

The structures and magnetic properties of small Fe_nB clusters

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Abstract. The geometric structures and magnetic properties of small Fe_nB clusters have been studied by using a linear combination of atomic orbitals approach with the density functional formalism, and the Kohn–Sham equation is solved self-consistently by the discrete variational method. It is found that it is favourable for the B atom to locate at the surface, not at the centre of the cluster, and that the tetrahedron for Fe_4B and the triangular prism for Fe_6B clusters are not the most stable structures. When one atom in an Fe_{n+1} cluster is replaced by a B atom, forming an Fe_nB cluster, the binding energy increases, while the moment of the Fe atom decreases. It is indicated that the environment and doping play important roles as regards the stability and magnetic properties of clusters.

1. Introduction

Atomic clusters constitute an intermediate phase, between the atomic and bulk phases, which shows anomalous physical and chemical properties in comparison with the behaviour of the corresponding bulk solids and free atoms. In recent years, more and more attention has been paid to the study of the clusters. Part of the motivation stems from the desire to understand how physical properties and structures evolve from atom to molecule to cluster to ultrafine particle, and in the end to the bulk phase. Further motivation is associated with the desire to use solid devices of smaller and smaller structures in technological applications. Early investigations on clusters were largely confined to single-component clusters; recently, in order to increase the number of variables for the purposes of material design and control, clusters composed of two or more elements have been attracting increasing attention. Many studies indicate that structures and properties of clusters will be changed greatly by doping—for example, the stability of the Al_{13} cluster can be substantially enhanced by doping with C, B^- [1] and transition-metal atoms [2]. Therefore many kinds of complex materials can be synthesized via atomic engineering.

Transition-metal clusters are of particular interest, because their significant catalytic and magnetic properties have led to useful technological applications, such as in high-density magnetic devices. In recent years, Fe_n clusters have been studied extensively and many exotic properties have been found [3–7]. We know that B can greatly improve the features of bulk Fe, and Fe–B-based crystalline and amorphous alloys have many useful properties (such as ferromagnetism, and creep and wear resistance), so they have been widely used in

modern aeronautical and astronautic technology and in many other industrial applications. How does the impurity B affect the structures and magnetic properties of the Fe_n clusters? No study on this problem has been reported to our knowledge. In this paper, we shall deal with this subject. In fact, the tetrahedron for Fe_4B and triangular prism for Fe_6B have been taken to be structural units in studies on amorphous Fe–B alloys [8, 9], but are these two structures stable as isolated clusters? Furthermore, Fiorani *et al* [10], and Linderoth *et al* [11] and Rivas *et al* [12] have successfully prepared ultrafine amorphous Fe–B particles, with which a new type of nanostructured material can be synthesized. Although the ultrafine particle is much larger in size than a cluster, investigations on clusters can shed some light on the properties of ultrafine particles. In this paper, we use spin-density functional theory together with the local density approximation to study the structure and magnetic properties of Fe_nB clusters.

2. The theoretical method

In 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 von Barth–Hedin type of exchange–correlation potential $V_{xc}(\mathbf{r})$ [13]. V_{ext} is an external potential including the Coulomb potential generated by ions. The numerical atomic wavefunctions are used as the basis set for the expansion of wavefunctions. Group theory is employed to symmetrize the basis functions:

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

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

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

Then a matrix equation can be obtained:

$$(\mathbf{H} - \varepsilon \mathbf{S}) \mathbf{C} = 0 \quad (4)$$

where \mathbf{H} is the Hamiltonian matrix and \mathbf{S} is the overlap matrix. The discrete variational method (DVM) [14] has been used to self-consistently solve the matrix equation. To get the electronic density of states (DOS) from the discrete energy levels ε_i , the Lorentz expansion scheme is used; the total DOS is defined as

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

with

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

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 number, and n and l are orbital and angular quantum numbers respectively. The total energy is evaluated from

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

where f_i is the occupation number, Z_I is the proton number of atom I , $\rho(r)$ is the charge density, and 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 E_b is determined from

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

where E_{tot} is the total energy of the cluster, and E_{ref} is the sum of the total energies of all of the isolated free atoms in the cluster. The average binding energy is defined as the ratio between the total binding energy and the total number of atoms.

Table 1. The equilibrium bond lengths (\AA) and average binding energies ε_b (eV) for Fe_nB clusters. h_{Fe} and h_B are the distances from the Fe or B atom at the vertex to the bottom, and z is the prism length for a triangular prism.

Cluster	Structure	Bond length	ε_b	Position for B
FeB	Linear	1.78	2.15	
Fe ₂ B	Linear	1.80	2.46	Centre
	Triangular	$R_{Fe-Fe} = 2.30$, $R_{Fe-B} = 1.77$	2.57	Vertex
Fe ₃ B	Triangular	3.10	2.42	Centre
	Tetrahedral	2.24, $h_B = 1.74$	2.85	Vertex
Fe ₄ B	Square	2.50	2.88	Centre
	Square pyramidal	2.23, $h_B = 1.92$	3.22	Vertex
	Tetrahedral	3.0	2.60	Centre
	Triangular bipyramidal	2.5, $h_{Fe} = 1.75$, $h_B = 1.501$	3.37	Vertex
Fe ₅ B	Pentagonal	2.24	3.24	Centre
	Pentagonal pyramidal	2.13, $h_B = 1.01$	3.63	Vertex
	Square pyramidal	2.70	2.98	Centre
	Triangular bipyramidal	2.80	2.55	Centre
	Octahedral	2.31, $h_{Fe} = 2.19$, $h_B = 1.53$	3.48	Vertex
Fe ₆ B	Hexagonal	2.25	3.320	Centre
	Hexagonal pyramidal	2.21, $h_B = 0.35$	3.09	Vertex
	Pentagonal pyramidal	2.23, $h_{Fe} = 1.41$	2.83	Centre
	Pentagonal bipyramidal	2.30, $h_{Fe} = 1.21$, $h_B = 1.15$	3.81	Vertex
	Octahedral	2.30	2.44	Centre
	Triangular prismatic	2.35, $z = 3.17$	3.36	Centre

3. Results and discussions

For all the structures considered, the atomic distances are optimized by maximizing the binding energy within the symmetry constraints. Mulliken population analysis has been

used to obtain the occupation numbers of the atomic orbitals; the magnetic moment is the difference between the occupation numbers in spin-up and spin-down states. The structure data obtained are listed in table 1. In the case of the cluster Fe_2B , we have calculated the linear and triangular geometric structures; the binding energy of the triangular structure is about 0.11 eV higher than that of the linear structure. For the Fe_3B cluster, we have studied the triangular and tetrahedral structures, and found that the tetrahedron has larger binding energy, which indicates that a transition from a two-dimensional structure to a three-dimensional one takes place. Among the possible structures—square, square pyramid, tetrahedron and triangular bipyramid—for Fe_4B , we find that the triangular bipyramid has the largest binding energy, and the binding energy of the tetrahedron with B at the centre is smaller. This suggests that the tetrahedral structure is not stable for the isolated Fe_4B cluster. For the Fe_5B cluster, the pentagonal bipyramid is the most stable structure, and octahedron comes next. For the Fe_6B cluster, the most stable structure is the pentagonal bipyramid rather than the triangular prism; this also indicates that the triangular prism structure is not stable for the isolated Fe_6B cluster. Therefore, from table 1, we can see that the tetrahedron for Fe_4B and triangular prism for Fe_6B are not the most stable structures; the situation is quite different to that of bulk amorphous Fe–B alloys, where these two clusters are adopted as stable structure units. These results indicate that the environment plays an important role as regards the stability of clusters. Meanwhile it is interesting to note that it is favourable for the B atom to locate at the surface, not at the centre of the cluster.

Table 2. The comparison as regards stable structures, average binding energies ε_b (eV) and moment μ (μ_B) between the Fe_nB cluster and the Fe_{n+1} cluster.

	Cluster	Structure	ε_b	μ
$n = 1$	FeB	Linear	2.15	3.866
	Fe_2	Linear	1.65	4.000
$n = 2$	Fe_2B	Triangular	2.57	3.775
	Fe_3	Triangular	2.03	3.980
$n = 3$	Fe_3B	Tetrahedral	2.85	2.997
	Fe_4	Tetrahedral	2.67	3.010
$n = 4$	Fe_4B	Triangular bipyramidal	3.37	3.388
	Fe_5	Triangular bipyramidal	3.20	3.450
$n = 5$	Fe_5B	Pentagonal pyramidal	3.63	2.384
	Fe_6	Octahedral	3.59	3.300
$n = 6$	Fe_6B	Pentagonal bipyramidal	3.81	2.844
	Fe_7	Pentagonal bipyramidal	3.75	2.850

One of the authors has studied the structures and properties of small Fe_n clusters ($n \leq 7$) in detail [5]. In order to demonstrate clearly the effects of the impurity B atoms on the structures and magnetic moments, a comparison between Fe_nB and Fe_{n+1} clusters has been made and shown in table 2, where the data for Fe_{n+1} clusters are from [5]. We can see that in Fe_nB clusters the average binding energy is an increasing function of n , and when one atom in an Fe_{n+1} cluster is replaced by one B atom, forming an Fe_nB cluster, the binding energy increases, while the moment of the Fe atom decreases. Except for in the Fe_5B cluster, the structure of the ground state remains unchanged when one Fe atom is replaced by a B atom, indicating that the B atom simply substitutes for one Fe atom when forming the Fe_nB cluster. However, the stable structure for Fe_5B is a pentagonal pyramid, not an octahedron as in the Fe_6 , which suggests that the structure of an Fe_n cluster can be

Table 3. The occupation numbers and moments of atomic orbitals for the stable structures of Fe_nB clusters. The numbers in brackets are moments (in μ_B); the orbitals are 3d, 4s and 4p for the Fe atom, and 2s and 2p for the B atom.

Cluster	3d	4s	4p	μ_{Fe}	2s	2p	μ_B
FeB	6.4468 (2.9949)	0.8480 (0.6862)	0.2475 (0.1851)	(3.8662)	1.8294 (-0.009)	1.6363 (-0.4567)	(-0.4657)
Fe ₂ B	6.3965 (3.2205)	0.9930 (0.3647)	0.3096 (0.1901)	(3.7753)	1.6257 (0.060)	1.9761 (-0.6167)	(-0.5506)
Fe ₃ B	6.5961 (2.7842)	0.9238 (0.0831)	0.3092 (0.1302)	(2.9974)	1.6433 (0.0056)	1.8691 (-0.6035)	(-0.5979)
Fe ₄ B	6.4571 (3.1718)	0.9569 (0.1624)	0.4476 (0.053)	(3.3878)	1.5526 (-0.0707)	2.0008 (-0.5442)	(-0.6143)
Fe ₅ B	6.5301 (2.1897)	0.7962 (0.0331)	0.4944 (0.1604)	(2.384)	1.4621 (-0.0093)	2.4313 (-0.3549)	(-0.3642)
Fe ₆ B	6.5089 (2.767)	0.7127 (0.01)	0.5550 (0.0674)	(2.844)	1.2068 (-0.1347)	2.9805 (-0.4508)	(-0.5905)

changed by doping with B.

The occupation numbers and moments of the atomic orbitals of the stable structures are shown in table 3. Comparing with the electronic configurations for the isolated Fe and B atoms, we find that the B atom is an electron acceptor with charges transferred from Fe atoms; this is because the electronegativity of B is larger than that of the Fe atom, and the charge transfers are in the region of 0.138–0.45 electrons per Fe atom and 0.45–1.10 electrons per B atom. In the Fe_{n+1} cluster, 4s electrons are transferred to 3d and 4p orbitals due to the sp–d hybridization [5]. In the Fe_nB cluster, 4s electrons of Fe are transferred not only to its own 3d and 4p orbitals but also to the B 2p orbital. Additionally, the B atom displays small negative moments, and the main contributions come from the 2p orbital, which has strong hybridizations with the orbitals of Fe in the spin-down (minority) band, leading to a slightly increased occupation of the B spin-down states. Such an induced ferromagnetism also exists in many glassy and crystalline transition-metal and transition-metal–metalloid alloys [15–17].

Recently, Hyeong-Chai Jeong and Steinhardt proposed a cluster approach for quasicrystals [18]; they believed that quasicrystal ordering is attributable to a small set of low-energy atomic clusters which determine the state of minimum free energy, and the structure of a solid can be determined from the lowest-energy atomic clusters. However, the situation is quite different in amorphous materials. As we have found, the tetrahedron for Fe_4B and the triangular prism for Fe_6B , which are presumed to be the structural units in Fe–B amorphous alloys, are not the most stable structures for isolated clusters. We can see that the behaviour of isolated clusters is quite different from that of the clusters in the bulk phase; the environment plays an important role as regards the stability and magnetic properties of clusters. In order to obtain the real properties of amorphous substances via a cluster approach, the interactions between the cluster and its environment must be taken into account. In the previous cluster model calculations for the amorphous Fe–B alloys [8], a single cluster is was used to simulate the bulk phase; from the above discussions, we can see that an improvement should be made by considering the interactions with the environment, and this study is still in progress.

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