Ferromagnetism in Small Clusters

J. Merikoski, J. Timonen, and M. Manninen
Department of Physics, University of Jyväskylä, SF-40100 Jyväskylä, Finland

P. Jena
Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284
(Received 1 October 1990)

Magnetization of small ferromagnetic clusters at finite temperatures has been studied using the Ising model and Monte Carlo techniques. The magnetization of finite clusters is reduced from the bulk value, and increases with the external magnetic field and with the cluster size. The results explain qualitatively the recent observations by de Heer, Milani, and Chatelain of the reduction with decreasing cluster size of the average magnetic moment in small iron clusters.

PACS numbers: 75.40.Mg, 05.50.+q, 36.40.+d

In a recent experiment on iron clusters consisting of 50 to 230 atoms, de Heer, Milani, and Chatelain[1] have found that the magnetization of these clusters increases with increasing size and applied magnetic field. They have concluded that the average magnetic moment per atom *increases* as clusters grow. This conclusion is in contrast not only to an earlier experimental study[2] on Fe clusters but also to a large number of theoretical calculations[3-8] on magnetic materials with reduced size and dimensionality. Experimentally, the size and dimensionality of materials can be controlled by growing them as clusters,[1,9] multilayers, and modulated structures.[10] These systems exhibit novel electronic and magnetic properties and are the subject of intense theoretical and experimental investigation. Magnetic properties of clusters of both magnetic and nonmagnetic elements have, for example, been shown to exhibit quantum size effects.[11-14] The calculated and observed trends are related[8] to the reduction in the average coordination number of the magnetic atom as the size or dimensionality of the system is lowered. This behavior can be understood qualitatively by recognizing that a lower coordination number causes a decrease in the orbital overlap between neighboring atoms, and, consequently, enhances the magnetic moment.

In this Letter we address the apparent contradiction between the recent result of de Heer, Milani, and Chatelain[1] and the vast existing literature[2-8] on the magnetic moments of systems with low dimensionality and small size. Using the familiar Ising model and the Monte Carlo method, we have calculated the temperature, external-magnetic-field, and cluster-size dependence of the magnetization of ferromagnetic clusters. We show that, even at temperatures well below the Curie temperature of the bulk metal, the magnetization of these clusters is reduced from the bulk value and increases with the external magnetic field. These results are in good agreement with those reported in Ref. 1. Therefore, we believe that the decrease in the magnetic moment observed in this experiment is due to the statistical behavior at finite temperatures of the clusters which have been studied. The temperature and size dependences of the magnetization of these clusters are large enough to completely mask any possible change in the value of the magnetic moments. We further show that the experimentally observed time dependence of the magnetization is related to the temperature dependence of the spin-lattice relaxation time.

For simplicity we use a model with localized spins, and because the behavior of the magnetization is not very sensitive to the actual form of the spin interactions,[15] we have used the nearest-neighbor Ising model,

$$H = J\sum_{\langle i,j\rangle} S_i S_j - g\mu_B B \sum_{i=1}^{N} S_i \,, \tag{1}$$

where $\langle i,j\rangle$ denotes a pair of nearest neighbors and $S_i = \pm 1$ is the spin variable at site i. We have assumed an fcc lattice structure for the clusters. These are formed such that layers of successive neighbors are added to an atom in the center. In this Letter we report results only for clusters with complete shells. The twelve smallest clusters are shown in Table I. Note that it is

TABLE I. Shell structure of twelve smallest clusters. N_j and C_j denote the number of spins and the average number of nearest neighbors of the spins in shell j, respectively.

Shell	N_j	$N=\sum N_j$	$C_j(N=55)$	$C_j(N=135)$	$C_j(N=225)$
1	1	1	12	12	12
2	12	13	12	12	12
3	6	19	8	12	12
4	24	43	7	12	12
5	12	55	5	11	12
6	24	79		8	12
7	8	87		9	12
8	48	135		6	10
9	6	141			8
10	36	177			7
11	24	201			6
12	24	225			5

not necessary to have an atom in the center of the cluster; we could equally well have chosen, e.g., a tetrahedral or an octahedral site to be the center.

The equilibrium properties of the clusters and the dependence of the average magnetization on temperature T (in units of $J k_B^{-1}$) and on the external field B (in units of $J\ g^{-1}\mu_B^{-1}$) are well described[15] by Monte Carlo simulations. The details of the relaxation mechanisms are not well understood in the iron-group metals,[16,17] so we use the usual transition probability together with importance sampling. The time-dependent magnetization of the clusters[1] relates to nonequilibrium properties which cannot be described by this method, but the time-dependent data[1] can nevertheless be qualitatively explained.

In the Monte Carlo (MC) simulations we have mostly used 3000 MC steps per spin which gives a reasonably smooth magnetization for clusters with $N > 100$. For smaller clusters we have occasionally used averaging over a few independent runs to reduce fluctuations.

We show in Fig. 1 our results for the magnetization per spin in zero external field as a function of temperature for a few clusters. It is evident that, below or slightly above the Curie temperature of the smallest cluster, magnetization increases with the cluster size. At temperatures well above the Curie temperatures the converse is true; the decay with temperature of the magnetization is slowest for the smallest cluster. The latter feature is a result of increasing fluctuations with decreasing size of the cluster, and of considering the absolute value of the magnetization. Close to the Curie temperature the average Monte Carlo magnetization drops very fast to zero because of rapid fluctuations in the sign of the magnetization. Our results agree with previous findings for Ising spins on a simple-cubic lattice.[18]

The increase of magnetization with the cluster size results from decreasing magnetization per spin with increasing shell number, and adding a new shell has the effect of pushing the inner shells towards higher magnetization. A similar behavior has been observed before in the studies of surface magnetization,[18] and it can easily be understood in terms of an effective field produced at each site by the neighboring spins.

In Fig. 2 we show the magnetization of three clusters of different size as a function of the external magnetic field for two different temperatures. The higher temperature is slightly above the Curie temperature of the largest cluster, and the lower temperature is between the Curie temperatures of the two smallest clusters. As expected, above the Curie temperature magnetization approaches zero with decreasing external field. This is the behavior observed in the experiments,[1] and it is therefore quite obvious that the *spin* temperature of the clusters in these experiments has been above the Curie temperature. It is also evident from Fig. 2 that the average magnetization increases with the cluster size in agreement with the

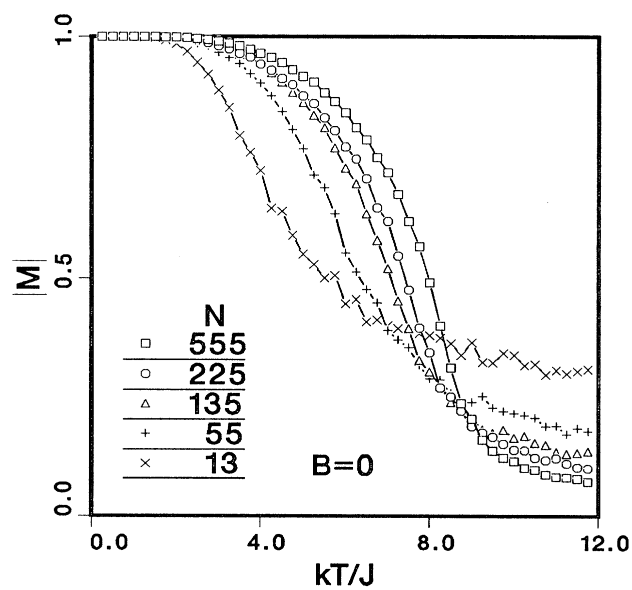

FIG. 1. The temperature dependence of the absolute value of the magnetization in zero external field of five small Ising clusters.

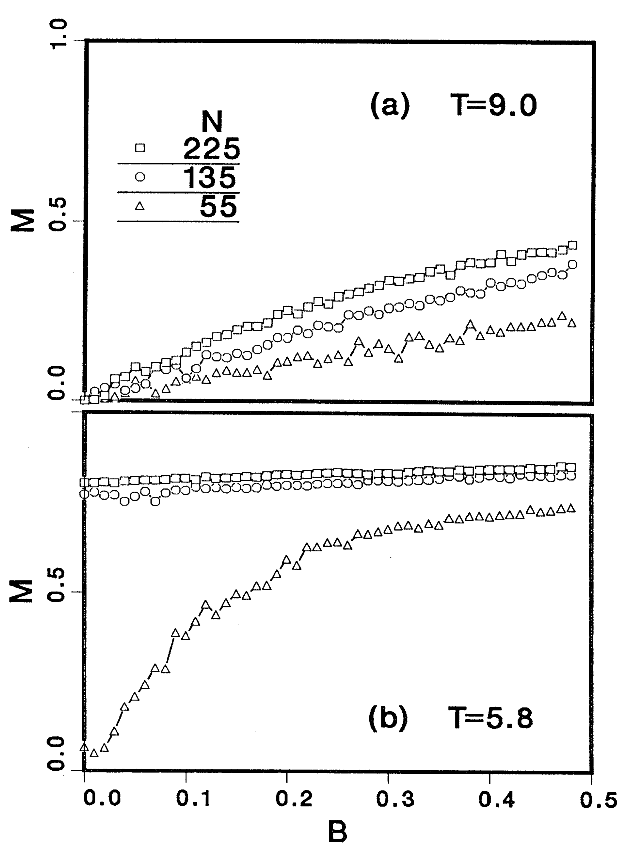

FIG. 2. Magnetization of three Ising clusters as a function of the external field for two different temperatures.

experimental results.[1] The fine structure observed in the experiments[1] is probably related to the structure of the clusters themselves, and to changes in the local magnetic moments and their interactions.

Now we are in a position to explain the time dependence of the experimentally observed[1] magnetization of the clusters. We concluded above that, in the clusters, the spin temperature must have been above the Curie temperature at the time of measurement. When the clusters go through the part of the apparatus which is kept at the desired temperature, they undergo 10^5–10^6 collisions, and it is argued in Ref. 1 that this is enough for them to reach thermal equilibrium. We believe that this is not true for the spin degrees of freedom. There are two factors in this case which increase the spin-lattice relaxation time; the finite size of the clusters and the large heat capacity of ferromagnetically coupled spins.[19] The heat capacity of the spins is of the same order of magnitude as that of the lattice, and this factor alone can increase the relaxation time appreciably.[19] It can be estimated that the clusters spend of the order of 10 μs in the constant-temperature part of the apparatus,[1] and this time is apparently much shorter than the relaxation time.

The clusters which enter the Stern-Gerlach magnet in the measurements[1] therefore have a spin temperature well above the Curie temperature, and a controlled lattice temperature. The magnetization which these clusters gain during the approximately 100 μs they spend inside the magnet depends strongly on the actual lattice temperature[16,17,20] because of the strong temperature dependence of the relaxation time.[21]

In addition to the total magnetization it would be convenient to have another measure of the approach to the bulk properties of the magnetization of small iron clusters. To this end we will consider how well the magnetization of small spin clusters satisfies the scaling properties of the bulk magnetization.[15] Our results are shown in Fig. 3 where we plot the scaled magnetization of the cluster with 555 spins as a function of the scaled reduced temperature. We show the result both for using the known[22] bulk values of the critical indices β and δ and for a "best fit" with these indices as parameters. It is quite clear that even clusters of this small size satisfy the scaling reasonably well and that experimental results should follow the same pattern. As we noted above, the temperature of the spins in the experiments on iron clusters[1] is not controlled, but a plot like the one shown in Fig. 3 can also be drawn as a function of the external field.[23] Scaling is not satisfied for very small values of the external field because the finite-size effects are then more prominent.

We have shown in this Letter that, at finite temperatures, the magnetization of small ferromagnetic clusters is smaller than that of bulk metal. Magnetization is found to increase with the cluster size, a feature which is related to reduction of magnetization in the surface layer as compared with the bulk magnetization under similar conditions. These results are in qualitative agreement with recent experimental observations.[1] The time dependence[1] of the magnetization is due to the temperature-dependent spin-lattice relaxation time. This relaxation time is enhanced in small ferromagnetic clusters because of finite-size effects and the large heat capacity of the spin system. If the temperature control of the spin systems could be improved in the experiments, the time-dependent measurements would provide a powerful way of studying the relaxation mechanisms in small clusters. We have also shown that, even without a good control of temperature, it is possible to make experimental tests of scaling behavior. It would be of interest in this respect to extend the existing scaling arguments as applied[18] to surface magnetism to spherical clusters.

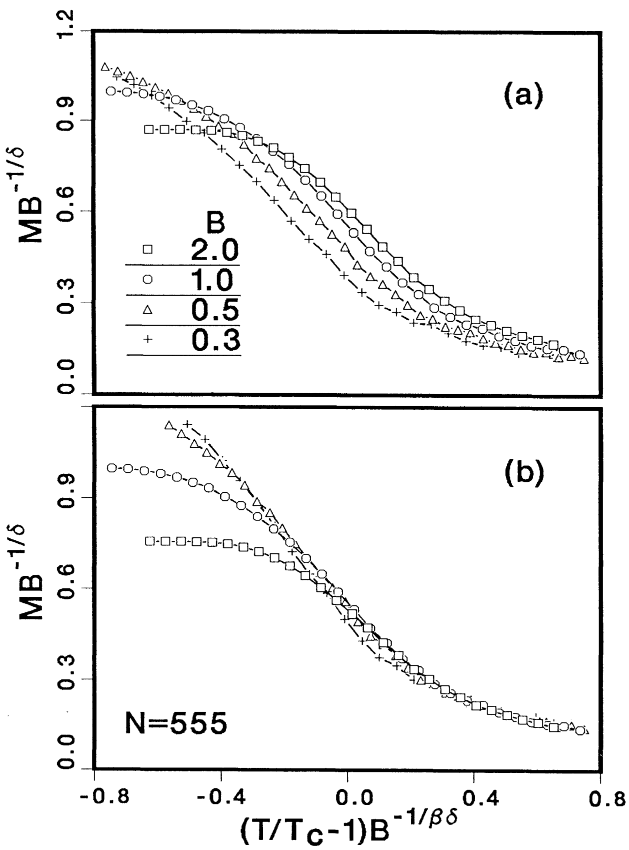

FIG. 3. Scaling of magnetization with the reduced temperature and the external field. (a) is based on using the bulk critical exponents, and in (b) $\beta\delta$ is kept constant and δ is changed such as to give the best scaling behavior for $T \geq T_c$.

One of the authors (P.J.) acknowledges the partial support of the National Science Foundation (U.S.-Finland exchange program) and the Army Research Office, and one of the authors (J.M.) thanks the Academy of Finland for financial support.

[1]W. A. de Heer, P. Milani, and A. Chatelain, Phys. Rev. Lett. **65**, 488 (1990).

[2]G. M. Cox, D. J. Trevor, R. L. Whetten, E. A. Rohlfing, and A. Kaldor, Phys. Rev. B **32**, 7290 (1985).

[3]C. Y. Yang, K. H. Johnson, D. R. Salahub, J. Kaspar, and R. P. Messmer, Phys. Rev. B **24**, 4673 (1981).

[4]K. Lee, J. Callaway, K. Kwong, R. Tang, and A. Ziegler, J. Chem. Phys. **31**, 1796 (1985).

[5]G. M. Pastor, J. Dorantes-Davila, and K. H. Benneman, Phys. Rev. B **40**, 7642 (1989).

[6]O. Jepsen, R. M. Nieminen, and J. Madsen, Solid State Commun. **34**, 575 (1980).

[7]S. Ohnishi, A. J. Freeman, and M. Weinert, Phys. Rev. B **28**, 6741 (1983).

[8]F. Liu, M. R. Press, S. N. Khanna, and P. Jena, Phys. Rev. B **39**, 6914 (1989).

[9]*Elemental and Molecular Clusters,* edited by G. Benedek, T. P. Martin, and G. Pacchioni (Springer, Berlin, 1988).

[10]J. J. Krebs, P. Lubitz, A. Chaiken, and G. A. Prinz, Phys. Rev. Lett. **63**, 1645 (1989); B. Heinrich, Z. Celinski, J. F. Cochran, W. B. Muir, J. Rudo, Q. M. Zhong, A. S. Arrot, and K. Myrtle, Phys. Rev. Lett. **64**, 673 (1990).

[11]R. Kubo, A. Kawabata, and S. Kobayashi, Annu. Rev. Mater. Sci. **14**, 49 (1984).

[12]W. P. Halperin, Rev. Mod. Phys. **58**, 533 (1986).

[13]B. K. Rao, P. Jena, and M. Manninen, Phys. Rev. B **32**, 477 (1985).

[14]F. Liu, S. N. Khanna, and P. Jena, Phys. Rev. B **42**, 976 (1990).

[15]For a review, see, e.g., K. Binder, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, London, 1976), Vol. 5B, pp. 1–105.

[16]C. J. Gorter, *Paramagnetic Relaxation* (Elsevier, Amsterdam, 1947).

[17]C. W. Haas and H. B. Callen, in *Magnetism,* edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. I, pp. 450–549.

[18]D. P. Landau, in *Monte Carlo Methods in Statistical Physics,* edited by K. Binder (Springer-Verlag, Berlin, 1979), pp. 337–355; J. Mathon, Rep. Prog. Phys. **51**, 1 (1988); H. C. Siegmann *et al.*, J. Phys. (Paris), Colloq. **49**, C8-9 (1988).

[19]P. W. Anderson, Phys. Rev. **88**, 1214 (1952).

[20]C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1967).

[21]It is evident from Fig. 3 of Ref. 1 that the clusters which follow the speed of the carrier gas at 77 K do not gain any appreciable magnetization so that, at this temperature, the relaxation time must be longer than 100 μs. Similarly, at 300 K the relaxation time must be quite close to 100 μs. Those clusters which undergo a velocity slip with respect to the carrier gas are heated [J. B. Anderson and J. B. Fenn, Phys. Fluids **8**, 780 (1965)], and their relaxation time becomes correspondingly shorter. This behavior is clearly displayed in Fig. 3 of Ref. 1.

[22]C. Domb, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, London, 1974), Vol. 3, pp. 357–484.

[23]There are several possibilities for testing the scaling behavior. In this respect see, e.g., H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford Univ. Press, New York, 1971).