

Competing structural and magnetic effects in small iron clusters

G. Rollmann, P. Entel *, S. Sahoo

Institute of Physics, University of Duisburg-Essen, Duisburg Campus, 47048 Duisburg, Germany

Received 24 April 2004; accepted 29 September 2004

Abstract

We present new results of ab initio total-energy calculations of small iron clusters, Fe_n with $2 \leq n \leq 15$, in which structural Jahn-Teller like distortion and competing non-collinear and collinear magnetic moments have been taken care of simultaneously. We used the density-functional method that employs pseudopotentials and the projector augmented wave method. The full relaxation of the atoms without imposing any symmetry constraints leads to unsymmetrical arrangements of the atoms (distorted clusters) and restores collinearity of the magnetic moments of all clusters considered so far. For $n \leq 7$ our results agree in part with previous ab initio calculations.

© 2005 Elsevier B.V. All rights reserved.

PACS: 36.40.Cg; 61.46.+w; 71.15.Mb

Keywords: Magnetism of iron clusters; First-principles calculations

1. Introduction

The physics of magnetic transition-metal (TM) clusters is still an intriguing and challenging topic both from an experimental and a theoretical point of view. Although certain properties of the clusters can be explored directly, like the bond lengths of the atoms from extended X-ray absorption fine structure measurements [1], the vibrational frequencies of free clusters from resonance Raman spectroscopy [2], the dependence of the magnetic moments of the free clusters on size and temperature using a Stern–Gerlach magnet and time-of-flight mass spectrometer [3] or the orbital and spin magnetic moments of supported clusters from X-ray magnetic circular dichroism technique [4,5], a systematic and accurate investigation of the structural, electronic and magnetic properties of small TM clusters is

still not feasible. With respect to theory the development of computational techniques relying on first-principles methods as well as the increase in computer capacity have allowed to study TM clusters containing up to a few hundred atoms—yet some fundamental problems are still there like the observation that different methods yield different results for the spin multiplicity and the magnetic moments of the clusters (see also the discussions in [6–9]) or like the competition of non-collinear versus collinear magnetism depending on the morphology of the clusters [10,11], on the Jahn–Teller distortions [12] and on the multi-twinned structures usually observed for the larger clusters [13]. For an overview of computational calculations on an ab initio basis including tight-binding calculations and a discussion of some of the problems addressed above we refer to [14].

There are some further interesting works which we would like to mention. A recent implementation of the density functional based self-consistent charge tight-binding method allowing to address larger TM clusters is discussed in [15]. Different aspects of magnetism of

* Corresponding author. Tel.: +49 203 379 3330; fax: +49 203 379 3665.

E-mail address: entel@thp.uni-duisburg.de (P. Entel).

small clusters have also been discussed on the basis of the Hubbard model allowing to deal with correlation effects [16–18] or on the basis of the Heisenberg model showing novel quantum effects for the case of antiferromagnetic exchange [19]. We finally notice that the magnetic moments of TM clusters, which for the free clusters are usually larger than corresponding bulk values, can significantly change for the case that the clusters are supported [20,21] or embedded [22,23].

In the present contribution we present results of total energy calculations in the framework of density functional theory allowing for full relaxation of the atoms in free clusters without any symmetry constraints. In contrast to most results reported in the literature we observe that for the case of iron clusters all geometries found correspond to distorted clusters even for the case of high-symmetry forms like the 13-atom icosahedron, and that the degree of distortion influences the magnitude of the magnetic moments.

2. Computational details

For each iron atom a number of eight valence electrons was taken into account, the remaining core electrons together with the nuclei were described by pseudopotentials following the projector augmented wave method as implemented in the Vienna ab initio simulation package [24]. For the exchange correlation functional we chose a form proposed by Perdew and Wang [25]. For all clusters considered the energy cutoff for the electronic wavefunctions was kept fixed at a

value of 335 eV throughout the calculations. For the supercell we have chosen a cube of size 12^3 \AA^3 which is large enough to ensure that the interaction of clusters with their images is negligible. Integration over the Brillouin zone was done for the Γ -point only. Besides atomic relaxation we also allowed for a fully non-collinear magnetization density as described in [11].

The ground state geometries of the iron clusters containing up to 15 atoms as obtained from our calculations are depicted in Fig. 1. The clusters do not possess the highest possible symmetry but are distorted to some degree. For the small Fe_n clusters ($n \leq 6$), the ground state structures are in agreement with the corresponding results reported in [8,9], whereas for Fe_7 we find the pentagonal bipyramid as in [12]. Comparison of results for the larger clusters is difficult because no similar calculations based on the generalized gradient approximation (GGA) exist.

An exception to this is Fe_{13} , whose potential energy surface has been studied extensively before by Bobadova-Parvanova et al. [28]. In close agreement to their results we obtain a distorted icosahedron with a collinear, ferromagnetic alignment of the spins and a total magnetic moment of $44 \mu_B$ as the isomer with the lowest total energy. An antiferromagnetic-like state with the moment of the central atom reversed and a total moment of $34 \mu_B$ is located 37.8 meV per atom higher. These relationships are shown in Fig. 2.

Fig. 3 shows results of geometry optimization for the Fe_5 cluster in the GGA starting from different initial geometries without imposing any symmetry constraints. We have also allowed for non-collinear arrangements of

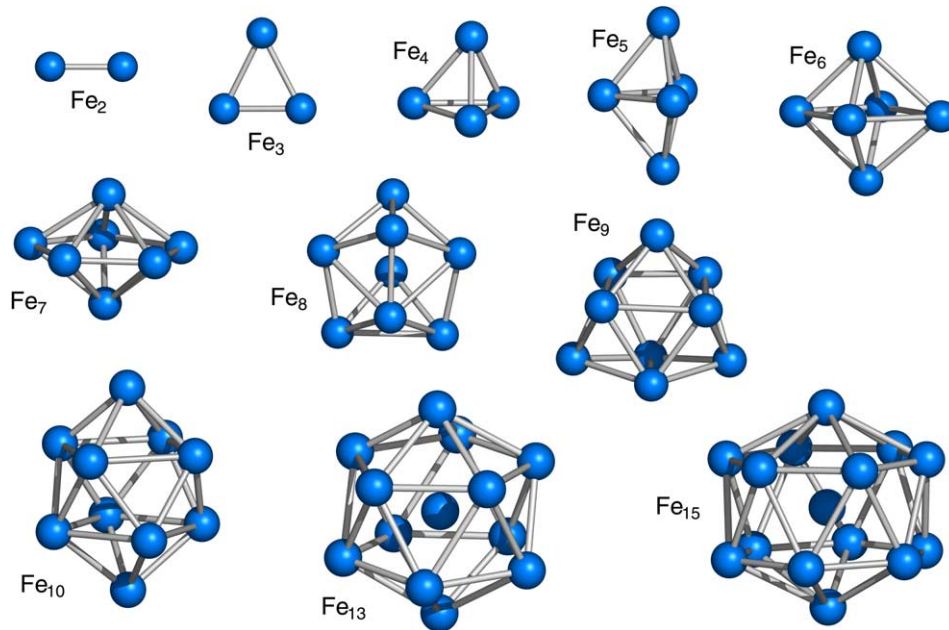


Fig. 1. Ground state geometries of iron clusters containing between 2 and 15 atoms as obtained from our GGA calculations. All structures exhibit some degree of distortion from the regular shape.

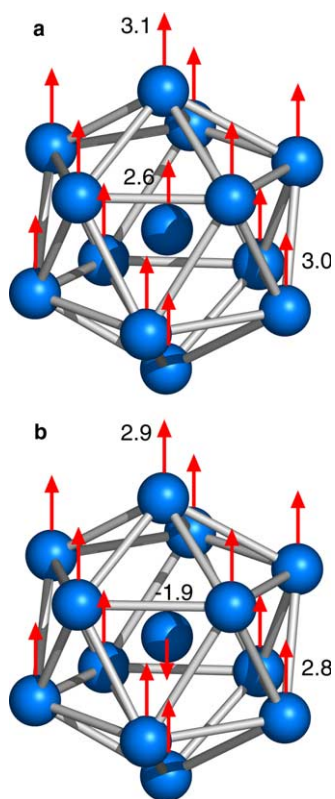


Fig. 2. The collinear, ferromagnetic ground state of the Fe_{13} cluster with distorted icosahedral shape ($M = 44 \mu_B$) (a) is by 37.8 meV lower in energy than the antiferromagnetic solution ($M = 34 \mu_B$) (b).

the magnetic moments. The ground state of the trigonal-bipyramidal (D_{3h} symmetry) cluster is characterized by a non-collinear magnetization density originating from a tilt in the moments of the apical atoms in opposite direc-

tions and corresponds to the state already found earlier [11,10]. By employing the local density approximation (LDA), Oda et al. and Hobbs et al. obtain a total magnetic moment of $14.5 \mu_B$, whereas it is calculated to $15.9 \mu_B$ when gradient corrections are included [11], present study]. The angle by which the moments of the apical atoms are tilted varies from 30° to 36° in the LDA calculations and is calculated to 31° by using GGA. The energetic relationships schematically shown in Fig. 3 reveal that the effect of the Jahn–Teller distortion on the magnetic moments is to restore collinearity. For all other clusters considered so far we have made the same observation, the ground state corresponding to a

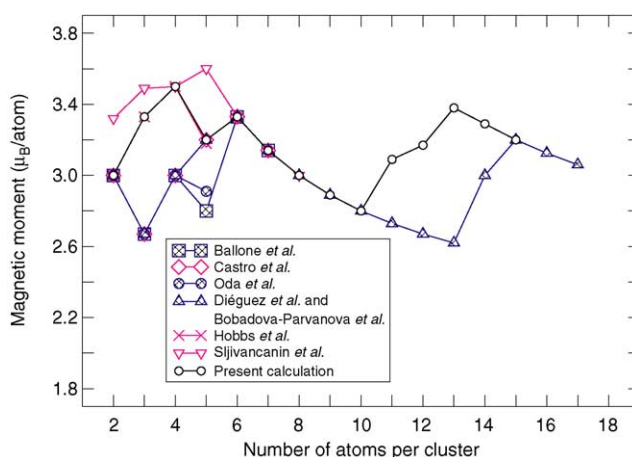


Fig. 4. Comparison of the magnetic moments obtained in the present calculation (black circles) with available data from other ab initio calculations (blue: LDA [6,10,15,26], magenta: GGA [11,21,27]). See text for discussion.

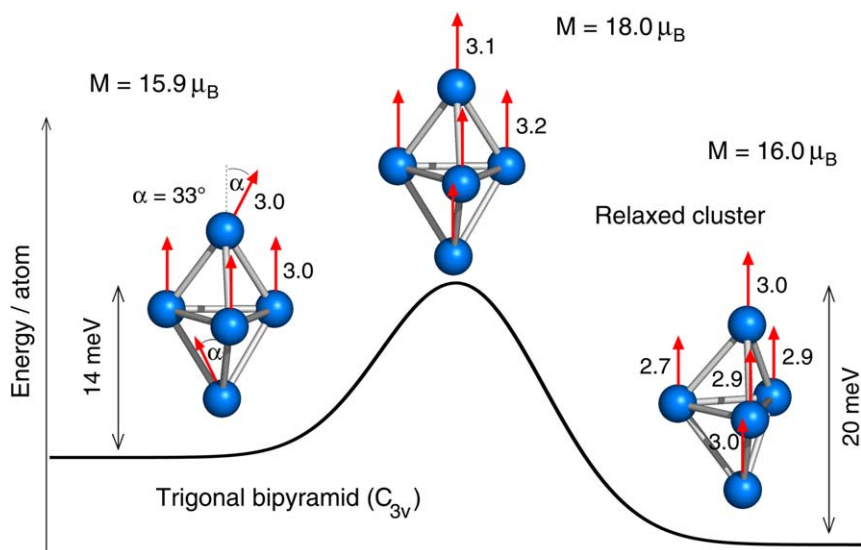


Fig. 3. Schematic sketch of the energetic and magnetic relationships between local minima on the potential energy surface of the Fe_5 cluster. The distorted trigonal bipyramid with restored collinear spin moments corresponds to the ground state geometry of Fe_5 . Magnetic moments are represented by arrows, their values are given by the numbers.

collinear ferromagnetic arrangement of the spin moments.

Fig. 4 shows the magnetic moments of the present GGA calculations together with results of former calculations using either the local density approximation (LDA) [6,10,15,26] or the GGA [11,21,27].

3. Conclusions

The results of ab initio calculations of TM clusters found in the literature are not consistent and seem to depend strongly on the details of the simulation method. We have shown that in order to obtain reliable values for the magnetic moments of the clusters, it is important to take into account relaxation of the atoms. We found that the ground state geometries of small iron clusters are distorted with collinear ferromagnetic arrangement of the magnetic moments. A systematic extension of the present calculations to include larger cluster sizes is needed. A few calculations for larger Fe_n clusters with bcc (Fe_{35} , Fe_{35}) and fcc structure (Fe_{38} , Fe_{43} , Fe_{55} , Fe_{62}) show that in this case a larger inward relaxation of the outer shells takes place in all cases, accompanied by an increase of local magnetic moments beyond $3 \mu_B$ [29]. A systematic search for additional distortion of these clusters has yet to be undertaken.

References

- [1] H. Purdum, P.A. Montano, G.K. Shenoy, T. Morrison, Phys. Rev. B 25 (1982) 4412.
- [2] T.L. Haslett, K.A. Bosnick, S. Fedrigo, M. Moskovits, J. Chem. Phys. 111 (1999) 6456.
- [3] I.M.L. Billas, J.A. Becker, A. Châtelain, W.A. de Heer, Phys. Rev. Lett. 71 (1993) 4067.
- [4] J.T. Lau, A. Fröhlich, R. Nietubyc, M. Reif, W. Wirth, Phys. Rev. Lett. 89 (2002) 057201.
- [5] P. Gambardella, S. Rusponi, M. Veronese, S.S. Dhesi, C. Grazioli, A. Dallmeyer, I. Cabria, R. Zeller, P.H. Dederichs, K. Kern, C. Carbone, H. Brune, Science 300 (2003) 1130.
- [6] O. Diéguez, M.M.G. Alemany, C. Rey, P. Ordejón, L.J. Gallego, Phys. Rev. B 63 (2001) 205407.
- [7] G.L. Gutsev, Phys. Rev. B 65 (2002) 132417.
- [8] S. Chrétien, D.R. Salahub, Phys. Rev. B 66 (2002) 155425.
- [9] G.L. Gutsev, C.W. Bauschlicher Jr., J. Phys. Chem. A 107 (2003) 7013.
- [10] T. Oda, A. Pasquarello, R. Car, Phys. Rev. Lett. 80 (1998) 3622.
- [11] D. Hobbs, G. Kresse, J. Hafner, Phys. Rev. B 62 (2000) 11556.
- [12] M. Castro, Int. J. Quant. Chem. 64 (1997) 223.
- [13] B. Rellinghaus, O. Dmitrieva, S. Stappert, J. Cryst. Growth 262 (2004) 612.
- [14] J.A. Alonso, Chem. Rev. 100 (2000) 637.
- [15] P. Bobadova-Parvanova, K.A. Jackson, S. Srinivas, M. Horoi, C. Köhler, G. Seifert, J. Chem. Phys. 116 (2002) 3576.
- [16] F. López-Urias, G.M. Pastor, Eur. Phys. J. D 9 (1999) 495.
- [17] M.A. Ojeda, J. Dorantes-Dávila, G.M. Pastor, Phys. Rev. B 60 (1999) 6121.
- [18] F. López-Urias, G.M. Pastor, K.H. Bennemann, J. Appl. Phys. 87 (2000) 4909.
- [19] J.B. Parkinson, J. Timonen, J. Phys.: Condens. Matter 12 (2000) 8669.
- [20] S. Pick, V.S. Stepanyuk, A.N. Baranov, W. Hergert, P. Bruno, Phys. Rev. B 68 (2003) 104410.
- [21] Ž. Šljivančanin, A. Pasquarello, Phys. Rev. Lett. 90 (2003) 247202.
- [22] R. Robles, R.C. Longo, A. Vega, C. Rey, V. Stepanyuk, L.J. Gallego, Phys. Rev. B 66 (2002) 064410.
- [23] Y. Xie, J.A. Blackman, Phys. Rev. B 66 (2002) 085410.
- [24] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
- [25] J.P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244.
- [26] P. Ballone, R.O. Jones, Chem. Phys. Lett. 233 (1995) 632.
- [27] M. Castro, C. Jamorski, D.R. Salahub, Chem. Phys. Lett. 271 (1997) 133.
- [28] P. Bobadova-Parvanova, K.A. Jackson, S. Srinivas, M. Horoi, Phys. Rev. B 66 (2002) 195402.
- [29] A.V. Postnikov, P. Entel, J.M. Soler, Eur. Phys. J. D 25 (2003) 261.