

## Influence of temperature on the systematics of magnetic moments of free Fe clusters

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 446205

(<http://iopscience.iop.org/0953-8984/19/44/446205>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 06:30

Please note that [terms and conditions apply](#).

# Influence of temperature on the systematics of magnetic moments of free Fe clusters

O Šipr<sup>1</sup>, S Polesya<sup>2</sup>, J Minár<sup>2</sup> and H Ebert<sup>2</sup>

<sup>1</sup> Institute of Physics of the AS CR v.v.i, Cukrovarnická 10, CZ-162 53 Prague, Czech Republic

<sup>2</sup> Department Chemie und Biochemie, Universität München, Butenandtstraße 5-13, D-81377 München, Germany

E-mail: [sipr@fzu.cz](mailto:sipr@fzu.cz) and [Hubert.Ebert@cup.uni-muenchen.de](mailto:Hubert.Ebert@cup.uni-muenchen.de)

Received 27 April 2007, in final form 5 September 2007

Published 16 October 2007

Online at [stacks.iop.org/JPhysCM/19/446205](http://stacks.iop.org/JPhysCM/19/446205)

## Abstract

We investigate how temperature affects the dependence of the average magnetic moments  $\bar{\mu}$  of clusters on their size and how the magnetic moment profile of an individual cluster varies with temperature  $T$ . The focus is on free spherical Fe clusters of 9–89 atoms. The interaction among individual magnetic moments is described by a classical Heisenberg spin Hamiltonian, with exchange coupling constants provided by *ab initio* calculations. Average magnetic moments  $\bar{\mu}$  for finite  $T$  were obtained via Monte Carlo simulations. We found that the exchange coupling depends on the cluster size and on the position of the atom in the cluster in a complex way, with no obvious systematics. The magnetic moment profile of an individual cluster becomes more uniform if  $T$  increases. The dependence of  $\bar{\mu}$  on the cluster size, in practice, does not depend on temperature if  $T$  is in the range of 0–300 K. Ground-state calculations for  $T = 0$  K should thus be able to describe experiments based on the deflection of a molecular beam in a magnet for  $T \neq 0$  K.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Free clusters of a few tens to hundreds of atoms form an interesting class of materials, both from fundamental and applications points of view. They contain a large portion of surface atoms, yet their properties cannot be obtained as a simple interpolation between the surface and the bulk. Magnetic moments of free clusters can be determined experimentally by measuring the deflection of a molecular beam in a Stern–Gerlach magnet [1]. By applying this technique, it was found that the magnetic moment per atom  $\bar{\mu}$  is larger in clusters than in the bulk and that it varies non-monotonously with the cluster size. Much theoretical research has recently been done on free clusters of transition metals. The calculations indeed provided non-monotonous dependence of  $\bar{\mu}$  on the cluster size (and also non-monotonous magnetic moment profiles for

individual particles). However, the calculated positions of minima and maxima of  $\bar{\mu}$  as a function of the number of atoms  $N$  in the cluster do not always agree with the experiment. One of the reasons for the disagreement could be that the experiments are done for clusters thermalized at temperatures  $T \approx 70\text{--}300$  K while the calculations are done for  $T = 0$  K.

In this paper, we focus on free Fe clusters of 9–89 atoms and investigate quantitatively how the dependence of  $\bar{\mu}$  on  $N$  varies with  $T$ . In particular, we check whether the positions of minima and maxima of  $\bar{\mu}(N)$  depend on  $T$  and whether calculations for  $T = 0$  K can be realistically expected to reproduce experiments performed at finite temperatures. We also study how the magnetic moment profile of an individual cluster changes if temperature is raised. Knowing this information will facilitate further interaction between theoretical and experimental research in this area and provide a deeper insight into finite-temperature magnetism of spatially confined systems.

Magnetism of free Fe clusters was studied both by theoretical and experimental methods in the past. Billas *et al* [1] measured average magnetic moments  $\bar{\mu}$  of free Fe clusters of 25–700 atoms at  $T = 120$  K. On the other hand, practically all theoretical work on magnetism of free Fe clusters was done for  $T = 0$  K. Calculations relying on a model tight-binding Hamiltonian cover ranges of up to 230 atoms [2–5]. *Ab initio* calculations were performed either using the pseudopotential scheme [6, 7] or within the multiple-scattering formalism [8] and cover sizes up to 400 atoms. In most calculations, bulk interatomic distances were assumed [3, 5, 8, 7]; in some cases, relaxation of interatomic distances was allowed [2, 4, 6]. A general trend was found that the local magnetic moments  $\mu_i$  increase in a quasi-oscillatory way when going from the center of the cluster outwards. Usually, only the spin magnetic moment  $\mu_{\text{spin}}$  was calculated. The orbital magnetic moment  $\mu_{\text{orb}}$  of Fe clusters was calculated only in a fully relativistic study of Šipr *et al* [8] and in the work of Tiago *et al* [7], where spin–orbit interaction was included in a variational step. Although the calculations reproduce some trends of the  $\bar{\mu}(N)$  dependence, none of the theoretical studies achieves a full agreement with experiment.

As concerns the studies of finite-temperature magnetism of clusters, most of them relied on the Heisenberg Hamiltonian with interaction parameters taken from the corresponding bulk [9–12]. Only recently, finite-temperature effects were described via a Heisenberg Hamiltonian with *ab initio* cluster-specific coupling parameters [13]. It was found that the crossover-temperature  $T_c$  depends on the cluster size non-monotonously. Calculations of Polesya *et al* [13] confirmed earlier findings [10–12] that magnetic moments at the cluster surface generally decay faster with increasing  $T$  than magnetic moments in the interior but they also found that this trend may be reversed for some distances from the center.

Finite-temperature magnetism of clusters was studied also by approaches that do not rely on the Heisenberg Hamiltonian. López-Urías *et al* [14] investigated magnetism of small clusters ( $N \leq 6$ ) at  $T \neq 0$  K within a single-band Hubbard model and found that for some values of the model parameters, clusters may exhibit an increase of  $\bar{\mu}$  with increasing  $T$  at low temperatures. Pastor *et al* [15] studied local spin-fluctuation energies for Fe and Ni clusters ( $N \leq 51$ ) within the functional-integral theory and found that spin-flip energies depend strongly on the size of the cluster and on the atomic site. Andriotis *et al* [16, 17] studied Ni clusters ( $N \leq 201$ ) by combining the classical potential approximation with the tight-binding molecular-dynamics method. The temperature dependence of  $\bar{\mu}$  of Ni clusters obtained by Andriotis *et al* [16] displays a similar pattern as  $\bar{\mu}$  of Fe clusters [13]. However, the crossover-temperature  $T_c$  was found to increase monotonously with the cluster size for Ni clusters [17], which is in contrast with the non-monotonous dependence found for Fe clusters by a different method [13].

In this work we will show that the dependence of average magnetic moments per atom  $\bar{\mu}$  of Fe clusters on their size does not change significantly if the temperature is raised from  $T = 0$  K

up to room temperature. For higher temperatures,  $\bar{\mu}$  of large clusters decays more quickly with increasing  $T$  than  $\bar{\mu}$  of small clusters. At the same time, increasing  $T$  makes magnetic moment profiles of individual clusters more uniform. We will also show that the total coupling of the magnetic moment of a particular atom is a complicated function of the distance of the atom from the center and of the cluster size, with no obvious systematics.

## 2. Computational scheme

We investigated free spherical Fe clusters constructed from 1–7 coordination shells of bcc iron (9–89 atoms), without geometry relaxation. The energetics connected with the deviation of spins from a ferromagnetic order was described by a classical Heisenberg spin Hamiltonian,

$$H_{\text{eff}} = - \sum_{i \neq j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j, \quad (1)$$

where  $J_{ij}$  is the exchange coupling constant between atoms  $i$  and  $j$  and  $\mathbf{e}_i$ ,  $\mathbf{e}_j$  are unit vectors pointing in the directions of the corresponding local magnetic moments. The exchange coupling constants  $J_{ij}$  were obtained from *ab initio* scalar-relativistic calculations of the ground-state electronic structure, via the formula of Liechtenstein *et al* [18]

$$J_{ij} = -\frac{1}{4\pi} \text{Im} \int^{E_F} dE \text{Tr} (t_{i\uparrow}^{-1} - t_{i\downarrow}^{-1}) \tau_{\uparrow}^{ij} (t_{j\uparrow}^{-1} - t_{j\downarrow}^{-1}) \tau_{\downarrow}^{ji}. \quad (2)$$

The above formula (for details see [18]) was derived by exploiting the multiple-scattering formalism, linear response theory, the spin-polarized local force theorem, and the long-wave approximation. The ground-state electronic structure was calculated within the multiple-scattering formalism, relying on the atomic sphere approximation (ASA) and on the parametrization of Vosko, Wilk, and Nusair for the exchange–correlation potential [19], using the SPRKKR code [20, 21]. A detailed description of our ground-state calculations can be found elsewhere [8, 22].

The average magnetic moment  $\bar{\mu}$  was calculated as the expectation value of the magnitude of the total magnetic moment of the cluster (per atom),

$$\bar{\mu} = \frac{1}{N} \left\langle \left| \sum_{i=1}^N \mu_i \mathbf{e}_i \right| \right\rangle, \quad (3)$$

where  $\mu_i$  is the (zero-temperature) magnetic moment at site  $i$ . Generally, the expectation value of any observable  $A$  which is a function of spin directions,  $A(\{\mathbf{e}_i\})$ , can be written for a given  $T$  as

$$\langle A \rangle = \frac{\text{Tr} \exp(-H_{\text{eff}}/kT) A}{\text{Tr} \exp(-H_{\text{eff}}/kT)}. \quad (4)$$

We evaluated the sum in (4) by a Monte Carlo (MC) method [23] using the standard Metropolis importance sampling algorithm [24]. The  $J_{ij}$  values obtained from (2) were taken as input parameters. The simulation started from a collinear orientation of all local moments at low temperature (0.5 K) and each step consisted of a random rotation of one spin. For each next temperature, the last spin configuration obtained for the previous temperature was used as the starting configuration. The total number of MC steps per atom was  $10^7$ – $10^8$  for each temperature. The first  $10^6$  or  $2 \times 10^6$  steps were used for equilibration and the rest for obtaining the averages of physical quantities.

The moment  $\bar{\mu}$  defined by (3) concerns the whole cluster. Earlier studies carried out for  $T = 0$  K found that the local magnetic moments increase in a quasi-oscillatory way when going from the cluster center towards its surface [2, 8]. In order to investigate the temperature

dependence of the magnetic moment profile of individual clusters, one has to determine the mean magnetic moment  $\mu_s^{(j)}$  related to a given shell. We define it as the expectation value of the projection of the magnetic moments of all atoms forming the shell (per atom) onto the direction of the magnetic moment of the whole cluster,

$$\mu_s^{(j)} = \frac{1}{N^{(j)}} \left\langle \sum_{k=1}^{N^{(j)}} \mu_k e_k \cdot \frac{\sum_{i=1}^N \mu_i e_i}{|\sum_{i=1}^N \mu_i e_i|} \right\rangle, \quad (5)$$

where  $k$  spans all  $N^{(j)}$  sites belonging to the  $j$ th shell. This definition is analogous to, for example, the ‘local intrinsic magnetization’ as defined in [12].

The  $J_{ij}$  constants characterize the coupling between spins of atoms  $i$  and  $j$ . In order to quantify the strength by which a spin of atom  $i$  is held in its direction by interacting with all the other atoms, we define the total coupling  $J^{(i)}$ ,

$$J^{(i)} \equiv \sum_{j \neq i}^N J_{ij}. \quad (6)$$

In a crystal, this quantity would be just the effective exchange interaction constant  $J^{(0)}$  which is connected, in the mean-field approximation, to the Curie temperature  $T_C$  via

$$J^{(0)} = \frac{3}{2} k_B T_C. \quad (7)$$

In a loose way, one could see  $J^{(i)}$  as a measure of the ‘local Curie temperature’ in a cluster (obviously, the true Curie temperature is not a local quantity and, moreover, phase transitions do not occur in finite systems).

For both free and supported clusters, it turned out to be useful to investigate the dependence of site-related magnetic properties on coordination numbers [8, 25, 26]. The influence of the nearest as well as the next-nearest neighbors can be incorporated into the effective coordination number  $n_{\text{eff}}$  defined as [27]

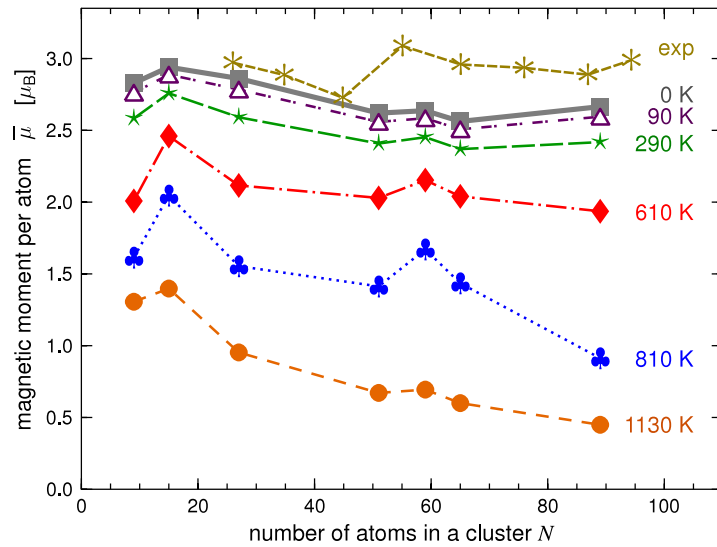
$$n_{\text{eff}} = n_1 + \beta n_2, \quad (8)$$

where  $n_1$  is the number of nearest neighbors and  $n_2$  is the number of next-nearest neighbors. The coefficient  $\beta = 0.25$  is determined by the distance dependence of the  $d$  electron hopping integrals [27, 28].

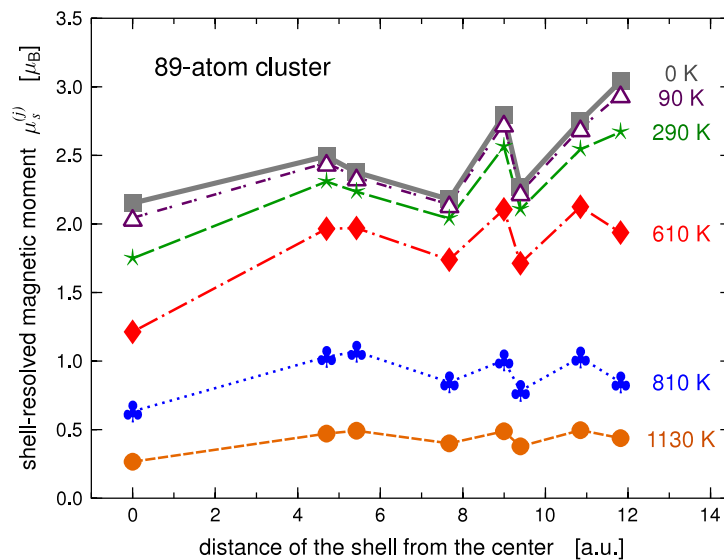
### 3. Results

Figure 1 shows the calculated average magnetic moments  $\bar{\mu}$  of clusters (see equation (3)), as a function of the number of atoms in the  $N$ -atom cluster, for several temperatures  $T$ . One can see that  $\bar{\mu}$  for  $T \neq 0$  K joins smoothly the zero-temperature results, thus confirming that our computational scheme is internally consistent. There is an overall decrease of  $\bar{\mu}$  with increasing  $T$  for all cluster sizes, in accordance with our earlier results [13]. As concerns the dependence of  $\bar{\mu}$  on  $N$ , significant deviations from the  $T = 0$  K situation appear only above room temperature. For large clusters,  $\bar{\mu}$  drops with increasing  $T$  more quickly than for small clusters. For comparison, the experimental results for  $T = 120$  K [1] are also shown in figure 1. Note that the experimental data contain errors (especially for low  $N$ ); we do not show the error bars here so that the plot remains legible.

The magnetic moment profile of an 89-atom cluster evaluated according to (5) is shown in figure 2 for several temperatures. Again, significant differences with respect to the  $T = 0$  K case appear only above room temperature. Generally, increasing  $T$  makes the magnetic moment profile flatter—the differences between local minima and maxima of  $\mu_s^{(j)}$  get smaller if  $T$  gets higher.

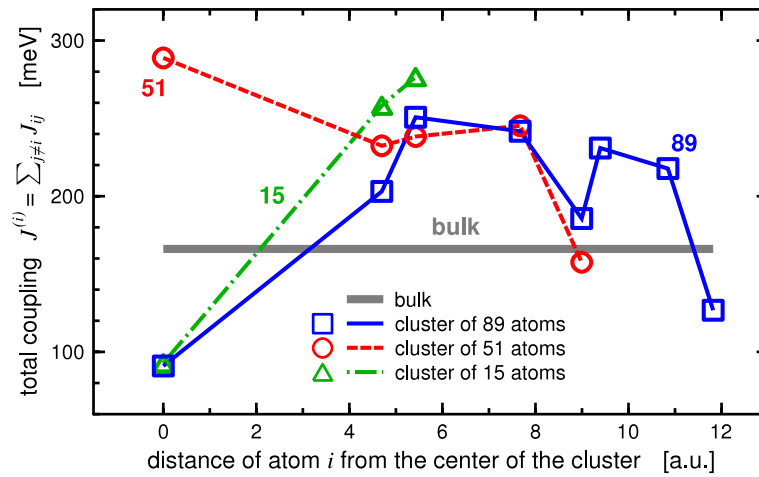


**Figure 1.** Average magnetic moments  $\bar{\mu}$  defined by (3) shown as function of the cluster size, for various temperatures (specified at the right edge of the graph). Experimental data of Billas *et al* [1] for  $T = 120$  K are shown as well.

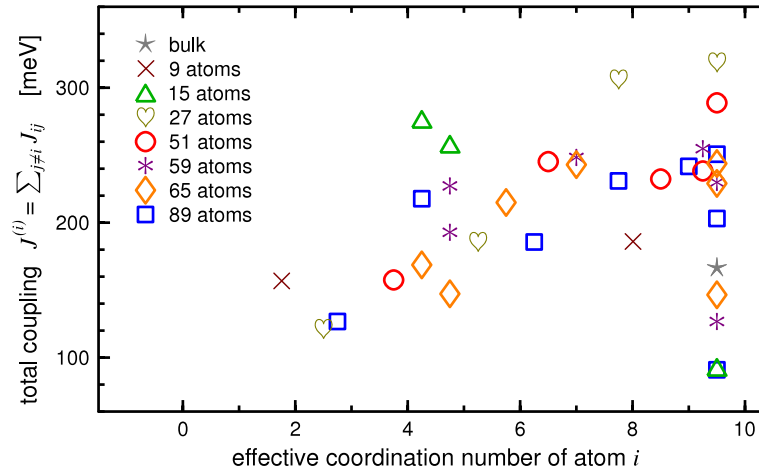


**Figure 2.** Dependence of the magnetic moments  $\mu_s^{(j)}$  assigned to individual shells of an 89-atom cluster on the distance of the shell from the center, for several temperatures (shown at the right edge of the graph).

Let us turn now to the exchange coupling constants. The site-related total coupling of spins  $J^{(i)}$  evaluated according to (6) is shown in figure 3 for selected clusters. For comparison, the coupling parameter  $J^{(0)}$  for an Fe crystal is also shown. One can see immediately that the coupling depends both on the size of the cluster and on the position of the atom within the cluster and that this dependence is quite complex. The same is true also for other cluster sizes



**Figure 3.** Total coupling  $J^{(i)}$  of spins in clusters of 15, 51, and 89 atoms. The coupling constant  $J^{(0)}$  for an Fe crystal is represented by the thick horizontal line.



**Figure 4.** Dependence of the total coupling  $J^{(i)}$  on the effective coordination number of the atom  $i$ . For each cluster size, data points are shown by different markers, as indicated in the legend.

(not shown in the plot for the sake of clarity). Interestingly, flipping the spins in the outer shells is not always easier than flipping the spins in the interior shells; for example, for the 15-atom cluster, the trend is just the opposite.

Figure 4 shows the dependence of the total coupling  $J^{(i)}$  of the spin at atom  $i$  on the effective coordination number  $n_{\text{eff}}$  of this atom. The figure contains data points for all the cluster sizes we investigated and, for comparison, for an Fe crystal as well. One can see that despite some tendency of  $J^{(i)}$  to increase linearly with increasing  $n_{\text{eff}}$  for  $n_{\text{eff}} \lesssim 8$ , no simple trend can be identified in figure 4. The same would be true if we put just the number of nearest neighbors  $n_1$  instead of  $n_{\text{eff}}$  on the horizontal axis (cf the definition (8)).

#### 4. Discussion

The main issue of this study was to find out whether the dependence of the average magnetic moment  $\bar{\mu}$  on the cluster size will change significantly if the temperature is raised from  $T = 0$  K (for which most calculations are done) to  $T \approx 100$  K (for which most experiments are performed). We found that up to room temperature,  $\bar{\mu}$  of free Fe clusters does not depend significantly on  $T$ . This implies that ground-state calculations should be able to reproduce the currently available experimental data.

The results shown in figure 1 demonstrate that  $\bar{\mu}$  decreases with increasing  $T$  more quickly for large clusters than for small clusters. This is in agreement with conclusions based on inspecting the  $\mu(T)$  curves for specific cluster sizes obtained either with uniform coupling constants [9, 11] or with cluster-specific constants  $J_{ij}$  [13]. However, there are exceptions to this rule; e.g.  $\bar{\mu}$  of the 9-atom cluster decreases with increasing  $T$  more quickly than  $\bar{\mu}$  of the 15-atom cluster (in the  $T \approx 300$ –600 K range). A surprising feature of the results shown in figure 1 is that the non-monotonous character of the dependence of  $\bar{\mu}$  on  $N$  gets more pronounced if the temperature increases from 0 K to  $T \approx 600$ –800 K (the maxima at 15 and 59 atoms are highest for  $T \approx 800$  K).

It follows from the temperature dependence of the magnetic moment profile of the 89-atom cluster (figure 2) that  $\bar{\mu}$  decreases with  $T$  more quickly at the cluster surface than in the interior. This agrees with earlier results obtained for  $J_{ij}$  constants taken from Fe crystal [10–12]. If proper cluster  $J_{ij}$  constants were used, it was found by inspecting the individual  $\mu_s^{(j)}(T)$  curves that this trend is not uniform (see figure 3 in [13]). Figure 2 illustrates this from yet another viewpoint: the average magnetic moment of atoms in the second shell (at 5.42 au) is smaller than the average magnetic moment of atoms in the first shell (at 4.70 au) for  $T = 0$  K while the situation is reversed for  $T \gtrsim 600$  K. Another point to mention is that  $\mu_s^{(j)}$  at cluster surfaces never drops to zero—not even for very high  $T$ .

A deeper insight into how temperature affects magnetism of clusters could be gained from site-related coupling constants  $J^{(i)}$ . One can see from figure 3 that their behavior can hardly be guessed beforehand; for some clusters, the  $J^{(i)}$  coupling parameter is largest in the center, for some clusters  $J^{(i)}$  is largest at the cluster surface, for some clusters  $J^{(i)}$  exhibits a non-monotonous (quasi-oscillatory) behavior. The  $J^{(i)}$  coupling parameter in clusters may be larger as well as smaller than in the bulk. So figure 3 can be seen as yet another demonstration that for a realistic description of finite-temperature magnetism of clusters, proper cluster-specific coupling constants have to be used.

The site-related coupling parameter  $J^{(i)}$  can be seen as an analog to the low-temperature limit of the local spin-fluctuation energies  $\Delta F_i$  studied for Fe clusters by Pastor *et al* [15]. Similarly to the case of  $J^{(i)}$ , it was found that  $\Delta F_i$  is a complicated function of the cluster size and of the position of the site  $i$  [15]. Moreover, Pastor *et al* found by analysing the energies  $\Delta F_i$  that for a 15-atom Fe cluster, the ferromagnetic order is particularly stable at the outermost shell while for a 51-atom cluster, atoms in the outermost shell show the tendency to spin reversals. This is in remarkable agreement with the behavior of  $J^{(i)}$  shown in figure 3: for a 15-atom cluster,  $J^{(i)}$  attains its maximum in the outermost shell while for a 51-atom cluster,  $J^{(i)}$  attains its minimum in the outermost shell.

The fact that there is only a weak relation between the  $J^{(i)}$  constants and  $n_{\text{eff}}$  (see figure 4) is in contrast to the finding that for supported Co clusters on Pt or Au, the  $J^{(i)}$  constants do depend on the coordination number of Co atoms in a nearly linear manner [26]. One should realize, however, that this difference might be caused not only by intrinsic differences but also by different size ranges: the supported Co clusters investigated in [26] contained up to 10 atoms while the free Fe clusters investigated here contain 9–89 atoms.



Let us now address how our results are affected by the approximations used. Our study focuses on clusters with bulk interatomic distances. This is certainly a limitation; real free Fe clusters will differ from this idealized geometric model. The true cluster geometry is still a matter of controversy: experimental and theoretical studies published so far do not lead to convergent conclusions [3, 6, 29–31]. We adopt the bulk bcc geometry as a reasonable first guess. We expect that our main conclusions about how  $\bar{\mu}$  changes with temperature are not specific to a particular geometry.

The potential we used for describing zero-temperature electronic structure was constructed using the ASA. We expect that this is not a serious limitation. It was demonstrated that the ASA is appropriate at metallic surfaces, unless one is interested in states localized above the surface (as in scanning tunneling microscopy) [32]. Likewise, it was shown recently that ASA potentials describe spectroscopic properties of free noble metal clusters properly [33].

Our calculation is scalar-relativistic, meaning that the orbital contribution  $\mu_{\text{orb}}$  to the magnetic moment of clusters is ignored. This should not affect the conclusions of this work. Earlier fully relativistic studies [8] found that, for  $T = 0$  K, the total magnetic moment of clusters is not very sensitive to the orbital contribution: including  $\mu_{\text{orb}}$  just caused a more or less uniform increase of  $\bar{\mu}$  by about  $0.05 \mu_{\text{B}}$ , independently of the cluster size. Likewise, including  $\mu_{\text{orb}}$  does not significantly alter the magnetic moment profile of individual clusters either (cf figures 1–2 of [8]).

The Hamiltonian (1) does not include the magnetic anisotropy energy (MAE). Earlier calculations for small supported Co clusters (up to 10 atoms) suggested that the MAE should not affect the temperature dependence of cluster magnetism significantly [34]. On the other hand, a study of free 13-atom clusters indicated that surface anisotropy could affect the temperature dependence of magnetism for low temperatures (provided that it is sufficiently large) [35]. Calculations relying on a model  $d$ -band Hamiltonian suggest that, for our cluster size range, the MAE is larger than in the bulk and that it crucially depends on the cluster size and geometry [36]. Recently it was even suggested [37] that variations of the MAE could be the main cause of the non-monotonous behavior of  $\bar{\mu}$  as observed in the experiment of Billas *et al* [1]. As a whole, it appears that the influence of the MAE on our results cannot be properly assessed at this stage.

One should also note that we rely on a *classical* Hamiltonian (1) to describe magnetic excitations. Incorporating quantum effects in calculations of finite-temperature magnetic properties is a demanding task. Recent examples include *ab initio* dynamical mean-field theory applied to bulk Fe and Ni [38], the quantum Heisenberg model applied to small rare-earth clusters [14, 39] or path-integral quantum Monte Carlo applied to light molecules and argon clusters [40, 41]. The quantum nature of magnetic excitations has to be taken into account in order to obtain, among others, the correct asymptotics in the low  $T$  regime. We do not expect that our conclusions about the systematics of magnetic moments and of exchange coupling would change if a quantum Hamiltonian instead of (1) was employed.

Our study implies that zero-temperature calculations of magnetic moments of free Fe clusters of  $N \lesssim 100$  atoms are adequate to be compared with the experimental results, e.g. at  $T = 120$  K [1]. We assume that the same will be true also for larger clusters and for other transition metals. In particular, let us recall that measurements of  $\bar{\mu}$  of free Mn clusters were performed for  $T = 68$  K [42], of free Co clusters for  $T = 78$  K [43], of free Ni clusters for  $T = 78$  K [43] and for  $T = 73$ – $303$  K [44], and of free Rh clusters for  $T = 93$  K [45]. In all these cases, ground-state calculations should be able—with reasonable accuracy—to reproduce the measured dependence of  $\bar{\mu}$  on the cluster size. The disagreement of current calculations with experiment, therefore, should not be ascribed to the influence of finite temperature. Rather, other effects such as structural transformation should be explored. An additional source of the

discrepancies between the experiment and the calculations may come from the fact that the experimental values have not been obtained directly but inferred from measured deflections in a Stern–Gerlach magnet. The magnetic moments can be derived from the experiment only after several assumptions concerning superparamagnetic behavior, single-domain magnetization, and spin relaxation have been made [43, 46, 47].

## 5. Conclusions

The dependence of the average magnetic moments  $\bar{\mu}$  of free Fe clusters of 9–89 atoms on the cluster size for temperatures up to  $T \approx 300$  K is essentially the same as for  $T = 0$  K; ground-state calculations should thus, in principle, be able to describe experiments based on deflection of molecular beams in a Stern–Gerlach magnet. The magnetic moment profile of an individual particle gets flatter if  $T$  increases. The total exchange coupling of the magnetic moment of a particular atom  $J^{(i)}$  depends in a complex manner on the cluster size as well as on the position of the atom in the cluster, with no obvious systematics.

## Acknowledgments

This work was supported by grant IAA100100637 of the Academy of Sciences of the Czech Republic. The research in the Institute of Physics AS CR was supported by project AV0Z-10100521 of the Academy of Sciences of the Czech Republic. Support by the Deutsche Forschungsgemeinschaft within the Schwerpunktprogramm 1153 ‘Cluster in Kontakt mit Oberflächen: Elektronenstruktur und Magnetismus’ and by the BMBF project 05KS4WMB/2 is gratefully acknowledged.

## References

- [1] Billas I M L, Becker J A, Châtelain A and de Heer W A 1993 *Phys. Rev. Lett.* **71** 4067
- [2] Pastor G M, Dorantes-Dávila J and Bennemann K H 1989 *Phys. Rev. B* **40** 7642
- [3] Guevara J, Parisi F, Llois A M and Weissmann M 1997 *Phys. Rev. B* **55** 13283
- [4] Andriotis A N and Menon M 1998 *Phys. Rev. B* **57** 10069
- [5] Franco J A, Vega A and Aguilera-Granja F 1999 *Phys. Rev. B* **60** 434
- [6] Postnikov A V, Entel P and Soler J M 2003 *Eur. Phys. J. D* **25** 261
- [7] Tiago M L, Zhou Y, Alemany M M G, Saad Y and Chelikowsky J R 2006 *Phys. Rev. Lett.* **97** 147201
- [8] Šipr O, Košuth M and Ebert H 2004 *Phys. Rev. B* **70** 174423
- [9] Binder K, Rauch H and Wildpaner V 1970 *J. Phys. Chem. Solids* **31** 391
- [10] Wildpaner V 1974 *Z. Phys.* **270** 215
- [11] Hendriksen P V, Linderorth S and Lindgård P A 1993 *Phys. Rev. B* **48** 7259
- [12] Kachkachi H and Garanin D A 2001 *Physica A* **300** 487
- [13] Polesya S, Šipr O, Bornemann S, Minár J and Ebert H 2006 *Europhys. Lett.* **74** 1074
- [14] Lopez-Urias F, Pastor G M and Bennemann K H 2000 *J. Appl. Phys.* **87** 4909
- [15] Pastor G M, Dorantes-Davila J and Bennemann K H 2004 *Phys. Rev. B* **70** 64420
- [16] Andriotis A N, Fthenakis Z G and Menon M 2006 *Europhys. Lett.* **76** 1088
- [17] Andriotis A N, Fthenakis Z G and Menon M 2007 *Phys. Rev. B* **75** 073413
- [18] Liechtenstein A I, Katsnelson M I, Antropov V P and Gubanov V A 1987 *J. Magn. Magn. Mater.* **67** 65
- [19] Vosko S H, Wilk L and Nusair M 1980 *Can. J. Phys.* **58** 1200
- [20] Ebert H 2002 *The Munich SPR-KKR package, version 2.1* <http://olymp.cup.uni-muenchen.de/ak/ebert/SPRKKR>
- [21] Ebert H 2000 *Electronic Structure and Physical Properties of Solids (Springer Lecture Notes in Physics vol 535)* ed H Dreyssé (Berlin: Springer) p 191
- [22] Šipr O and Ebert H 2005 *Phys. Rev. B* **72** 134406
- [23] Binder K 1997 *Rep. Prog. Phys.* **60** 487

- [24] Landau D P and Binder K 2000 *A Guide to Monte Carlo Simulations in Statistical Physics* (Cambridge: Cambridge University Press)
- [25] Mavropoulos P, Lounis S, Zeller R, Dederichs P H and Blügel S 2006 *Appl. Phys. A* **82** 103
- [26] Šipr O, Bornemann S, Minár J, Polesya S, Popescu V, Šimůnek A and Ebert H 2007 *J. Phys.: Condens. Matter* **19** 096203
- [27] Tománek D, Mukherjee S and Bennemann K H 1983 *Phys. Rev. B* **28** 665
- [28] Zhao J, Chen X, Sun Q, Liu F and Wang G 1995 *Phys. Lett. A* **205** 308
- [29] Diéguez O, Alemany M M G, Rey C, Ordejón P and Gallego L J 2001 *Phys. Rev. B* **63** 205407
- [30] Pellarin M, Bagueard B, Vialle J L, Lermé J, Broyer M, Müller J and Perez A 1994 *Chem. Phys. Lett.* **217** 349
- [31] Wang L S, Cheng H S and Fan J 1995 *J. Chem. Phys.* **102** 9480
- [32] Papanikolaou N, Nonas B, Heinze S, Zeller R and Dederichs P H 2000 *Phys. Rev. B* **62** 11118
- [33] Gusso M 2006 *J. Phys.: Condens. Matter* **18** 1211
- [34] Minár J, Bornemann S, Šipr O, Polesya S and Ebert H 2006 *Appl. Phys. A* **82** 139
- [35] Hernández L and Pinettes C 2005 *J. Magn. Magn. Mater.* **295** 82
- [36] Guirado-López R 2001 *Phys. Rev. B* **63** 174420
- [37] Xie Y and Blackman J A 2003 *J. Phys.: Condens. Matter* **15** L615
- [38] Liechtenstein A I, Katsnelson M I and Kotliar G 2001 *Phys. Rev. Lett.* **87** 067205
- [39] López-Urriáz F, Díaz-Ortiz A and Morán-López J L 2002 *Phys. Rev. B* **66** 144406
- [40] Shumway J 2006 *Computer Simulation Studies in Condensed-Matter Physics XVII (Springer Proceedings in Physics vol 103)* ed D P Landau, S P Lewis and H B Schüttler (Berlin: Springer) p 181
- [41] Parletta C, Guidotti C and Arrighini G P 2004 *Theor. Chem. Acc.* **111** 407
- [42] Knickelbein M B 2001 *Phys. Rev. Lett.* **86** 5255
- [43] Billas I M L, Châtelain A and de Heer W A 1997 *J. Magn. Magn. Mater.* **168** 64
- [44] Apsel S E, Emmert J W, Deng J and Bloomfield L A 1996 *Phys. Rev. B* **76** 1441
- [45] Cox A J, Louderback J G and Bloomfield L A 1993 *Phys. Rev. Lett.* **71** 923
- [46] Bucher J P and Bloomfield L A 1993 *Int. J. Mod. Phys. B* **7** 1079
- [47] Xu X, Yin S, Moro R and de Heer W A 2006 *Phys. Rev. Lett.* **95** 237209