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The magnetic properties of Fe_3 TMB clusters

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Abstract

The magnetic properties of Fe_3 TMB clusters (TM: 3d transition metal) are studied systematically using the discrete-variational local-spin-density-functional method; the equilibrium bond length, binding energy, ionization potential and magnetic moments are determined. It is found that the magnetic moment of Fe displays an even-odd alternation upon changing the atomic number Z of the TM atom, larger moment of Fe for the even Z and smaller for the odd. If the TM is still Fe, the moment of the host Fe is the largest, the next largest is Ni but not Co as in $\text{Fe}_{60}\text{TM}_{20}\text{B}$ amorphous alloys. Sc, Ti, V and Cr are antiferromagnetically coupling to Fe moment, the rest are coupling ferromagnetically. Fe_3MnB cluster has the largest average magnetic moment, it is expected to synthesize a new type of nanostructured magnetic material with this kind of clusters.

1. Introduction

Magnetism is one of the most interesting and challenging problems in cluster physics as well as material science. From a fundamental point of view, cluster offers a unique opportunity to study how the magnetic properties change as the local electrons of an isolated atom start to delocalize through several atoms, and how the itinerant magnetism characteristic of the solid state develops with increasing cluster size. Moreover, the magnetic behavior of itinerant 3d electrons is known to be very sensitive to the lattice structure and to the local environment of the atoms. Early investigations on clusters are largely confined to one-component cluster, in order to increase the number of variables for the purpose of material design and control, clusters composed of two or more elements

have been attracting increasing attention. We know that in industrial applications, Fe–B based amorphous alloys with some additional elements such as Ni, Co, Mn, C, P, Si have formed the popularly used amorphous soft magnetic materials, while $\text{Fe}_{80}\text{B}_{20}$ with a few percent of rare earth Nb substitution can exhibit very hard magnetic properties [1]. Recently, Dudek et al. [2] found experimentally that in metallic glasses of the type $\text{Fe}_{80-x}\text{TM}_x\text{B}_{20}$ (TM: 3d transition metal, x : at% of TM) the substitution of Fe by Co causes a significant increase of magnetization by increasing the moments of Fe in this alloy, the opposite cases are for Mn, Cr, V and Ti. For $\text{Fe}_{60}\text{TM}_{20}\text{B}_{20}$, the magnetic moments of Fe are 0.69, 0.0, 0.0, 0.81, 2.85 and 2.15 for TM = Ti, V, Cr, Mn, Co and Ni, respectively, the moments for TM change according to following sequence: $\mu_{\text{Co}} > \mu_{\text{Ni}} > \mu_{\text{Mn}} > \mu_{\text{Cr}} > \mu_{\text{Ti}} > \mu_{\text{V}}$ [2]. How is the situation in this kind of clusters? In this paper, by using density functional theory with the local spin density approximation,

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we will discuss Fe₃TMB clusters, which have the same at% in composition as that in Fe₆₀TM₂₀B₂₀ alloys.

2. Theoretical method

In the density functional theory, the Hamiltonian for electrons has the following form in atomic units:

$$H = \sum_i -\frac{1}{2} \nabla_i^2 + \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}(\mathbf{r}) + V_{ext}. \quad (1)$$

We have used the Barth–Hedin type for the exchange-correlation potential $V_{xc}(\mathbf{r})$ [3]. V_{ext} is an external potential including the Coulomb potential generated by ions. The numerical atomic wave functions are used as the basis set for the expansion of wave functions. The group theory is used to symmetrize the basis functions

$$\Phi_j = \sum_i D_{ij} \phi_j \quad (2)$$

where ϕ_j is an atomic wave function, Φ_j is a symmetrized basis function, D_{ij} is the so-called symmetry coefficient which is determined only by the symmetry of clusters. In this work we have used 3d, 4s and 4p orbitals of Fe and TM atoms and 2s, 2p orbitals of B atom as the basis set ϕ_j . The wave functions of the electrons in the clusters are expanded in the symmetrized basis function Φ_j :

$$\Psi_i = \sum_j C_{ij} \Phi_j. \quad (3)$$

Then a matrix equation can be obtained:

$$(H - \epsilon S) C = 0 \quad (4)$$

where H is the Hamiltonian matrix and S is the overlap matrix. The discrete variational method (DVM) [4] has been used to self-consistently solve the matrix equation. To get the electronic density of states (DOS) from the discrete energy level ϵ_i , the Lorentz expansion scheme is used, the total DOS is defined by

$$D(E) = \sum_{n,l,\sigma} D_{nl}^\sigma(E) \quad (5)$$

with

$$D_{nl}^\sigma(E) = \sum_i A_{nl,i}^\sigma \frac{\delta/\pi}{(E - \epsilon_i)^2 + \delta^2} \quad (6)$$

where σ is the spin index, i labels the eigenfunction and a broadening factor $\delta = 0.42$ eV is used. $A_{nl,i}^\sigma$ is the Mulliken population numbers, n and l are orbital and angular quantum numbers, respectively. The total energy is evaluated by

$$E_{tot} = \sum_i f_i \epsilon_i - \frac{1}{2} \iint \frac{\rho(\mathbf{r}) \rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + \int \rho(\mathbf{r}) (\mu_{xc} - V_{xc}) d\mathbf{r} + \frac{1}{2} \sum_{IJ} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (7)$$

where f_i is the occupation number, Z_I is the proton number of atom I , $\rho(\mathbf{r})$ is the charge density, μ_{xc} is a universal potential related to V_{xc} by

$$\frac{d}{d\rho} \rho \mu_{xc} = V_{xc}. \quad (8)$$

The binding energy is determined by the difference between the total energy of the cluster and that of a reference system selected to minimize the numerical errors,

$$E_b = E_{tot} - E_{ref}. \quad (9)$$

In our calculations, the number of the Diophantus sample points per atom is 1000, and the convergence accuracy of the self-consistent charge process is 10^{-4} e.

3. Results and discussion

We have studied the structures and magnetic properties of Fe_{*n*} clusters and Fe_{*n*}B clusters in detail [5, 6]. We found that substituting a Fe atom in Fe_{*n*+1} cluster with B atom forming Fe_{*n*}B cluster, it is favorable for B atom to locate at the surface not in the center of the cluster, the lowest-energy structures for both Fe₅ and Fe₄B clusters are triangular bipyramids. Now let us replace a Fe atom in the Fe₄B cluster with another TM atom forming Fe₃TMB cluster. What happens to equilibrium structure is the question. In the study of magnetism for cluster, only the higher symmetry structures are

Table 1

The equilibrium bond length R (Å) and average binding energy ϵ_b (eV), ionization potential IP (eV), μ_{Fe} , μ_{TM} , μ_B the moments for Fe, TM and B atom, respectively, μ the average moment of cluster; h_{TM} and h_B the distances between TM or B atom at the vertex to the bottom

Cluster	Bond length	ϵ_b	IP	μ_{Fe}	μ_{TM}	μ_B	μ
Fe ₃ ScB	2.60 $h_{Sc} = 2.08, h_B = 1.04$	3.462	5.01	3.252	− 1.137	− 0.618	1.60
Fe ₃ TiB	2.50 $h_{Ti} = 2.00, h_B = 1.25$	3.737	5.56	3.256	− 2.018	− 0.750	1.40
Fe ₃ VB	2.55 $h_V = 1.84, h_B = 1.15$	3.682	6.01	3.123	− 2.721	− 0.703	1.19
Fe ₃ CrB	2.80 $h_{Cr} = 1.86, h_B = 0.95$	2.896	5.62	3.381	− 4.580	− 0.561	1.11
Fe ₃ MnB	2.60 $h_{Mn} = 2.03, h_B = 1.04$	2.995	5.80	3.276	4.615	− 0.443	2.80
Fe ₃ FeB	2.50 $h_{Fe} = 1.75, h_B = 1.51$	3.361	5.93	3.450	3.363	− 0.615	2.62
Fe ₃ CoB	2.60 $h_{Co} = 1.89, h_B = 0.94$	3.213	6.35	3.346	2.477	− 0.516	2.496
Fe ₃ NiB	2.50 $h_{Ni} = 2.00, h_B = 1.25$	3.445	5.15	3.446	1.179	− 0.679	2.167

Table 2

The occupation numbers and moments of atomic orbitals

Cluster	3d (Fe)	4s (Fe)	4p (Fe)	3d (TM)	4s (TM)	4p (TM)	2s (B)	2p (B)
Fe ₃ ScB	6.4118 (2.932)	0.9268 (0.238)	0.4449 (0.082)	1.5598 (− 0.805)	0.9949 (− 0.220)	0.2903 (− 0.113)	1.4287 (− 0.0338)	2.3757 (− 0.5847)
Fe ₃ TiB	6.4438 (2.870)	0.9004 (0.268)	0.4768 (0.117)	2.5525 (− 1.649)	0.9734 (− 0.224)	0.3331 (− 0.145)	1.470 (− 0.0687)	2.2052 (− 0.6813)
Fe ₃ VB	6.4462 (2.7892)	0.8483 (0.292)	0.4174 (0.130)	3.5259 (− 2.418)	1.0140 (− 0.194)	0.5285 (− 0.313)	1.4475 (− 0.054)	2.3486 (− 0.649)
Fe ₃ CrB	6.3858 (3.024)	0.8872 (0.237)	0.2787 (0.119)	4.9414 (− 4.006)	0.9598 (− 0.239)	0.5300 (− 0.335)	1.4579 (− 0.0269)	2.4584 (− 0.5341)
Fe ₃ MnB	6.4169 (3.013)	0.9104 (0.162)	0.3597 (0.102)	5.4653 (4.333)	1.0691 (0.220)	0.5517 (0.062)	1.4385 (− 0.0203)	2.4143 (− 0.4232)
Fe ₃ FeB	6.4428 (3.1593)	0.9102 (0.209)	0.4396 (0.081)	6.5002 (3.209)	1.0971 (0.020)	0.4716 (0.133)	1.5526 (− 0.0707)	2.0008 (− 0.5442)
Fe ₃ CoB	6.4004 (3.027)	0.8362 (0.233)	0.3700 (0.086)	7.4315 (2.386)	1.2276 (0.0446)	0.5239 (0.047)	1.4195 (− 0.0111)	2.5658 (− 0.5054)
Fe ₃ NiB	6.4359 (3.064)	0.8595 (0.252)	0.4364 (0.130)	8.4819 (1.280)	1.1730 (− 0.002)	0.3954 (0.082)	1.4523 (− 0.0529)	2.3021 (− 0.6267)

Note: The numbers in brackets are moments.

often considered, because the higher symmetry is favored for the magnetism [7–10]. We have taken Fe₃CoB cluster as an example, by comparing the binding energies of tetrahedron, square-pyramid and triangular bipyramid, the last one is found to be the lowest-energy structure. Because of the sim-

ilarity among all the Fe₃TMB clusters considered, we adopt triangular bipyramid as equilibrium structure for all the Fe₃TMB clusters, the atomic distances are optimized by maximizing the binding energy with the symmetry constraints. Mulliken population analysis has been used to obtain the

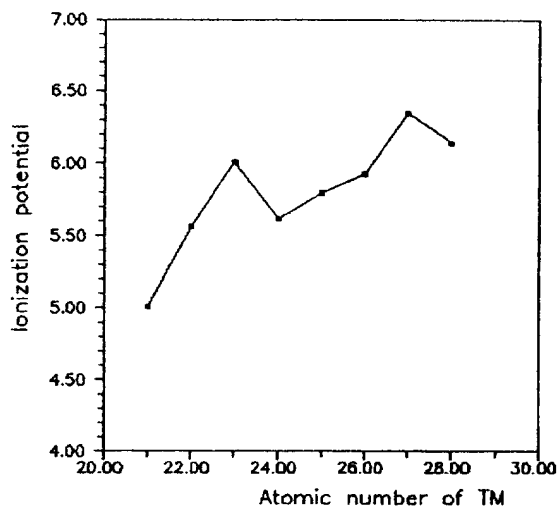


Fig. 1. The dependence of ionization potential IP on the atomic number of TM.

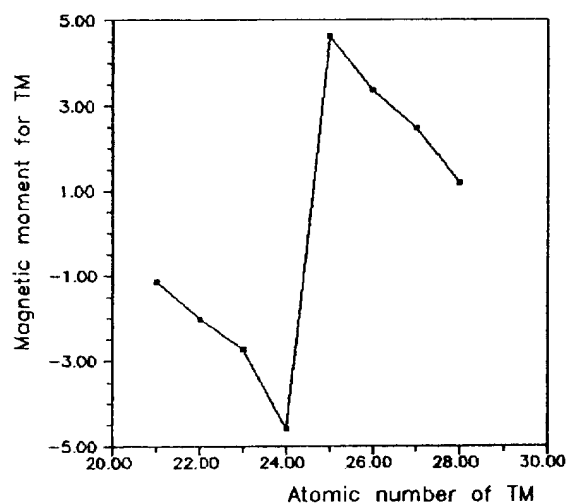


Fig. 3. The dependence of magnetic moment of TM on the atomic number of TM.

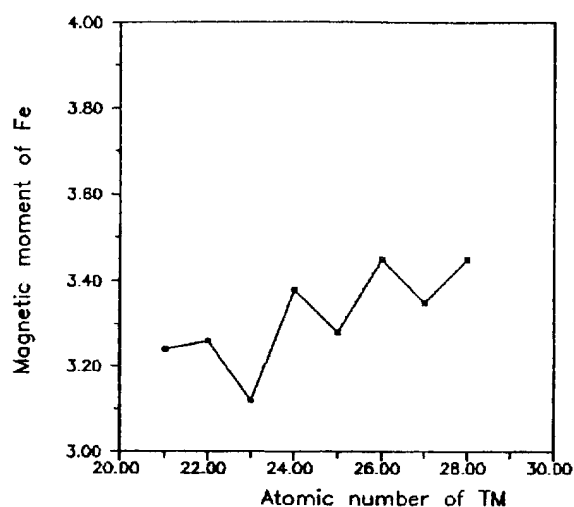


Fig. 2. The dependence of magnetic moment of Fe on the atomic number of TM.

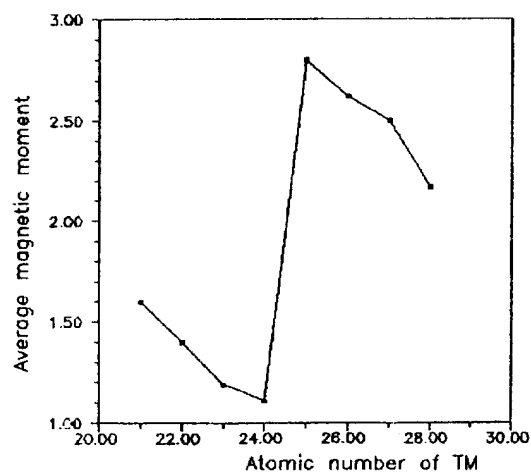


Fig. 4. The dependence of average magnetic moment on the atomic number of TM.

occupation number of atomic orbitals, the magnetic moments are the difference between the occupation numbers in spin-up and spin-down states, the vertical ionization potentials are the total energy differences between neutral and positively charged clusters at the equilibrium distances of the neutral clusters. The data for bond length (\AA),

binding energy per atom (eV), ionization potential IP (eV) and magnetic moments are listed in Table 1, the occupation numbers and moments of atomic orbitals are shown in Table 2. The dependences of IP, magnetic moments for Fe and TM, the average magnetic moment of the cluster on atomic number Z of TM atom are given in Figs. 1–4, respectively.

We can see from the Table 2 that B atom is an electron acceptor with charges transferred from Fe or/and TM, meanwhile, the 4s electrons of Fe are also transferred to 3d and 4p orbitals of Fe atoms. Similar situations are true for Sc and Ti, but opposite is true for V, Cr, Mn, Fe, Co and Ni, for which the TM atom gets electrons. The 4s electrons of Fe taking part in the charge transfer process is confirmed by the Mossbauer spectroscopy for amorphous $\text{Fe}_{80-x}\text{M}_x\text{B}_{20}$ (M: P, C, Si) [11]. Sc, Ti, V and Cr are antiferromagnetic coupling to Fe moment, while Mn, Fe, Co and Ni are ferromagnetic coupling to Fe moment. It is interesting to notice that if the substitution TM is still Fe, the magnetic moment for the host Fe is largest, the second one is for Ni, but not Co as in $\text{Fe}_{60}\text{TM}_{20}\text{B}_{20}$ amorphous alloy. The most striking feature is that the magnetic moment of host Fe displays even–odd alternation upon changing the atomic number Z of TM, the even Z makes the moment of Fe larger, and the odd Z brings out the contrary. The analysis indicates that if Z is even the number of total valent electrons is odd, the unpaired electron is associated with the increase of moment. As far as the magnetic moments of substitution TM atom are concerned, the largest is for Mn and the smallest is for Sc. The Fe_3MnB cluster has the largest average moment among all the clusters considered. Hence we can hope that a new type of nanostructured magnetic material may be synthesized with this kind of clusters.

Fig. 5 shows the density of state (DOS) and the orbital-resolved partial DOS (PDOS) for Fe_3MnB cluster, where the Fermi energy is shifted to zero. We can see that the total DOS is dominated by the Fe-3d PDOS which is much higher than others, the Fe-4p and Mn-4p states are basically above the Fermi level, while B-2s states and part of B-2p states are far below the Fermi level, so B atom must be electron acceptor in agreement with the Mulliken population analyses in Table 2, and the Fe-3d and Mn-3d states have considerable hybridizations resulting in ferromagnetic coupling between them.

To sum up, we have systematically studied the magnetic properties of Fe_3TMB clusters. Most remarkably, the moment of host Fe displays even–odd alternation upon changing the atomic

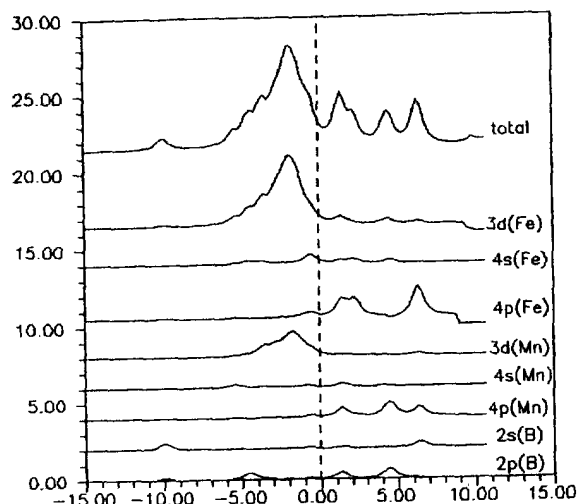


Fig. 5. The density of state and partial density of state for Fe_3MnB cluster, the abscissa is for energy (eV) and the vertical axis is for DOS and PDOS (arb. units).

number of TM atom. Although Fe_3TMB cluster has the same at% in composition as in $\text{Fe}_{60}\text{TM}_{20}\text{B}_{20}$, their properties are quite different. Furthermore, Fe_3TMB cluster has the largest average moment, and it might provide a new class of nanostructured magnetic materials.

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