PHYSICAL REVIEW B VOLUME 47, NUMBER 20 15 MAY 1993-II

Ground-state properties of small iron clusters

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(Received 23 November 1992)

Ground-state structures of small iron clusters, $N \leq 18$, are determined from simulated-annealing calculations. Total energies are calculated using the effective-medium theory, and the d-band energy is included using the tight-binding approximation. The main effects of the partially filled d band are a higher symmetry of the ground-state structures than those assumed by simple metals such as Na and Cu and a tendency to produce hollow structures. We find a correlation between the presence of unscreened atoms in the iron-cluster ground states and measured ionization potentials and reactivities with H_2.

Transition-metal clusters are interesting because of the complex interplay between effects of discreteness, magnetism, and the presence of partially filled d bands. Although calculations of the atomic structures of simple-metal clusters exist,[1,2] similar calculations on transition-metal clusters have not been done, primarily because many more valence electrons are involved.

Recent interesting experimental results on the magnetic properties of iron clusters make these systems particularly desirable for theoretical investigation. An anomalous increase of the Stern-Gerlach deflection of iron clusters with temperature has been reported,[3] while for similar experiments on cobalt[4] the magnetism always decreases with temperature. The latter result is explained by assuming the clusters to be super-paramagnetic with a spin temperature decreasing the Stern-Gerlach deflection.[5] In models trying to explain the anomalous behavior of iron,[6,7] the anisotropy of iron clusters is believed to play an important role. However, in order to estimate the anisotropy of small iron clusters, the atomic arrangement of the clusters is needed.

In this paper we present an approximate total-energy scheme that allows simulated-annealing determination of ground-state structures of transition metals, and iron clusters are used as a prototype system. We find a correlation between measured H_2 reactivities and ionization potentials and the level of screening of the most exposed atom in the cluster ground-state configuration as a function of cluster size. This correlation gives a very transparent explanation of the variation of hydrogen reactivity with iron cluster size. The reactive clusters are simply the ones that pack in a non-close-packed manner and therefore have surface atoms with relatively low coordination number. Here we have not gone further into an investigation of the magnetic anisotropy of the clusters. This requires a presumably more involved total-energy calculation that includes the electronic structure. Previously[8] the expectation value of the spin-orbit coupling has been calculated within a Hartree-Fock treatment of amorphous iron.

The basic idea behind the effective-medium theory (EMT) is to estimate the binding energy of an atom in a metallic system by approximating the surroundings by a simpler "effective medium."[9] The reference system is usually chosen as a homogeneous electron gas of a suitable density. The EMT has been applied in a number of studies of energetics of metal surfaces including descriptions of clean and adsorbate-induced surface relaxations and reconstructions,[9-12] self-diffusion at surfaces,[13] and a study of small copper clusters.[2]

The electron density for a system of atoms is approximated by a superposition of screened-atom densities. This leads to an expression[9] for the binding energy of the system which can be written

$$E_{\text{tot}} = \sum_{\text{atoms } i} E_c(\bar{n}_i) + \sum_{\text{atoms } i} \Delta E_{\text{AS}}^{(i)} + \Delta E_{\text{1-el}} \quad (1)$$

where the sums run over all the atoms in the system. In Eq. (1) the first term contains the *cohesive function* E_c which is determined from calculations of the energy of one atom embedded in a homogeneous gas of density $\bar{n}_i$. For all metals the cohesive function exhibits a single minimum at a density n_0 characteristic of the element. This density corresponds to the equilibrium lattice constant of the metal, and the second derivative of the cohesive function around the minimum is proportional to the bulk modulus of the metal.[9]

The *atomic-sphere correction energy* ΔE_{AS} describes the difference in electrostatic interaction between the atoms in the system under consideration and in a close-packed (fcc) arrangement where the electrostatic interactions are already included in the cohesive function in the atomic-sphere approximation. This energy is predominantly positive and originates from core-core repulsion in insufficiently screened metallic systems.

The *one-electron energy correction* $\Delta E_{\text{1-el}}$ describes the energy due to the deference in the local density of states (DOS) for an atom in the metallic system compared with the same atom in the reference system. This term can be neglected in most situations for simple metals and late transition metals,[9] but is important for a description of the band energy of transition metals with partially filled d bands. Details of the effective-medium calculation procedure can be found in Ref. 2.

In order to calculate the one-electron energy correction we have chosen to apply a tight-binding (TB) model. This simple approach has been shown to give a good description of copper atoms at low coordination numbers. The EMT with a tight-binding one-electron correction reproduces the essential physics of Cu clusters, as shown in a previous study,[2] and has given a good description of the self-diffusion of Cu on a Cu(111) surface.[13] Matrix elements for s and d orbitals for Fe have been taken from a parametrization based on self-consistent linear-combination-of-atomic-orbitals (LCAO) calculations[14] on Fe dimers where the TB approach was combined with a moment expansion model. In this work, since we only work with finite clusters, the $6N\times 6N$ tight-binding matrices have been diagonalized explicitly. The one-electron energy correction can now be expressed as the following difference:

$$\Delta E_{1\text{-el}} = E_{1\text{-el}}^{\text{TB}}(\{\mathbf{r}_i\}) - \sum_{\text{atoms } i} E_{1\text{-el}}^{\text{ref}}(\bar{n}_i) \ . \tag{2}$$

The magnetism of iron is included through a difference in on-site matrix element which leads to the correct shift in DOS for the bcc crystal.

The EMT parameters were fitted to three experimental quantities, the equilibrium lattice constant, the bulk modulus, and the shear modulus,[16] using the bcc lattice as the reference system for the one-electron correction.

In the EMT formulas as well as in the calculation of the reference one-electron energy we have included two nearest-neighbor shells. Since only a few atom pairs have larger interatomic distances than the bulk equilibrium second-nearest-neighbor distance in the cluster size range considered, we have not included any cutoffs in the calculation of $\bar{n}$ and of the TB matrix of a cluster.

In EMT bulk and surface calculations, E_c is normally described with a third-order expansion around its minimum. Atoms at cluster surfaces may reside at densities too low for this to be sufficient; to improve the functional form of E_c, we have added an exponential function in $\bar{n}$ fitted to linear-muffin-tin-orbital (LMTO) calculations for bcc iron at very large lattice constants. This term is negligible at bulk equilibrium densities, but gives a very good fit at low densities.

First-principles calculations on iron microclusters have been performed for up to four atoms.[15] The ground-state geometries found here are the same as the ones we find—an equilateral triangle for Fe_3 and a tetrahedron for Fe_4. Bond length and cohesive energy for the cluster ground states from Ref. 15 and from our calculations are listed in Table I. Note that the zero of cohesive energy is not very well determined in the EMT. There are differences in the absolute magnitude of both quantities, but the variation with size and structure is very similar with the two methods. As the EMT parametrization relates to bulk properties, we expect the quality of the model to be better for systems with larger coordination numbers.

We find the ground-state structure of Fe to be fcc rather than the actual bcc. This energy balance is very fine, though, and is due to magnetic effects far beyond this model.[15] The failure to predict the ferromagnetic bcc bulk structure for iron should not discourage one from investigating the effects of finite size and surfaces on the ground-state structure of Fe clusters, effects which are much larger.

With the total-energy method described above we have performed simulated-annealing Monte Carlo calculations of an average of 3000 sweeps through all coordinates, cooling from $\simeq 2000$ K down to $\simeq 20$ K, and subsequently minimized to find a local-energy minimum. Of the order of 10 annealings have been performed for each cluster size.

In order to estimate the degree of convergence of the present simulated-annealing calculations, we have calculated the standard deviation of the annealed energy based on 17 anneals for $N=8$ and 17 anneals for $N=13$, each consisting of 3000 sweeps with a cooling from $T=0.3$ to 0.00178 eV. Removing "outlying" points more than two standards deviations away from the average, we are left with 13 energy values for each with a standard deviation of 4.4 and 10.2 meV on the minimized total energy, respectively, corresponding to effective temperatures of 1.5 ± 0.4 and 2.5 ± 0.7 meV. These numbers are consistent with the final value of the temperature of 1.78 meV in these runs. The effective temperature should be higher than the final temperature because of the very rapid quenching; however, this effect is partially canceled by the energy minimization following each anneal. A rough estimate of the accuracy of a ground-state energy would be a few times the harmonic value $\sqrt{(3N-6)/2}T_{\text{eff}}$ with the effective temperature $T_{\text{eff}}=2$ meV, which reaches a maximum value of 10 meV for $N=18$.

The ground-state total energy of Fe_N approximately follows a curve defined by an energy proportional to N and a surface term proportional to $N^{2/3}$. To determine the possible existence of magic numbers and particularly

TABLE I. Ground-state bond lengths, cohesive energies, and magnetic moments for iron clusters of sizes 2–4. The columns marked LCAO refer to Ref. 15, and the columns marked EMT to this work.

Size	Structure	Bond Length (a_0) LCAO	Bond Length (a_0) EMT	Cohesive energy (eV/atom) LCAO	Cohesive energy (eV/atom) EMT	Magnetic moment (μ_B/atom) LCAO	Magnetic moment (μ_B/atom) EMT
2		3.74	3.99	2.025	2.032	3	3
3	Linear	4.23	3.63	1.787	1.668	2	2.67
3	Equilateral	3.86	4.23	2.602	3.113	2.67	3
4	Square	3.87	4.28	2.780	3.003	2	2.5
4	Tetrahedral	4.25	4.49	3.073	3.424	3	2.5

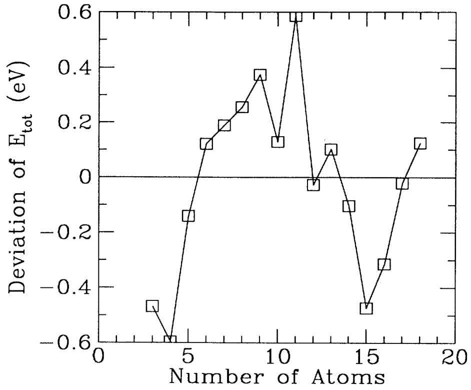

FIG. 1. Deviation of the total energy from a fit to Eq. (3) as a function of cluster size N.

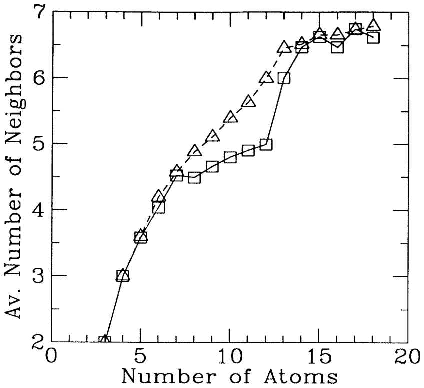

FIG. 3. Average number of nearest neighbors per atom for ground-state structures calculated with (□) and without (△) inclusion of the one-electron correction.

stable or unstable structures, Fig. 1 displays the deviation of the total energy from a two-parameter fit,

$$E_{\text{fit}}(N)=aN+bN^{2/3}\ . \tag{3}$$

Notable features in Fig. 1 are the instability of Fe_{11} and the stability of Fe_4 and Fe_{15}. In order to analyze the origins of these features we show deviation plots similar to Fig. 1 for the energy contributions ΔE_{AS} from Eq. 1 and $E^{\text{TB}}_{\text{1-el}}$ from Eq. 2 in Fig. 2. The atomic-sphere correction energy has a striking drop between $N=12$ and $N=13$ coinciding with the size where one well-defined central atom appears in the equilibrium cluster geometry. This is to be expected, since ΔE_{AS} depends sensitively on coordination number. In other words, the central atom decreases the "surface energy" of the cluster drastically.

The one-electron energy somewhat compensates the atomic-sphere correction for $N\geq 9$, but also exhibits a zig-zag pattern. To explain the former trend we note that the cohesive function will generally hold atoms at a fixed background density, which approximately corresponds to a fixed second moment of the local density of states. Under these constraints, atoms with a low coordination number and a correspondingly stronger coupling to each neighbor will have a more well-defined splitting between bonding and antibonding states and thus a larger bonding energy. Since the reference one-electron energy $E^{\text{ref}}_{\text{1-el}}$ only depends on $\bar{n}$, the effect of the one-electron energy correction should be to decrease the coordination of cluster atoms.

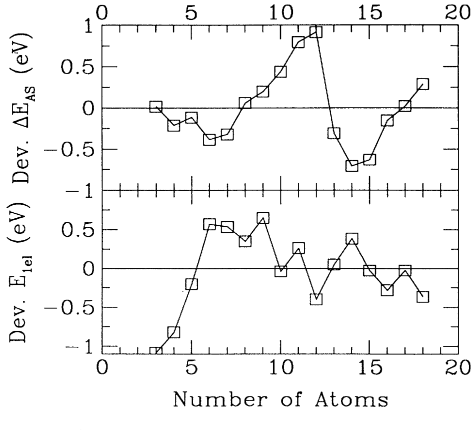

FIG. 2. Deviation of atomic-sphere correction energy ΔE_{AS} (upper panel) and TB one-electron energy $E^{\text{TB}}_{\text{1-el}}$ (lower panel) from fits like Eq. (3) as a function of cluster size.

A comparison between the ground-state configurations of Fe_N calculated with our full total-energy expression and the ground-state configurations in a calculation where we set $\Delta E_{\text{1-el}}=0$, shows that the one-electron correction indeed has this effect. In Fig. 3 we compare the average coordination number for the two sequences of ground-state structures. The average coordination number was calculated by weighting each atomic pair by a Fermi function in distance, centered between bulk nearest- and next-nearest-neighbor distances. Inspection shows that the former structures are hollow for $N\leq 12$, whereas the latter kind have one central atom covered by a partial second layer for $N\geq 9$.

Now for the zig-zag trend of Fig. 2. There is a common characteristic of the configurations at $10\leq N\leq 15$, illustrated in Fig. 4, which can be described with an axis going through two atoms (plus a central atom for $N\geq 13$) and two rings of atoms around the axis: For example, Fe_{12} is a perfect icosahedron; Fe_{10} has two four-atom rings; and Fe_{15} has two six-atom rings. This means that the clusters $N=10$, 12, 13, and 15 have two adjacent commensurate rings, whereas Fe_{11} and Fe_{14} have adjacent rings of different numbers of atoms. This correlates with the larger one-electron binding for the former group as illustrated in Fig. 2. It has not been possible to find the exact eigenstates of the TB matrices that are responsible for the energy differences; we are looking for a 0.4-eV effect in a total one-electron energy of about $N\times 8$ eV.

In conclusion: Fe_4 and Fe_{15} deviate from the fit Eq. (3) in the negative direction, because they are close packed as well as symmetric. Fe_{11} deviates in the positive direction because of the incompatibility of its two deviates in the positive direction because of the incompatibility of its two atomic rings.

The trend of the atomic-sphere correction energy from Fig. 2 is similar to the measured trends of the reactivity

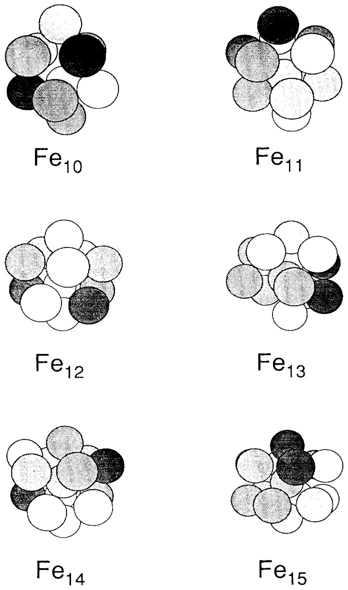

FIG. 4. Ground-state structures of Fe_N, $10 \leq N \leq 15$. Fe_{11} and Fe_{14} do not have two adjacent "rings" of identical numbers of atoms. Fe_{13} is atypical; it is not a perfect centered icosahedron.

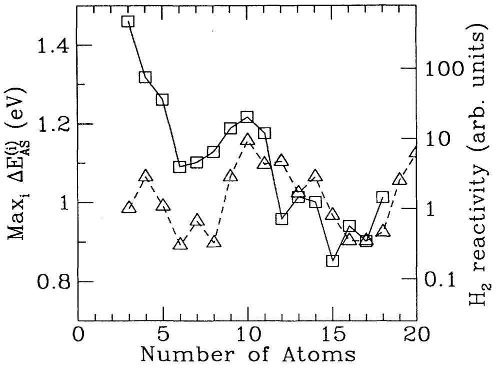

FIG. 5. Maximum atomic-sphere correction energy ΔE_{AS} for one atom in the ground-state structure of Fe_N as a function of N (□, left axis). Logarithm of experimental reactivity with H_2 (Δ, right axis), from Ref. 17.

of Fe_N with molecular hydrogen[17] and of the ionization potential of Fe_N.[18] All have a local maximum around $N=10$ and a local minimum around $N=15$. We have plotted in Fig. 5 the maximum value of the atomic-sphere correction for any one atom in each equilibrium structure, as well as measured reactivity with molecular hydrogen on a logarithmic scale.

A high value of the atomic-sphere energy $\Delta E_{AS}^{(i)}$ corresponds to ineffective screening of atomic cores and may be associated with the presence of a point or edge on the cluster surface. Thus, a high maximal atomic-sphere energy corresponds to the presence of sites with a reduced dipole moment and therefore a lower work function and ionization potential. The hydrogen molecule that approaches such a site can more easily pick up an electron from the cluster and dissociate.

In the case of Cu, the trend of the ionization potential[19] seems to be determined more by the angular-momentum-level bunching of the s electrons leading to magic numbers for clusters of simple metals.[20,2] This level bunching determines the position of the highest occupied level. In the case of Fe with the Fermi level cutting through the d band, there is a much smaller variation of the energy of the highest occupied level.

Summarizing, with a simple but quantitative total-energy calculational scheme, the effective-medium theory supplemented with a tight-binding description of the d-band formation, we have been able to determine ground-state geometries of small iron clusters of size $N \leq 18$ with simulated annealing.

The presence of a partially filled d band has two prominent effects on the ground-state geometry. First, there is a higher global symmetry than in the case of a filled d band, and second, the structures for $9 \leq N \leq 12$ are hollow instead of consisting of a central atom plus a partial second layer.

Energetically, the possibility of assuming rather symmetric geometries is reflected in the low energies of Fe_{10}, Fe_{12}, and Fe_{15} compared to Fe_{11} and Fe_{14}. Although the 13 cluster has the possibility of arranging itself in a perfect centered icosahedron, it does not do this and it does not have a relatively low energy. This may be an effect of the trend of $\Delta E_{1\text{-el}}$ to decrease coordination numbers in this borderline case between having and not having a central atom.

It is found that the most exposed atoms in the clusters $9 \leq N \leq 12$ high atomic-sphere energies corresponding to an incomplete screening. The trend in this quantity corresponds to the observed trends in the ionization potential and H_2 reaction rates. This indicates that the exposed atoms, having an electrostatic potential closer to vacuum, might be the preferred sites for chemical reactions.

Stimulating discussions with W.D. Knight, A. Maiti, J.K. Nørskov, and C. Elsässer are gratefully acknowledged. We thank C. Elsässer for doing the bulk LMTO calculations necessary for the parameter fitting. One of us (O.B.C.) acknowledges support from IBM, and from the Danish Natural Science Research Council. Computing resources at San Diego Supercomputer Center were provided by a NSF grant. This work was supported by National Science Foundation Grant No. FD91-20269 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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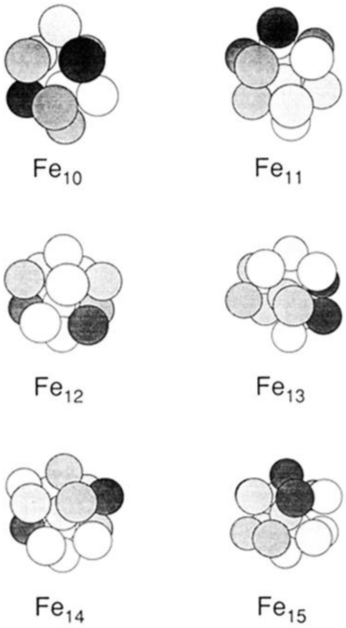

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