Novel structures of Co-Cu bimetallic clusters and their magnetic properties

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The structural and magnetic properties of Co_{18-m}Cu_{m} (0 ≤ m ≤ 18) clusters are investigated with a genetic algorithm (GA) and a spd-band model Hamiltonian in the unrestricted Hartree-Fock approximation respectively. In general, Cu atoms tend to occupy the surface, while Co atoms prefer to the interior of the clusters. Layered structures appear in some clusters with given stoichiometric compositions. The introduction of Cu atoms leads to large increase of the magnetic moment of Co-rich circumstance and nearly zero magnetism of the Cu-rich ambient. The interaction between Cu and Co atoms induces nonzero magnetic moment for Cu atoms. The total magnetic moments tend to decrease with the increase of Cu atoms. However, some particular large magnetic moment are found to be closely related to the structures. The environment of Cu and Co atoms have a dominant effect on the magnetism of the cluster.

57.75.+a, 75.40Mg, 36.40.Cg, 61.46.+w

Bimetallic clusters are an exciting research field due to their potential applications in the automobile industry and oil refined as catalysts. Such nanoscale alloys may present a number of structures and phases that are different from those of corresponding pure metals. Previously, there are intensive studies on homogeneous metal clusters. But the reports on the bimetallic clusters are scarce, especially for transition-metal bimetallic clusters because of the complexity in their electronic structure.

In this report, we exploit the structural and magnetic properties of bimetallic Co-Cu clusters. The main reason for choosing Co-Cu is that the physical properties of bulk Co and Cu are very different. We may get a clear picture of the various properties of the bimetallic clusters versus the different composition ratios. Moreover, Co and Cu alloys are non-miscible. The clusters may give a qualitative analysis from the mecoscopical points.

Although the reliable results on clusters can be obtained on basis of quantum chemistry or density function theory (DFT), the well-known NP problem leads to expensive computational costs. Alternatively, empirical potentials fitted from the bulk materials have been extensively employed to study the structures and properties of clusters. In this letter, we obtain the lowest energy structures of Co_{18-m}Cu_{m} (0 ≤ m ≤ 18) by a genetic algorithm (GA) with a Gupta-like many-body potential. The parameters for inhomogeneous Cu-Co interaction are derived from the average of the Cu-Cu and Co-Co parameters. In the GA scheme, a number of random initial configurations are generated in the beginning. Then any two candidates in the population can be chosen as parents to generate a child cluster by mating operation. The obtained child cluster can be selected to replace its parent, if it has lower binding energy but its configuration is different from any one in the population.

We have checked the validity of current parameterization by ab initio calculation on the smallest clusters, i.e., homogeneous and inhomogeneous dimers and trimers. The ab initio calculation is performed by using DMol package based on density functional theory (DFT). During the DMol electronic structure calculations, the effective core potential (ECP) and a double numerical basis including d-polarization function (DND) are chosen. The density function is treated within the generalized gradient approximation (GGA) with exchange-correlation potential parameterized by Wang and Perdew. A direct comparison of the ab initio and empirical results on the structural information such as equilibrium bond length and bond angle for those small clusters is given in Table I. One can find that all the bond angles of either homogeneous or inhomogeneous trimers are well described by empirical potential. Except Co₂ dimer, the difference of bond length between DFT and empirical calculation is less than 0.05Å. We have further verified our empirical scheme by calculating the clusters Co₁₃ and Cu₁₃. The average bond length and average binding energy per atom of Co are 2.55Å and 3.22 eV, which are 2.44 Å and 3.66±0.36 eV from first-principles calculations. For Cu₁₃, the bond length and the binding energy are 2.50Å and 2.59 eV, in agreement with the results of TB-LMTO, 2.52Å and 2.46 eV. From the above comparisons, the overall agreement of our present model potential with accurate ab initio is rather reasonable. Therefore, we can use such Gupta-like potential in the global structural optimization of 18-atom Cu-Co bimetallic clusters, in which ab initio calculations up to long time scale is computational prohibitive.

Table I. Bond length (d) and bond angle (θ) are compared with the spin-polarized DFT-GGA method (in parenthesis) for small Co, Cu or Co-Cu clusters.

|        | Co₂      | Cu₂      | CuCo     |
|--------|----------|----------|----------|
| d (Å)  | 2.203 (2.107) | 2.235 (2.225) | 2.219 (2.258) |

|        | Co₃      | Cu₃      | Cu₂Cu     | Cu₂Co     |
|--------|----------|----------|-----------|-----------|
| d (Å)  | 2.230 (2.262) | 2.337 (2.348) | 2.308 (2.361) | 2.324 (2.388) |
| θ      | 60.0 (60.0)  | 60.0 (60.0)  | 61.4 (62.1)  | 58.8 (56.5)  |
Fig.1 gives the morphology structures corresponding to different stoichiometric composition of Co$_{18-m}$Cu$_m$ ($0 \leq m \leq 18$). Great modifications are found in the bimetallic clusters. The most stable structures for the clusters with $m = 0, 2, 15 - 18$ are double icosahedron minus an atom in the layer, while the rest ones prefer to the bell-like structures. These imply that the mixing process has a great influence on the ground state structures. This may be original from the fact that 18-atom constitutes a great influence on the ground state structures. These imply that the mixing process has a higher surface energy and cohesive energy favors to the atom with the smaller surface energy and cohesive energy, thus lead to the appearance of layered structure and the segregation of Cu atoms. The bizarre structure characters may bring some peculiar properties. Our previous studies have shown some peculiar thermal behavior in Co-Cu bimetallic clusters. In the following, we investigate the electronic and magnetic properties by parameterized unrestricted Hartee-Fock approximation.

The Hamiltonian, written in a local orbital basis set, has the expression:

$$ H = \sum_{i,\alpha,\sigma} \epsilon_{i\alpha\sigma} \hat{n}_{i\alpha\sigma} + \sum_{\alpha,\beta,\sigma} t_{ij}^{\alpha\beta} \hat{c}_{i\alpha\sigma}^{\dagger} \hat{c}_{j\beta\sigma} $$

where $\hat{c}_{i\alpha\sigma}^{\dagger}$ ($\hat{c}_{ij\beta\sigma}$) are the creation (annihilation) operators and $\hat{n}_{i\alpha\sigma}$ is the number operator of an electron. The $t_{ij}^{\alpha\beta}$ is the hopping integral between different sites and orbitals. The orbital state $\alpha$ involved in calculation includes $s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, d_{3z^2-r^2}$. The single-site energy $\epsilon_{i\alpha\sigma}$ is given by

$$ \epsilon_{i\alpha\sigma} = e_{i\sigma}^0 + U\Delta n(i) - \frac{1}{2}\sigma J\mu(i) + \sum_{j \neq i} \Delta n(j)V_{ij} $$

where $e_{i\sigma}^0$ refers to the orbital energy levels in the paramagnetic solutions of the bulk. $\Delta n(j)$ denotes the charge change. The Coulomb interaction $V_{ij}$ is described as

$$ V_{ij} = \frac{U}{1 + (UR_{ij}/e^2)} $$

The orbital energy and the hopping integrals are taken to be the bulk values obtained from Andersen’s linear muffin-tin orbital atomic sphere approximation (LMTO-ASA) paramagnetic band. The hopping are assumed to be spin independent and are averaged for the heteronuclear. Exchange integrals other than $J_{\alpha\beta}$ are neglected and $J_{\alpha\beta}(Co) = 0.99 eV$. The direct integral $U_{dd}(Co)$ is obtained from Ref. and $U_{ss}/U_{dd}$ relations are from the atomic tables. We take $U_{dd} = U_{pp} = U_{sp}$ and $U_{ss} = U_{pd} = \frac{U_{dd} + U_{ss}}{2}$. For Cu, all the parameters come from Ref.

of the bulk Cu, 3.544 eV and 1.934 Jm$^{-2}$, are smaller than those of the bulk Co, 4.386 eV and 2.709 Jm$^{-2}$. Another possible reason is the atomic size effect. In our simulations, the first-nearest distance of Cu is 2.556A, larger than that of Co 2.507A. Thus, Co are more easily surrounded by Cu atoms.
The magnetic moment can be determined by integrating the majority and minority local densities of state (LDOS) up to Fermi energy:

$$\mu_{i\alpha} = \int_{-\infty}^{0} \left[ \rho_{i\alpha\uparrow}(e) - \rho_{i\alpha\downarrow}(e) \right] de.$$  \hspace{1cm} (4)

The LDOS is directly related to the diagonal elements of the local Green function by means of the recursion method.

$$\rho_{i\alpha\sigma} = -\frac{1}{\pi} \text{Im}[G_{i\alpha\sigma,i\alpha\sigma}(\epsilon)].$$  \hspace{1cm} (5)

Fig. 2 gives the total magnetic moment of Co$_{18-m}$Cu$_m$ bimetallic clusters as a function of the concentration of Co atoms. The total magnetic moments decrease from 33.61$\mu_B$ to 0$\mu_B$ as the Cu concentrations vary from $m = 2$ to $m = 13$. The curve can be divided into three sections. The first section is the Co-rich circumstance with $m = 1 - 5$, where the introduction of a small amount of Cu atoms enhances the magnetism of the clusters. The contribution to the magnetism mainly comes from the Co atoms far away from Cu atoms. It may be due to the large charge transfer between Cu and Co atoms. The second section is the comparative composition ratio with $m = 6 - 12$, in which the magnetic moments fluctuate with the cluster size. For the clusters with concentrations $m = 6 - 8$, the case is very similar to the first. But in the case of $m = 9 - 11$, the interior pentagonal bipyramid significantly contributes to the magnetism of the cluster. Thus, relatively large magnetic moments are found for these clusters. The third section is the Cu-rich clusters with $m = 13 - 17$. Cu atoms seem to have a "screen" effect on the magnetic moments and lead to zero magnetic moment in these clusters.

![FIG. 2. The total magnetic moments of Co$_{18-m}$Cu$_m$ bimetallic clusters as a function of the concentrations of Cu atoms.](image)

The magnetism of the cluster is found closely related to the environments of Co and Cu atoms and the cluster geometrical characters. For example, the total magnetic moment of Co$_{16}$Cu$_2$ is much larger than those of Co$_{17}$Cu$_1$ and Co$_{15}$Cu$_3$. The main reason is due to the large charge transfer between Co-Cu. Obviously, the number of Co-Cu bond in Co$_{16}$Cu$_2$ is much more than that of Co$_{17}$Cu$_1$ and Co$_{15}$Cu$_3$. The more the number of Co-Cu bond in the cluster, the larger the charge transfer, which induces a large magnetic moment. Similarly, the large magnetic moments for Co$_{11}$Cu$_7$ and Co$_9$Cu$_{10}$ are obtained, compared with Co$_{10}$Cu$_8$ and Co$_7$Cu$_{11}$. Contrary, the total magnetic moments for Co$_{13}$Cu$_5$ is found much larger than that for Co$_{12}$Cu$_6$, even the number of Co-Cu bond in the former is more than the latter one. As discussed above, Co$_{13}$Cu$_5$ is a good layered structure with 5 Cu atoms in the same layer and 13 Co atoms constituting an icosahedron. Although the high symmetry compresses the magnetism of the clusters, the 5 Cu atoms has an less effect to the icosahedron. It is well-known that the smaller the cluster size, the larger the magnetic moments. Therefore, a large magnetic moment is obtained for the cluster Co$_{13}$Cu$_5$.

![FIG. 3. Average magnetic moments of Co and Cu atoms as a function of the concentrations of Cu atoms.](image)

It is also worthy to note the nonzero magnetic moment of Cu atoms in some bimetallic clusters. Fig. 3 shows the average moments of Co and Cu as a function of the concentration of Cu. Although the average magnetic moment of Cu atoms is zero or nearly zero in most cases, particularly high magnetic moments are found in the clusters with $m = 1 - 3$ and less pronounced peaks are found at $m = 6, 12$. For the case of Co atoms, the hybridization with the Cu atoms leads to an oscillatory behavior for the average magnetic moment. These may be due to the different charge transfer. For Co atoms, the charges are transferred from $sp$ orbitals to $d$ orbital, contrary to the case of Cu atoms that the charges are transferred from $d$ orbital to $sp$ orbitals. Further, the charge transfer takes place from Co atoms to Cu atoms for the clusters with Cu concentration $m < 13$, while the case is reverse for $m \geq 13$. For the case of $m = 3, 6, 12$, the charge transfer from Co atoms to Cu atoms is found very large, which induces the large magnetism of Cu atom.

To explore the origin of peculiar magnetic properties, we show the total density of states (DOS) and $sp,d$ DOS of the pure and represented bimetallic clusters in Fig. 4. The
cluster Fermi level is presented as a dashed vertical line and shifted to zero. In general, the DOS near to Fermi level play a primary role in determining the magnetism of the clusters. Obviously, the contribution of \( d \) electrons is found dominantly, while the \( sp \) electrons contribution is low. The contribution of \( d \) electrons in \( Co_{18}Cu_2 \) is larger than that in \( Co_{18} \), which leads to a large increase of the magnetic moments in \( Co_{18}Cu_2 \). Similarly, the contribution of \( d \) electrons in \( Co_{16}Cu_2 \) is also larger than that in \( Co_{13}Cu_5 \), thus their corresponding magnetism are different from each other. For \( Co_{10}Cu_8 \), the contribution of \( d \) electrons is relatively less near to the Fermi level compared with other cases, which leads to a particular small magnetic moments. Moreover, the hybridization between \( sp \) and \( d \) orbitals among Co-Cu, Co-Co and Cu-Cu atoms in \( Co_{10}Cu_8 \) is also smallest among these four cases, while it is largest in \( Co_{16}Cu_2 \). This also enhances the magnetism of \( Co_{16}Cu_2 \).

In summary, the geometrical and magnetic properties of bimetallic clusters \( Co_{18-m}Cu_m \) have been studied by a genetic algorithm and a spin polarized tight-binding Hamiltonian. The main conclusions can be made as follows: (1) Great modifications are found for the 18-atom bimetallic clusters due to different composition ratios. This suggests that we can alter the composition ratios to attain new structures. (2) Ordering effect and segregation effect influence the atomic configurations of the bimetallic clusters simultaneously, which leads to the segregation of the Cu atoms to the surface and some layered structures. These may explain why there are no corresponding ordered compounds of Co-Cu bulk in the low temperature. (3) The introduction of Cu atoms causes a dramatic increase of magnetism in Co-rich circumstance and nonzero moments for Cu atoms. Particular large moments can be associated with the environments of Co and Cu atoms and the geometrical characters. (4) Cu atoms have an "screen" effect on the cluster magnetism in Cu-rich ambient and enhance the magnetics in Co-rich environment.

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