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Structure and magnetic properties of Co-Cu bimetallic clusters

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The structural and magnetic properties of $Co_{18-m}Cu_m$ $(0 \leqslant m \leqslant 18)$ clusters are investigated with a genetic algorithm 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 a 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 environments of Cu and Co atoms have a dominant effect on the magnetism of the cluster.

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Bimetallic clusters are an exciting research field due to their potential applications in the automobile industry and oil refined as catalysts.[1,2] 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 metallic clusters. But the reports on the bimetallic clusters are scarce,[3–9] 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 nonmiscible. The clusters may give a qualitative analysis from the mecroscopical points.

Although the reliable results on clusters can be obtained on basis of quantum chemistry or density function theory,[6–9] the well-known NP problem leads to expensive computational costs. Alternatively, empirical potential fitted from the bulk materials have been extensively employed to study the structures and properties of clusters.[4,5,10–14] In this paper, we obtain the lowest energy structures of $Co_{18-m}Cu_m$ $(0 \leqslant m \leqslant 18)$ by a genetic algorithm (GA) with a Gupta-like many-body potential.[11] The parameters for inhomogeneous Cu-Co interaction are derived from the average of the Cu-Cu and Co-Co parameters. In the GA scheme,[15–18] 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 first check the validity of current parameterization by *ab initio* calculation on the smallest clusters, i.e., homogeneous and inhomogeneous dimers and trimers. The *ab initio* calculations are performed by using DMol package based on density functional theory (DFT).[19] 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) (Ref. 20) with exchange-correlation potential parameterized by Wang and Perdew.[21] 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 Co_2 dimer, the difference of bond length between DFT and empirical calculation is less than 0.05 Å. We have further verified our empirical scheme by calculating the clusters Co_{13} and Cu_{13}. The average bond length and average binding energy per atom of Co are 2.45 Å and 3.22 eV, which are 2.44 Å (Ref. 22) and 3.66 ± 0.36 eV (Ref. 9) from first-principles calculations. For Cu_{13}, the bond length and the binding energy are 2.50 Å and 2.59 eV , in agreement with the results of TB-LMTO, 2.52 Å and 2.46 eV.[23] Moreover, the binding energy of a Cu_{38} cluster in fcc structure from Gupta potential is 2.86 eV, while the more accurate TB-LMTO result is about 2.7 eV.[23] From the above comparisons, the overall agreement of the present model potential with accurate *ab initio* calculations is reasonable in a rather wide cluster size range. 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.

Figure 1 gives the morphology structures corresponding to different stoichiometric composition of $Co_{18-m}Cu_m$ $(0 \leqslant m \leqslant 18)$. 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.

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.

	Co_2	Cu_2	CuCo	
d(Å)	2.203 (2.107)	2.235 (2.225)	2.219 (2.258)	
	Co_3	Cu_3	Co_2Cu	Cu_2Co
d(Å)	2.230 (2.262)	2.337 (2.348)	2.308 (2.361)	2.324 (2.388)
θ (degree)	60.0 (60.0)	60.0 (60.0)	61.4 (62.1)	58.8 (56.5)

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 double-icosahedron with a defect. The existence of a defect may easily induce a structural transition. Hence, we can alter the composition ratios to attain some new structures.

Segregation effect is found in the ground state structures of bimetallic clusters: Cu atoms tend to occupy the surface, while Co atoms prefer to the interior. The early occupied sites by Cu atoms have lower coordination number (CN), then the higher CN. Take Co_5Cu_{13} as an example. Eleven Cu atoms occupy the sites with CN's being 5 or 6, and the other 3 Cu atoms are in the layer with $CN's=8$. Moreover, the same kinds of atoms tend to assemble together in the same layer. The assembling Cu atoms tend to maximize the number of Cu-Cu and Co-Co bonds. This phenomenon may be due to the great difference of the surface energy and the cohesive energy between Co and Cu. To minimize the total energy, the atom with the smaller surface energy and cohesive energy tends to occupy the surface, while the atom with a higher surface energy and cohesive energy favors to the interior. The average cohesive energy and surface energy 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 2.556 Å , larger than that of Co 2.507 Å . Thus, Co are more easily surrounded by Cu atoms.

Another interesting finding is the appearance of layered structures in the bimetallic clusters. For $Co_{13}Cu_5$, five Cu atoms occupy the lower CN sites while thirteen Co atoms constitute an icosahedron. Similar features are found in the clusters Co_8Cu_{10} and Co_7Cu_{11},etc. These imply the existence of some ordering effects to maximize the number of Co-Cu bond. The ordering effect and the segregation effect coexist and compete with each other in the cluster, 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 Cu-Co bimetallic clusters.[24] In the following, we investigate the electronic and magnetic properties by parametrized unrestricted Hartee-Fock approximation.

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

$$H=\sum_{i,\alpha,\sigma} \epsilon_{i\alpha\sigma}\hat{n}_{i\alpha\sigma}+\sum_{\substack{i\neq j\\ \alpha,\beta,\sigma}} t_{ij}^{\alpha\beta}\hat{c}^{+}_{i\alpha\sigma}\hat{c}_{i\beta\sigma}, \qquad (1)$$

where $\hat{c}^{+}_{i\alpha\sigma}(\hat{c}_{i\beta\sigma})$ 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 α involved in calculation includes $s,p_x,p_y,p_z,d_{xy},d_{yz},d_{xz},d_{x^2-y^2},d_{3z^2-r^2}$. The single-site energy $\epsilon_{i\alpha\sigma}$ is given by

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

Here ϵ_d^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

$$V_{ij}=\frac{U}{1+(UR_{ij}/e^2)}. \qquad (3)$$

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 bands.[25] The hopping are assumed to be spin independent and are averaged for the heteronuclear. Exchange

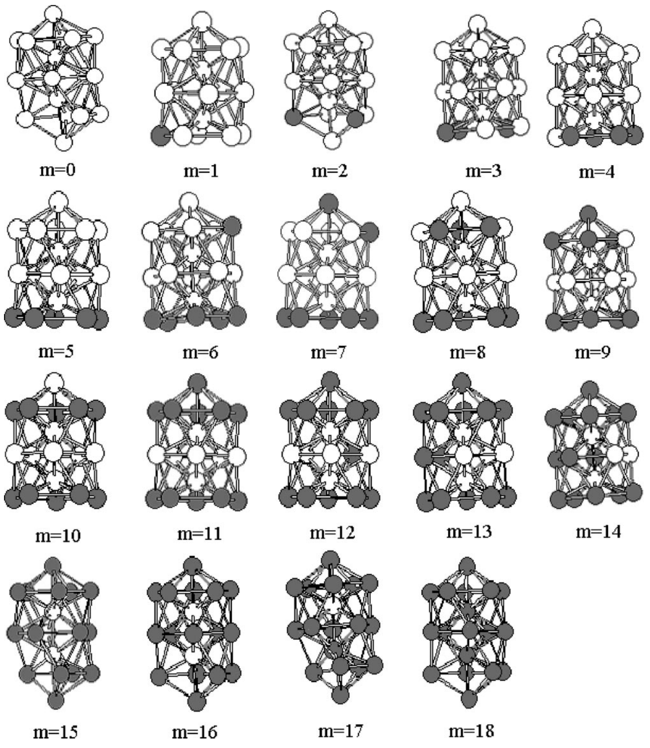

FIG. 1. Structures of $Co_{18-m}Cu_m$ with some concentrations.

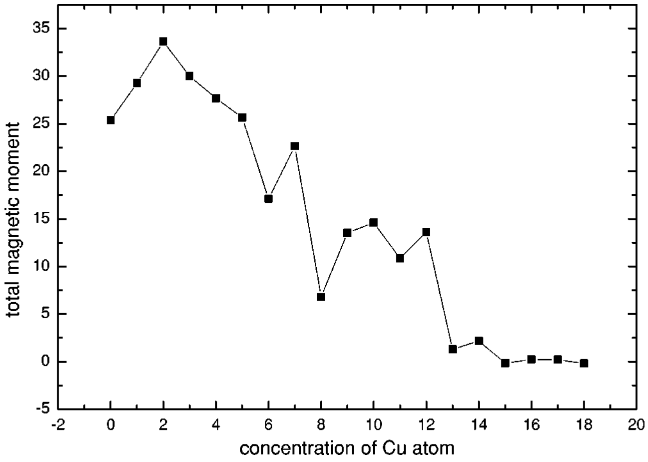

FIG. 2. The total magnetic moments of $\mathrm{Co}_{18-m}\mathrm{Cu}_m$ bimetallic clusters as a function of the concentrations of Cu atoms.

integrals other than J_{dd} are neglected and $J_{dd}(Co) = 0.99$ eV.[26] The direct integral $U_{dd}(Co)$ is obtained from Ref. 27, and U_{ss}/U_{dd} relations are from the atomic tables. We take $U_{dss}=U_{pp}=U_{sp}$ and $U_{sd}=U_{pd}=(U_{ss}+U_{dd})/2$.[28] For Cu, all the parameters come from Ref. 28.

The magnetic moment can be determined by integrating the majority and minority local densities of state(LDOS) up to Fermi energy

$$\mu_{i\alpha}=\int_{-\infty}^{\epsilon_F}[\rho_{i\alpha_\uparrow}(\epsilon)-\rho_{i\alpha_\downarrow}(\epsilon)]d\epsilon. \tag{4}$$

The LDOS is directly related to the diagonal elements of the local Green function by means of the recursion method[29]

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

Figure 2 gives the total magnetic moment of $\mathrm{Co}_{18-m}\mathrm{Cu}_m$ bimetallic clusters as a function of the concentration of Cu 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 to 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.

The magnetism of the cluster is found closely related to the local environments of Co and Cu atoms. For example,

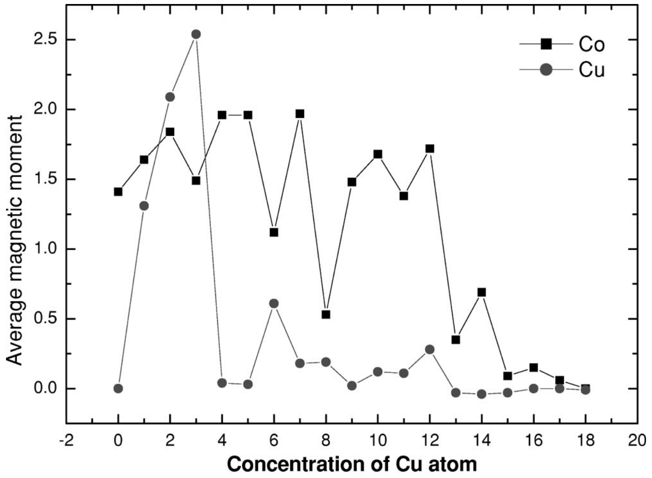

FIG. 3. Average magnetic moments of Co and Cu atoms as a function of the concentrations of Cu atoms.

the total magnetic moment of $\mathrm{Co}_{16}\mathrm{Cu}_2$ is much larger than those of $\mathrm{Co}_{17}\mathrm{Cu}_1$ and $\mathrm{Co}_{15}\mathrm{Cu}_3$. The main reason is due to the large charge transfer between Co-Cu. Obviously, the number of Co-Cu bond in $\mathrm{Co}_{16}\mathrm{Cu}_2$ is much more than that of $\mathrm{Co}_{17}\mathrm{Cu}_1$ and $\mathrm{Co}_{15}\mathrm{Cu}_3$. In general, the more the number of Co-Cu bonds in the cluster, the larger the charge transfer, which leads to a higher magnetic moment. Similarly, the large magnetic moments for $\mathrm{Co}_{11}\mathrm{Cu}_7$ and $\mathrm{Co}_8\mathrm{Cu}_{10}$ are obtained, compared with $\mathrm{Co}_{10}\mathrm{Cu}_8$ and $\mathrm{Co}_7\mathrm{Cu}_{11}$. As an exception, the total magnetic moments for $\mathrm{Co}_{13}\mathrm{Cu}_5$ is much larger than that of $\mathrm{Co}_{12}\mathrm{Cu}_6$, even the number of Co-Cu bonds in $\mathrm{Co}_{13}\mathrm{Cu}_5$ is less than the $\mathrm{Co}_{12}\mathrm{Cu}_6$. This effect can be understood by the unique structure of $\mathrm{Co}_{15}\mathrm{Cu}_3$. As shown in Fig. 1, $\mathrm{Co}_{13}\mathrm{Cu}_5$ is a good layered structure. The five Cu atoms are in the same layer and the thirteen Co atoms constitute an complete icosahedron. The five Cu atoms have relatively less effect on the magnetic moments of the Co_{13} icosahedron. On the contrary, the additional Cu atom in the $\mathrm{Co}_{12}\mathrm{Cu}_6$ has more pronounced disturbance on the magnetism of the Co_{12} with uncompleted icosahedron structure. The reduced symmetry in the Co_{12} may also lead to smaller magnetic moment, as compared with icosahedral Co_{13}. The structures may be due to the existence of spin-ordering in these clusters. However, we have checked the local on-site magnetic moments for several alloy clusters and found no particular ordering from current tight-binding calculations. The reason might be the lack of spin-coupling term in the tight-binding Hubbard model. More accurate investigation can be carried out by *ab initio* methods, which require significantly larger computational time.

It is also worthy to note the nonzero magnetic moment of Cu atoms in some bimetallic clusters. Figure 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

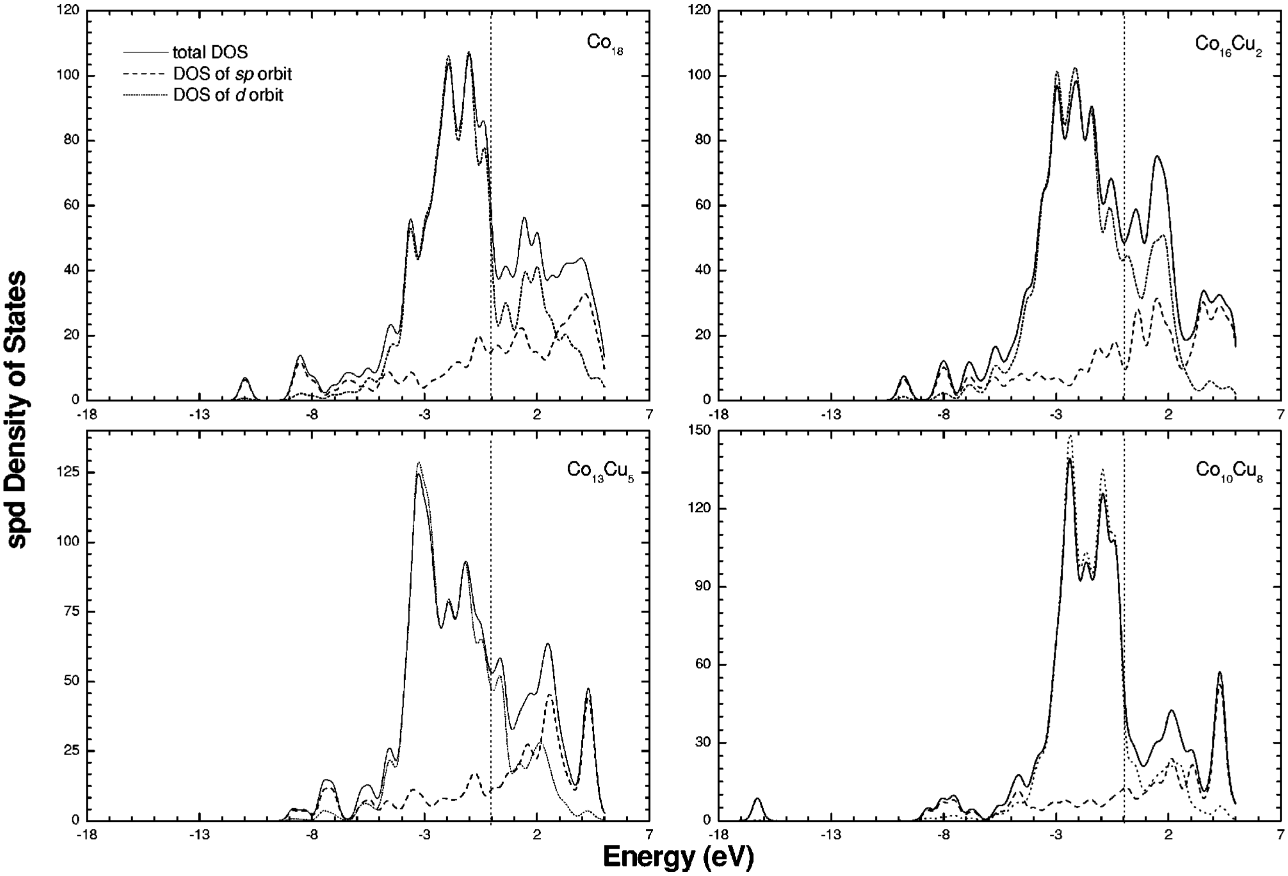

FIG. 4. Total, *sp*, and *d* orbitals DOS for some compositions: (a) Co$_{18}$; (b) Co$_1$6Cu$_2$; (c) Co$_{13}$Cu$_5$, (d) Co$_{10}$Cu$_8$; The vertical dashed lines indicate the DOS integrated Fermi level.

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 $m \geqslant 13$. 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$_{16}$Cu$_2$ is larger than that in Co$_{18}$, which leads to a large increase of the magnetic moments in Co$_{16}$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) Significant modifications are found for the 18-atom bimetallic clusters with 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 low temperature. (3) The introduction of Cu atoms causes a dramatic enhancement of magnetism in Co-rich circumstance and nonzero moments for Cu atoms. Particular large moments can be associated with the local 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 magnetism in Co-rich environment.

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[1] J.H. Sinfelt, *Bimetallic Catalysts: Discoveries, Concepts and Applications* (Wiley, New York, 1983).

[2] K.C. Taylor, *Automobile Catalytic Converters* (Springer, New York, 1984).

[3] G.E. Lopez and D.L. Freeman, J. Chem. Phys. **98**, 1428 (1993).

[4] M.J. L pez, P.A. Marcos, and J.A. Alonso, J. Chem. Phys. **104**, 1056 (1996).

[5] E.B. Krissinel and J. Jellinek, Int. J. Quantum Chem. **62**, 185 (1997).

[6] P. Mlynarski *et al.*, Vacuum **54**, 150 (1999).

[7] S.B. Zhang, M. L Cohen, and M.Y. Chou, Phys. Rev. B **36**, 3455 (1987).

[8] H.P. Cheng, R.N. Barnett, and U. Landman, Phys. Rev. B **48**, 1820 (1993).

[9] P. Mlynarski, M. Iglesias, and M. Perero, Vacuum **54**, 143 (1999).

[10] C. Rey, J. Garc-Fodeja, and L.J. Gallego, Phys. Rev. B **54**, 2942 (1996).

[11] F. Cleri and V. Rosato, Phys. Rev. B **48**, 22 (1993).

[12] Z.B. Guvenc, J. Jellinek, and A.F. Voter, in *Physics and Chemistry of Finite System: From Clusters to Crystals*, edited by P. Jena, S.N. Khanna, and B.K. Rao (Kluwer, Dordrecht, 1992), Vol. I, p. 411.

[13] S.K. Nayak, S.N. Khanna, and B.K. Rao, J. Phys.: Condens. Matter **10**, 10853 (1998).

[14] D.M. Deaven and K.M. Ho, Phys. Rev. Lett. **75**, 288 (1995).

[15] Y.H. Luo, J.J. Zhao, S.T. Qiu, and G.H. Wang, Phys. Rev. B **59**, 14 903 (1999).

[16] T.X. Li *et al.*, Phys. Lett. A **A267**, 403 (2000).

[17] J.L. Wang *et al.*, Solid State Commun. **117**, 593 (2001).

[18] J.L. Wang *et al.*, Chem. Phys. Lett. **341**, 529 (2001).

[19] DMOL is a density functional theory (DFT) package distributed by MSI. B. Delley, J. Chem. Phys. **92**, 508 (1990).

[20] J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).

[21] Y. Wang and J.P. Perdew, Phys. Rev. B **43**, 8911 (1991).

[22] David A. Hales *et al.*, J. Chem. Phys. **100**, 1049 (1994).

[23] U. Lanomers and G. Borstal, Phys. Rev. B **49**, 17 360 (1994).

[24] J.L. Wang *et al.*, Solid State Commun. **119**, 13 (2001).

[25] O.K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984); O.K. Andersen, O. Jepsen, and D. Gloetzel, in *Highlights of Condensed Matter Theory*, edited by F. Bassani, F. Fumi, and M. Tosi (North-Holland, Amsterdam, 1985).

[26] G. Stollhoff, A.M. Oles, and V. Heine, Phys. Rev. B **41**, 7028 (1990).

[27] T. Bandyopadhyay *et al.*, Phys. Rev. B **39**, 3517 (1990).

[28] G. Fabricius *et al.*, Phys. Rev. B **49**, 2121 (1994).

[29] R. Haydock, V. Heine, and M.J. Kelly, J. Phys. C **8**, 2591 (1975).