Estimation of electronic and structural influence on the thermal magnetic properties of clusters

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Using an effective Heisenberg model for clusters the spin-wave spectrum is calculated by direct diagonalization. The inclusion of a nonuniform magnetization profile at zero temperature, nonuniform exchange interactions as a result of structural relaxations, longer-range interactions, and of magnetic surface anisotropy have been studied. Very small effects are found on the thermal magnetic properties relative to those predicted for the simple nearest-neighbor Heisenberg model by Hendriksen, Linderoth, and Lindgård [J. Phys. C **31**, 5675 (1993); Phys. Rev. B **48**, 7259 (1993)].

The magnetic properties of clusters of transition metal atoms have recently been studied in order to elucidate how ferromagnetism evolves from the atom to the bulk. Free molecular beam experiments[1,2] have revealed larger magnetic moments per atom in small iron clusters, than expected in the bulk. Neutron scattering experiments have been performed on clusters supported in a matrix[3] and accurate magnetization measurements have been made.[4] Calculations for nanometer-sized particles by Pastor *et al.*[5] have shown that the magnetization at zero temperature has a nonuniform profile with larger moments at the surface. Experimental investigations seem to confirm this.[6] We have previously discussed the intrinsic thermodynamic magnetic properties of clusters using spin-wave theory[7,8] for a Heisenberg model, where a fixed magnitude of the spins $S_i = S$ and site-independent nearest-neighbor exchange interaction were assumed. Here we wish to discuss the consequences of the more realistic model in which we allow for a magnetization profile at $T = 0$ and a structural relaxation, which in turn will give rise to a site-dependent exchange interaction. Also longer-range interactions and possible effects of anisotropy will be discussed. The spin-wave theory at finite temperature and the thermodynamics for the itinerant magnets are exceedingly difficult.[9] However, it is a good approximation to assume that the $3d$-electron spins around a site i are performing a coherent precession which can be represented by the precession of an effective site-dependent spin S_i. The results by Pastor *et al.*[5] for the relatively large clusters with $N = 51$ atoms will form the basis for the present discussion of the influence of the electronic modifications on the thermodynamic magnetic properties of nanometer-sized particles.

The theory and the method of calculation have recently been described in detail;[7,8] therefore only a few basic steps will be given here. We consider an effective Heisenberg model

$$\mathcal{H} = -\frac{1}{2}\sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j. \tag{1}$$

Contrary to the previously studied model[7,8] we shall here allow both the exchange interaction J_{ij} and the spin values S_i at $T = 0$ to vary with the sites i, j in the cluster. We shall also consider the effect of interactions beyond the nearest neighbors. The equation of motion for the spin deviation operator S_i^+ for a ferromagnetic cluster can in a symmetrized, site-dependent random phase approximation be solved self-consistently by a direct numerical diagonalization, yielding both the N discrete eigenvalues E_p and the corresponding (normalized) eigenfunctions ψ_i^p for each state p. The states with the minimum relative change from site to site and few nodal planes have the lowest energy. These states have large amplitudes at the surface, and since they are the first to be populated at finite temperatures it is clear that a more rapid decrease of the magnetization is predicted for the surface layers. The magnetization is given by[8,10]

$$M_i(T) = S - \sum_{p=1}^{N-1} |\psi_i^p|^2 n(E_p)\,, \tag{2}$$

where $n(E_p) = [\exp(E_p/k_BT) - 1]^{-1}$ is the Bose weight of the state p. The spectrum (E_p) is discrete with a sizable gap ΔE to the first excited state, which for a $N = 749$ α-iron cluster is $\Delta E/k_B = 30$ K. Interestingly, the mean magnetization $M(T)$ can in a large temperature interval (up to 35% of T_c), be well fitted[7,8] to an effective power law $M(T) - M(0) = \Delta M(T) = BT^\alpha$. However, the parameters have no direct physical meaning. The energy gap ΔE gives in principle rise to an exponential behavior of the mean magnetization deviation $\Delta M(T) = S - \frac{1}{N}\sum_i \langle S_i^z\rangle$. Since $\sum_i |\psi_i^p|^2 = 1$ and the first excited state is three times degenerate for overall cubic symmetry (i.e., not only for ideal bcc or fcc symmetry) the low temperature behavior can be written

$$\frac{\Delta M(T)}{M(0)} = \frac{3}{N}\left[n(\Delta E) + n(2\Delta E)\right] + \cdots, \tag{3}$$

where we have used that there is a second triplet at $\approx 2\Delta E$, and where the dots represent $n(E_p)$ functions for $E_p \gtrapprox 2\Delta E$. The energy gap can be obtained by a fit[11] to Eq. (3) using a temperature range $k_BT \leq \frac{1}{3}\Delta E$. For impure systems with lower symmetry the degeneracy will be lifted; however, for small splittings a fit to

Eq. (3) might still be preferable. The energy gap is directly related to the exchange interactions. We generalize here the expression obtained by Hendriksen *et al.*[7,8] to include the interactions J_m to several neighbor shells m,

$$\Delta E(r_c) = \tilde{J} S f^2(r_c) \,, \tag{4}$$

where $f(r_c) = \pi a/(1.42 r_c + 0.58a)$, r_c is the cluster radius in units of the lattice constant a, and $\tilde{J} = J_1 + J_2 + 4J_3$ for bcc and $\tilde{J} = J_1 + J_2 + 3J_3$ for fcc. In Fig. 1 the magnetization is shown as a function of T and reciprocal cluster radius $1/r_c$ for the center spin (short-dashed line), the average moment (solid line), and the outer shell (long-dashed line). The average moment calculated by the spin-wave theory extrapolates naturally (thin line) to the T_c values calculated using a generalization of the spherical model.[8] For a 51 bcc cluster T_c is found to be reduced to 59% of the bulk value T_c(bulk). For increasing cluster sizes T_c is seen (thin dashed line) to approach T_c(bulk) for $1/r_c \to 0$, following an expected scaling behavior.[8] It is clearly of interest to investigate how robust these results are to the electronic modifications of the model, which are expected to be relevant for small metallic clusters.

Only for the very smallest clusters with a few atoms are the electronic and structural properties calculated from first principles. Since we are here interested in nanometer-sized particles we shall base our discussion on the calculation of the moment distribution in a $N = 51$ unrelaxed bcc iron cluster by Pastor *et al.*[5] They used the unrestricted Hartree-Fock decoupling of the Hubbard model, which can be written (neglecting the band indices)

$$\mathcal{H}_{\rm el} = \sum_{i \neq j,\sigma} t_{ij} c^\dagger_{i\sigma} c_{j\sigma} + \sum_{i,\sigma} \epsilon_{i\sigma} c^\dagger_{i\sigma} c_{i\sigma} - E_{dc},$$
$$\epsilon_{i\sigma} = \epsilon^0_d + U\Delta n(i) - \tfrac{1}{2}\sigma \mathcal{J} \mu(i) \,, \tag{5}$$

where t_{ij} is the tight binding hopping term, σ the spin index, and $\epsilon_{i\sigma} - \epsilon^0_d$ is a "penalty field" term. This strongly discourages large (square) amplitudes of $|c^\dagger_{i\sigma}|^2 = \hat{n}_\sigma(i)$ in the outer shells in order to minimize charge transfer $\Delta n(i) = n_\uparrow(i) + n_\downarrow(i) - n_0$ in the presence of the large Hubbard U term. The number of electrons (charge) around site i is $n_\sigma(i) = \langle \hat{n}_\sigma(i) \rangle$ and n_0 is the average charge. The magnetic moment in units of μ_B is $\mu(i) = n_\uparrow(i) - n_\downarrow(i) \propto S_i$ of Eq. (1), and the exchange integral $\mathcal{J}$ splits the $\sigma = \uparrow$ and $\downarrow$ states. E_{dc} and ϵ^0_d are constants. The diagonalization problem of Eq. (5) for $c^\dagger_{i\sigma}$ is identical with that for S^+_i. It is instructive, as an alternative to the traditional projected density of states argument,[5] to think about the problem in terms of the wave functions found for the spin-wave problem. For the electrons it is essential to include the charge transfer penalty, which strongly mixes the states in energy since U/t_{ij} is large, shifting the large amplitude surface states to high energies. The shell moment for a 51 bcc cluster calculated self-consistently[5] including the penalty term Eq. (5) is shown in Fig. 2, solid line. A lower than average moment in the center and a strongly increasing moment S_i for the outer shells were found. This can easily be incorporated in the solution of Eq (1). We find that it leads to a small increase of the calculated T_c of 5%, mainly due to the larger average moment $\mu_0 = 1.10\mu$(bulk) found for the cluster by Pastor *et al.*[5] The calculated magnetization extrapolates naturally to the calculated T_c; see Fig. 1. The calculated T_c values will be compared for various models in Table I.

Another modification to consider is variations in J_{ij} due to structural relaxation of the cluster, which can strongly alter the overlap terms in the exchange integrals. In an unrelaxed cluster it is not possible to have a nonuniform moment distribution at $T = 0$ without a certain charge transfer. Suppose for simplicity that we have fully occupied $\uparrow$ bands $n_\uparrow(i) = n^0_\uparrow$, and so the moment variation arises solely from the $\downarrow$ bands $n_\downarrow(i) = n^0_\downarrow + \Delta n(i)$. Then it is easy to see that the charge transfer is related to the moment profile by $\Delta n(i) = \mu(\text{bulk}) - \mu(i)$. Let us make a crude model for the lattice relaxation by requiring that the electron density around each nucleus be equal to that of the bulk and enforcing this by adjusting the Wigner-Seitz radius $r_{\rm WS}$ to account for excess electrons. For iron (atomic state: argon-$3d^6 4s^2$) with eight conduction electrons per nucleus we then argue as follows. In

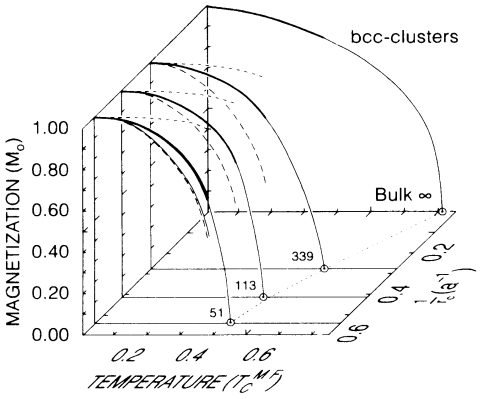

FIG. 1. The calculated magnetization versus temperature and inverse cluster radius $1/r_c$ of the center spin (short-dashed line), the average magnetization (solid line), and that of the outer shell (long-dashed line). The thin lines extrapolate to the calculated T_c. The number of spins is indicated as well as T_c(bulk) for $1/r_c = 0$. For the 51 cluster the thin additional lines indicate the small modification due to influence of the magnetization profile (normalized to 1).

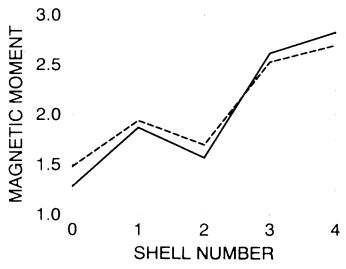

FIG. 2. The calculated magnetization profile (in units of μ_B) of a 51 bcc-iron cluster calculated by Pastor *et al.* (Ref. 5), solid line. The average moment is $2.45\mu_B$. The effective moment profile, including the lattice relaxations, is shown as a dashed line.

TABLE I. Comparison between the calculated values of the effective transition temperature T_c for a 51 bcc-iron cluster. For the NN case $T_c(\text{bulk}) = 0.71\ T_c^{\text{MF}}(\text{bulk})$ (Ref. 12).

Effect considered	$\frac{T_c}{T_c^{MF}(\text{bulk})}$	$\frac{T_c}{T_c(\text{bulk})}$
$\mu(i) = S$ (NN), J_1 from T_c (Ref. 8)	0.417	59%
$\mu(i)$ profile (Ref. 5), unrelaxed, $x = 0$	0.415[a]	62%
$\mu_{\text{eff}}(i)$ profile, relaxed, $x = +10$	0.415[a]	62%
$\mu_{\text{eff}}(i)$ profile, relaxed, $x = -10$	0.418[a]	62%
$\mu(i) = S$ (3NN), J from T_c	0.473	63%
$\mu(i) = S$ (NN), J_1 from D	0.417	82%

[a]For comparison the magnetization profiles are scaled to yield the average moment $\mu_0 = S$.

a sphere with volume $\frac{4\pi}{3} r_{\text{WS}}^3$ there are eight electrons in the bulk, whereas for the cluster there are $8 + \Delta n(i)$ in the volume $\frac{4\pi}{3} r_i^3$. Consequently, we need to adjust the radius as $r_i = r_{\text{WS}}[1 + \frac{1}{3\times 8}\Delta n(i)]$. We now distort the bcc cluster by packing these spheres of unequal radii $(0.98 r_i)$. The relative distance between the spins can be written $r_{ij} = R + \Delta r_{ij} = R\{1 + \frac{1}{48}[\Delta n(i) + \Delta n(j)]\}$, where $R = a\sqrt{3}/2$ is the bulk distance. We apply the argument to the 51 bcc cluster studied by Pastor *et al.*[5] The result is an expansion of the core of the cluster and a contraction of the outer shells, with lattice constant changes of the order of 1%, as generally expected.[5] For all atoms the displacements are along the cubic symmetry directions, except for the outermost shell, which is more drastically reconstructed. However, the nearest-neighbor coordination number is *unchanged* by these displacements and the bond directions are only slightly modified. Now, suppose the exchange constant in Eq. (1) depends strongly on the distance between the spins $J(R + \Delta r) \approx J(R)(1 + x\frac{\Delta r}{R})$, where $|x| \approx 10$. The site-dependent Heisenberg interaction in the relaxed cluster is then

$$J_{ij} = J(r_{ij}) \approx J(R)\left\{1 + \frac{x}{48}[\Delta n(i) + \Delta n(j)]\right\}. \qquad (6)$$

The estimated changes in the exchange interactions are $\leq 10\%$ due to the structural relaxations. This modification of J_{ij} can be included in Eq. (1), by using $J_{ij} = J(R) = J_1$ and instead introducing the effective moments $\mu_{\text{eff}}(i) = \mu(\text{bulk}) - [1 - \frac{x}{48}]\Delta n(i)$. Notice that for $x = 0$ we have the unrelaxed result.[5] For iron x is expected from various experimental facts[12] to be positive $x \approx +10$.[13] Therefore, including the lattice relaxation in this crude model tends to effectively reduce the moment profile, as shown in Fig. 2, dashed line, and only perturb the already minimal effect of a magnetization profile for iron. We can understand why the effect is so small on the thermal magnetic properties. This permits us to assume that it holds true also for larger clusters. The magnetization profile[5] does act as a "penalty field" for large amplitudes at the surface. However, contrary to the electron case, the field strength is far too small to significantly shift the energy sequence of states and change the wave functions. A refined calculation of the $T = 0$ magnetization profile and a somewhat larger effect of the relaxation on the exchange interactions will not alter this conclusion.

Let us additionally consider the possibility that we need a model with longer-range interactions to describe α-iron. It has previously been found[14] that in order to fit both T_c and the spin-wave stiffness constant D a model including interactions to the first three neighbor shells (3NN) is necessary. The calculated $T_c(\text{bulk})$ becomes too high by 40% if one includes only $J_1 = J$, which fits D. One could take the interactions to be all equal: $J_1 = J_2 = J_3 = J/6$. The constants J_1, J_2, J_3 cannot be fitted from the spin-wave dispersion relation because this gets overdamped when entering the Stoner excitation band. The effective 3NN model reproduces the first moment of the Stoner band better than the NN model and is therefore better for thermodynamic calculations, as it is able to correctly obtain both D and $T_c(\text{bulk})$. For small clusters there is no Stoner band—but discrete levels. It is therefore not evident whether the effective 3NN model works well also in this case. The result is shown in Table I. In the 3NN model T_c increases to 47% of $T_c^{\text{MF}}(\text{bulk})$. However, at the same time $T_c(\text{bulk})$ increases, to 0.75 $T_c^{MF}(\text{bulk})$.[14] Therefore, relative to $T_c(\text{bulk})$ the long-range model for the 51 bcc-iron cluster has only a slightly higher T_c than the nearest-neighbor model; see Table I. In the above arguments we have determined the relevant exchange interactions from the bulk transition temperature. For the itinerant magnetic metal cluster it may be more appropriate to use the NN model but with the larger J_1, which fits the spin-wave stiffness constant. This does increase T_c for the cluster; see Table I. A measurement of ΔE, using neutron scattering or low temperature magnetization experiments, would give the most direct determination of the exchange interactions in the clusters.

Finally, a modification of the magnetic properties is conceivable if the magnetic anisotropy is different in the clusters than in the bulk. We have previously[8] considered the effect of a shape anisotropy originating, for example, from the dipolar interactions in terms of a uniaxial anisotropy field. Experimental values of this field for 3–6 nm α particles shows that the anisotropy energy is much smaller than the exchange energy per unit volume, and hence such anisotropy has negligible effect on the thermal properties.[8] Another effect is crystal field anisotropy which could be much larger than in the bulk due to the presence of the surface and of the structural relaxation. No definite calculations are available on this question, so let us qualitatively discuss the effects assuming a spherical cluster. The contraction of the surface layers suggests a larger than bulk anisotropy at the surface. The lowering of the symmetry due to the missing neighbors will

produce a crystal field with a predominant axial term in the radial direction with a term in the Hamiltonian of the form DS_ξ^2, where ξ is the component along a radius vector. The anisotropy constant is either $D > 0$ or $D < 0$. In the last case, if $|D|$ is large compared to the exchange interaction a hedgehoglike spin structure would be expected. This is on the other hand not likely, at least for iron clusters, where the exchange interaction is much larger than the anisotropy in the bulk. For anisotropy energies with a magnitude $|D| \leq 10\%$ of J the exchange interaction will ferromagnetically align the spins with some canting, schematically shown in Fig. 3 for the radial and the tangential cases. The surface anisotropy will increase T_c only of the order of a few percent. This is a consequence of the competition between the aligning exchange interaction and the radial or tangential anisotropy field. The clusters will be magnetically harder for the tangential anisotropy than for the radial because of less destructive competition. This is interesting because it is opposite to the effect of uniaxial and planar anisotropy in bulk systems. The surface anisotropy will in general make the surface layers magnetically harder, similar to the above discussed electronic effects. However, unless the surface anisotropy energy is much larger than the exchange interaction, only small effects on the thermal properties can be expected.

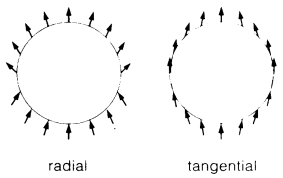

FIG. 3. Influence of an enhanced surface crystal field anisotropy term DS_ξ^2 on the magnetic ground state of the cluster (schematic) for $D < 0$ (radial) and $D > 0$ (tangential).

We have considered extensions of the nearest-neighbor Heisenberg model for metallic clusters and shown that our previous results are robust to the most compelling modifications. Measurements of the magnetization, T_c and of the spin-wave dispersion for iron and other clusters would be interesting in order to test the predictions and for getting a deeper understanding of the cluster and the itinerant magnetism.

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

[2] J. P. Bucher, D. C. Douglass, and L. A. Bloomfield, Phys. Rev. Lett. **66**, 3052 (1991); S. N. Khanna and S. Linderoth, *ibid.* **67**, 742 (1991); S. Linderoth and S. N. Khanna, J. Magn. Magn. Mater. **104-107**, 1574 (1992); D. M. Cox, D. J. Trevor, R. L. Whetten, E. A. Rohlfing, and A. Kaldor, Phys. Rev. B **32**, 7290 (1985).

[3] I. Mirebeau, C. Bellouard, M. Hennion, J. L. Dormann, C. Djega-Mariadassou, and M. Tessier, J. Magn. Magn. Mater. **104-107**, 1560 (1992); J. R. Childress, C. L. Chien, J. J. Rhyne, and R. W. Erwin, *ibid.* **104-107**, 1585 (1992).

[4] S. Linderoth, L. Balcells, A. Labarta, J. Tejada, P. V. Hendriksen, and S. A. Sethi, J. Magn. Magn. Mater. **124**, 269 (1993).

[5] G. M. Pastor, J. Dorantes-Dávila, and K. A. Bennemann, Phys. Rev. B **40**, 7642 (1989); J. Dorantes-Dávila, H. Dreyssé, and G. M. Pastor, *ibid.* **46**, 10432 (1992); A. Vega, J. Dorantes-Dávila, L. C. Balbás, and G. M. Pastor, *ibid.* **47**, 4742 (1993).

[6] F. Bødker, S. Mørup, C. A. Oxborrow, S. Linderoth, M. B. Madsen, and J. Niemantsverdriet, J. Phys. Condens. Matter **4**, 6555 (1992); J. Jing, X. Yang, Y. Hsia, and U. Gonser, Surf. Sci. **233**, 351 (1990); U. Heer, J. Ring, R. Birringer, U. Gonser, and H. Gleiter, Appl. Phys. Lett. **50**, 472 (1987).

[7] P. V. Hendriksen, S. Linderoth, and P.-A. Lindgård, J. Phys. C **31**, 5675 (1993).

[8] P. V. Hendriksen, S. Linderoth, and P.-A. Lindgård, Phys. Rev. B **48**, 7259 (1993).

[9] T. Moriya, *Magnetic Fluctuations in Itinerant Electron Magnetism*, Springer Series in Solid State Physics Vol. **56** (Springer, Berlin, 1985).

[10] In Ref. 7 the sum is erroneously multiplied by S. Since $S = 1$ was used it has no consequence on the results.

[11] The fit to Eq. (3) is somewhat difficult. First of all it requires a good knowledge of $M(T \to 0)$. Secondly, in a best fit the values calculated from the truncated sum Eq. (3) must lie systematically below the experiments with a deviation increasing from zero at $T \to 0$ to 10% at $T = \frac{1}{3}\Delta/k_B$, since we have estimated that at this temperature the neglected contribution from the higher energy terms in Eq. (2) amounts to 10%. A procedure is to make a least squares fit in the interval $0 < T < \frac{1}{3}\Delta/k_B$ and then increase this Δ by $\approx 10\%$ and test the systematic deviation.

[12] D. H. Martin, *Magnetism in Solids* (Iliffe, London, 1967).

[13] For completeness we have also given the results for $x = -10$.

[14] P.-A. Lindgård (unpublished) preliminary calculations for iron based on the correlation theory, P.-A. Lindgård, Phys. Rev. **B 27**, 2980 (1983).