atom clusters, $T = 146$ K for 130-atom clusters, and $T = 230$ K for 240-atom clusters. It is interesting to note that the theoretical curves are in good agreement with experiment. We would like to point out that these temperatures are based on the assumption that μ is the same for all cluster sizes. Since the parameter controlling the paramagnetic behavior is μ^2/T, any variations in μ with cluster size would alter the above temperature estimates. de Heer, Milani, and Châtelain estimat-

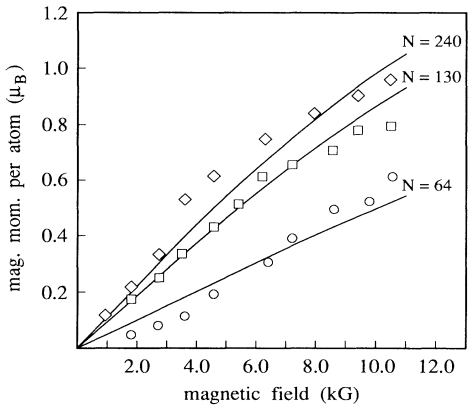

FIG. 1. Magnetic moment per atom as a function of magnetic field for Fe_N clusters having 64, 130, and 240 atoms calculated using Eq. (2) and temperatures of 135, 146, and 230 K, respectively. Continuous curves are the theoretical values and ○, □, and ◇ are the experimental results [2] corresponding to clusters having 56–72, 120–140, and 225–256 atoms, respectively.

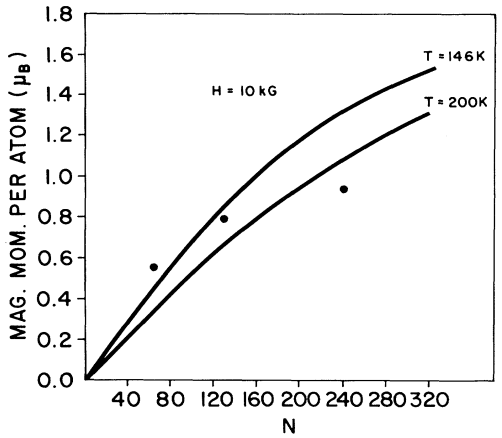

FIG. 2. Variation of the magnetic moment per atom as a function of the number of atoms in Fe clusters for temperatures of 146 and 200 K. Solid circles are the experimental values [2].

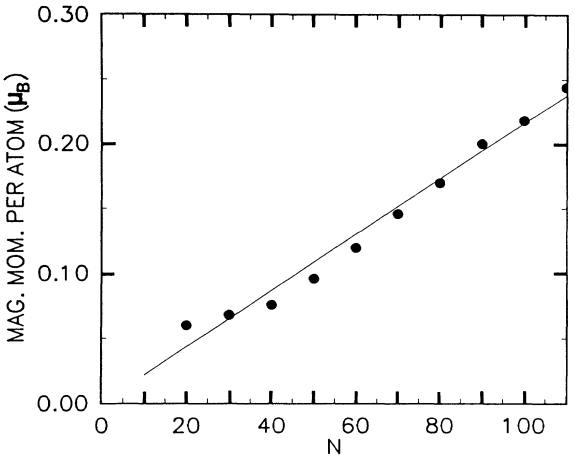

FIG. 3. Variation of the magnetic moment per atom as a function of the number of atoms in Co clusters for $T=170$ K and $H=0.53$ T. Continuous curve is the theoretical values and solid circles are the experimental results [3].

ed the cluster temperatures to be between 75 and 225 K. The theoretical temperatures $135 \leq T \leq 230$ lie in the experimental range. The theoretical increase in μ_{eff} with H is linear at low fields as also shown by experiments. This is also clear from Eq. (2), since in the limit of $N\mu H \ll k_B T$, Eq. (2) reduces to

$$\mu_{\text{eff}} \approx N\mu^2 H/3k_B T\,, \tag{3}$$

showing that μ_{eff} varies linearly with H for low fields.

We now consider the variation of μ_{eff} with particle size. In Fig. 2 we show μ_{eff} as a function of N for $H=10$ kG and $T=146$ and 200 K. It is clearly seen that μ_{eff} increases with the particle size. We have also shown in Fig. 2 the experimental μ_{eff} for clusters with mean sizes 64, 130, and 240 atoms. As mentioned above, the observed μ_{eff} indicate that the temperature of the clusters is increasing with size.

We now discuss the measurements of Bucher *et al.* [3] on Co_N clusters. The unique aspect of these measurements is the possibility to isolate the residency and the flight time of clusters. By making measurements as a function of residency time indicating the period during which the clusters equilibrate with the carrier gas, one can bring cluster temperatures closer to the surrounding source temperatures. For 115-atom Co_N clusters, these authors find that the measured μ_{eff} increases with the residency time and saturates to a constant value of $0.402\mu_B$ for residency times longer than 1.6 ms at fields $H=0.307$ T and temperature $T=83$ K. These measured values allow one to determine μ in clusters using Eq. (2). One obtains $\mu=2.08\mu_B$. A comparison of this value with the bulk moment of $1.72\mu_B$ shows that the moment in small clusters is indeed enhanced over the bulk value (by about 20%). Bucher *et al.* have also measured μ_{eff} in Co clusters having between 20 and 110 atoms for residency times of 850 μs and source temperature 82 ± 1 K. Since the measurement as a function of residency time indicates that it takes about 1.6 ms for the clusters to attain source temperatures, these clusters have temperatures higher than the source temperatures. Employing Eq. (1) and μ_{eff} for Co_{85} clusters determined above, the cluster temperature can be estimated to be 277 K. Assuming this temperature for all clusters and $\mu=2.08\mu_B$, μ_{eff} vs N can be calculated. This is shown in Fig. 3, along with the experimental values. One finds a remarkable agreement between the calculated and the experimental data, establishing, once again, the validity of the theoretical model.

To conclude, we have shown that the observed magnetic behavior of transition-metal clusters can be understood by assuming that they are superparamagnetic particles. We have assumed the atomic moments to be ferromagnetically aligned, i.e., disregarding the internal spin excitations. The decrease in the measured moments with decreasing size seen in recent experiments is then a consequence of fluctuations due to thermal and rotational effects. We would like to add that Eq. (2) is valid only in the limit of vanishing magnetic anisotropy. This will not be the case if the clusters are so cold that the thermal energies are less than the magnetic anisotropy energies. At these temperatures, the moments will be blocked and the cluster would exhibit spontaneous magnetization. We have also ignored effects arising due to detailed cluster shapes and isomers. These are being investigated and will be published in a coming paper.

This work was supported in part by a grant from the Army Research Office (DAAL-03-89-K-0015). One of us (S.N.K.) is grateful to L. Bloomfield and J. P. Bucher for discussions.

[1] *Small Particles and Inorganic Clusters,* edited by C.

Chapon, M. F. Gillet, and C. R. Henry [Z. Phys. D **12** (1989)]; *Physics and Chemistry of Small Clusters,* edited by P. Jena, B. K. Rao, and S. N. Khanna (Plenum, New York, 1987).
[2] W. A. de Heer, P. Milani, and A. Châtelain, Phys. Rev. Lett. **65**, 488 (1990).
[3] J. P. Bucher, D. C. Douglas, P. Xia, B. Haynes, and L. A. Bloomfield, Z. Phys. D (to be published).
[4] F. Liu, M. R. Press, S. N. Khanna, and P. Jena, Phys. Rev. B **39**, 6914 (1989).
[5] D. M. Cox, D. J. Trevor, R. L. Whetten, E. A. Rohlfing, and A. Kaldor, Phys. Rev. B **32**, 7290 (1985).
[6] J. Merikoski, J. Timonen, M. Manninen, and P. Jena, Phys. Rev. Lett. **66**, 938 (1991).
[7] *Introduction of Solid State Theory,* edited by C. Kittel (Wiley, New York, 1971), p. 532.
[8] L. Néel, C. R. Acad. Sci. **224**, 1488 (1947).
[9] I. S. Jacobs and C. P. Bean, in *Magnetism,* edited by G. T. Rado and H. Suhl (Academic, New York, 1963).
[10] G. Xia, S. H. Liou, A. Levy, J. N. Taylor, and C. L. Chien, Phys. Rev. B **34**, 7573 (1986).