Structures and magnetic properties of Fe and Ni monoatomic chains encapsulated by an Au nanotube*

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Structures and magnetic properties of transition metal (TM) Fe or Ni monoatomic chains (MACs) encapsulated by a Au (5, 5) nanotube (Fe@Au and Ni@Au) are investigated using the density functional theory (DFT). The calculated results show that both Fe@Au and Ni@Au prefer to adopt ferromagnetic (FM) orders as ground states. In particular, the Fe@Au keeps the magnetic properties of free-standing Fe MAC, indicating that this system may be viewed as a new candidate in electromagnetic devices.

Keywords: transition metal monoatomic chains, Au nanotube, structure, magnetic property

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1. Introduction

In recent years, transition metal (TM) nanowires, which exhibit special spin-polarized transport and magnetic properties, have received much attention due to their potential applications in high speed and low power electronic circuits.[1−7] A critical step toward application is to stabilize the TM nanowires without significantly changing their unique magnetic properties. One of the promising methods is to encapsulate the TM nanowires in different nanotubes and form TM@nanotube systems.[8−19] These TM@nanotube systems may be more stable and will exhibit exciting properties. For example, when the TM nanowires (such as Fe and Co) were doped in C nanotube, the hybrid structures have substantial magnitism and the boron nitride (BN) nanotube coated Ni nanowire shows half-metallic behaviour.[9,10]

Au nanotubes have been synthesized in recent experiments.[20] Since Au nanotubes are more chemically stable[21] than BN nanotubes and C nanotubes, they are expected to be more suitable for encapsulating TM nanowires. Au nanotubes could be regarded as rolling up a gold sheet at the lattice sites of a two-dimensional (2D) triangular lattice. The basis lattice vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ are used to define the 2D lattice ($|\boldsymbol{a}| = |\boldsymbol{b}| = 2.9$ Å).[20] A vector $\boldsymbol{C}$ (m, n) is defined as $= m\boldsymbol{a} + n\boldsymbol{b}$, where $m$and n are integers, and the Au nanotube is specified as Au (m, n) with $\boldsymbol{C}$.

A recent density functional theory (DFT) investigation[22] revealed that the Fe monoatomic chain (MAC) encapsulated in Au (6, 0) nanotubes has a large spin polarization at the Fermi level. Another study showed that for Co and Mn MACs encapsulated in Au (5, 5) nanotubes, the magnetic phase transition will happen when the interatomic distance gradually increases.[23] In order to have a more systematic understanding of the physical and chemical properties of TM@Au, in the present work we focus on Fe and Ni MACs doped in Au (5, 5) nanotubes (see Fig. 1). In addition, the Co MAC encapsulated by Au (5, 5) nanotube is also calculated for the sake of verification and comparison.

2. Theory and calculation method

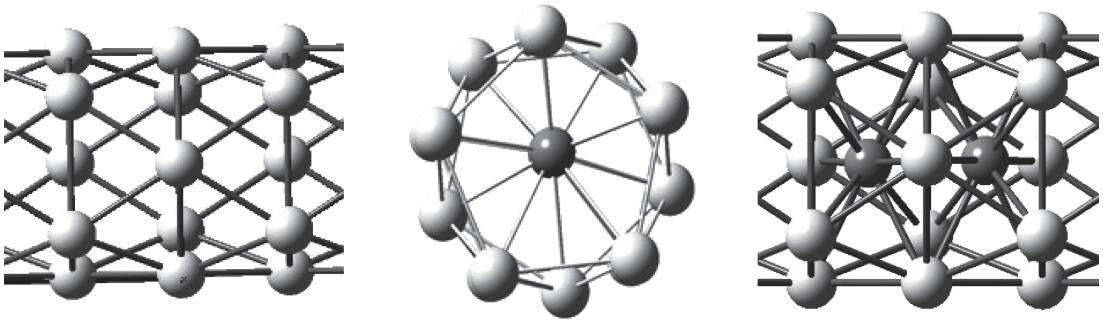
The accurate DFT was use to determine the structure and magnetic properties of TM@Au systems. In particular, the frozen-core full-potential projector augmented-wave (PAW) method implemented in the Vienna *ab initio* simulation package (VASP) was employed.[24−26] The exchange and correlation potentials were treated by spin-polarized generalized gradient approximation (GGA) with the Perdew–

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Burke–Ernzerhof (PBE) functional.[27−29] Spin–orbit coupling (SOC) was taken into account to calculate the orbital magnetic moment and magnetocrystalline anisotropy energy (MAE).

The convergence was achieved when the difference of the total energies in the last two consecutive steps was less than 10^{-5} eV and the maximum force allowed on each atom was 0.01 eV/Å. The kinetic energy cutoff was taken as 380 eV. For the purpose of improving the self consistent field convergence, the Methfessel–Paxton smearing method was employed.[30]

The TM@Au was placed in a unit cell with the dimensions of $20\times20\times c$ Å^3, where c was the lattice constant of the unit cell along the $z$axis (the direction of the Au tube or TM chain). The distance between adjacent Au tubes was at least 15 Å, which should be large enough to ignore the interaction between the adjacent tubes. The Brillion zone was meshed by the gamma-centered Monkhorst–Pack method[31] with $1\times1\times43$ grids for TM@Au.



(a) (b) (c)

Fig. 1. (a) Side view of the Au (5, 5) tube; (b) top view of TM@Au; (c) side view of TM@Au. The chain is along the z-axis direction. The white and grey balls correspond to Au and TM atoms, respectively.

3. Results and discussion

3.1. Geometric structure and energy

The optimized unit length and radius of the pure Au (5, 5) tube are 4.57 and 2.46 Å, respectively. The calculated interatomic distances for Fe, Co, and Ni free-standing MACs in the FM state are 2.25, 2.15, and 2.17 Å, respectively. They are all in good agreement with the reported calculations,[4,20] indicating that the method used here should be suitable and reliable.

Because the calculated results show that the unit length of the Au (5, 5) tube is about twice the interatomic distances for Fe, Co, and Ni MACs, in our theoretical model two TM atoms were doped in every unit cell of the Au tube. The lattice constants along the z-axis direction of TM@Au and the total energy differences between TM@Au tubes in the antiferromagnetic (AFM) state and in the FM state are shown in Table 1. The lattice constants of Fe@Au, Co@Au, and Ni@Au in the FM state are 4.79, 4.74, and 4.72 Å, while in the AFM state they are 4.87, 4.79, and 4.75 Å, respectively. The calculated results show that when the TM atom chains are encapsulated in the Au tube, the TM interatomic distances are mainly determined by the lattice parameter of the Au tube, and the lattice constants of TM@Au are all increased compared with the bare Au tubes. This phenomenon can be explained by the strong repulsion force between the Au atom and the TM atom when the MACs are doped in a Au tube with a very small radius (2.46 Å). According to the calculated results, the AFM states are all higher in energy than the FM states for Fe@Au, Co@Au, and Ni@Au. All the three kinds of TM@Au are more stable in the FM state, and thus only the FM state will be discussed in the following.

The formation energy ($E_{\rm f}$) of TM@Au in the FM state was calculated. The formation energy is defined as

$$E_{\rm f}({\rm TM@Au}) = 2E({\rm TM}) + E({\rm tube}) - E({\rm TM@Au}), \quad (1)$$

where $E(\cdot)$ is the total energy of the TM atom, nanotube, or the TM@Au system. As shown in Table 1, the formation energy is 8.41, 9.23, and 10.65 eV for Fe@Au, Co@Au, and Ni@Au, respectively. For comparison, the formation energy of the free-standing Fe,

Co and Ni atomic chains are also calculated to be 1.54, 3.85, and 5.41 eV for Fe, Co and Ni atomic chains, respectively. The formation energy of TM@Au is much higher than that of the corresponding MAC, indicating that the Fe, Co and Ni atomic chains encapsulated by the Au nanotube are more stable. In addition, the stability of the hybrid structures of TM@Au can be shown by comparison with the TM@CNT and TM@BNNT structures, whose formation energies are all less than 1 eV per TM atom.[9,10]

Table 1. Lattice constant (c/Å) of different TM@Au nanotubes, the total energy difference ($E_{\rm AFM}$–$E_{\rm FM}$/eV per atom) between the AFM phase and the FM phase, and the formation energy of TM@Au ($E_{\rm f}$/eV) in the FM state.

System	Magnetic phase	c/Å	$E_{\rm AFM}-E_{\rm FM}$/eV per atom	$E_{\rm f}$/eV
Fe@Au	FM	4.79	0.59	8.41
	AFM	4.87		–
Co@Au	FM	4.74	0.48	9.23
	AFM	4.79		–
Ni@Au	FM	4.72	0.42	10.65
	AFM	4.75		–

3.2. Magnetic moment and magnetocrystalline anisotropy energy

The calculated orbital magnetic moments and spin magnetic moments of the TM atoms in bare MACs and TM@Au nanotubes in the FM state are shown in Table 2. Compared with the free Fe chain, the orbital moments of the Fe atom in the Fe@Au tube decrease when the magnetic moment is parallel or perpendicular to the chain, while for the orbital moments of the Co atom, the situation is opposite. The orbital moment of the Ni atom in the Ni@Au tube decreases when the magnetic moment is parallel to the chain direction, and increases when the magnetic moment is perpendicular to the chain direction compared with the free Ni chain. In addition, the orbital moments of Fe, Co, and Ni atoms in the MACs along the chain are 0.16 $\mu_{\rm B}$, 0.20 $\mu_{\rm B}$, and 0.57 $\mu_{\rm B}$, respectively. They are coincident with the previous calculation.[4]

Table 2. Orbital magnetic moment $M_{\parallel}^{\rm o}$ (in units of $\mu_{\rm B}$ per atom) and spin magnetic moment $M_{\parallel}^{\rm s}$ (in units of $\mu_{\rm B}$ per atom) of TM atoms in free-standing MACs and TM@Au tubes along the chain direction. Orbital magnetic moments $M_{\perp}^{\rm o}$ (in units of $\mu_{\rm B}$ per atom) and spin magnetic moments $M_{\perp}^{\rm s}$ (in units of $\mu_{\rm B}$ per atom) of TM atoms in free-standing MACs and TM@Au tubes perpendicular to the chain direction.

System	$M_{\parallel}^{\rm o}$	$M_{\parallel}^{\rm s}$	$M_{\perp}^{\rm o}$	$M_{\perp}^{\rm s}$
Fe chain	0.16	3.00	0.12	3.02
Fe@Au	–0.05	3.00	0.04	2.98
Co chain	0.20	2.10	0.16	2.08
Co@Au	0.46	1.88	0.51	1.79
Ni chain	0.57	1.10	0.10	1.06
Ni@Au	0.19	0.55	0.23	0.47

Furthermore, the orbital magnetic moments of the three kinds of TM atoms in the TM@Au tubes perpendicular to the chain direction are all bigger than the corresponding orbital magnetic moment along the chain direction. As is well known, the magnetic direction with the bigger orbital moment will be lower in total energy. To further understand the result of the orbital magnetic moments, the MAEs of the TM@Au tubes are also studied.

The MAEs of the TM@Au tubes in the FM state are calculated with the total energy different approximation. The MAE is defined as the difference between the energies perpendicular to and along the z axis, and its values for Fe@Au, Co@Au, and Ni@Au are shown in Table 3. The MAE of Co@Au coincides with a recent result.[23] It means that all the hybrid systems of the TM@Au are more stable when the moment is perpendicular to the chain direction.

The MAEs of the freestanding MACs and the MACs in TM@Au (2 TM atom per cell) are also displayed in Table 3. When the lattice constants transform from the free chains to the MACs in TM@Au, the easy magnetization axes of the Fe and Co atom chains all change from being along the z axis to being perpendicular to the z axis, and their MAEs all drop slightly. After being encapsulated by Au nanotubes, the MAEs of Fe@Au and Co@Au all increase (from −2.58 to −4.42 meV for Fe; from −0.21 to −5.53 meV for Co) due to the overlap of Au electrons and TM electrons. For the Ni chain, when the lattice constant transforms from the free chains to the MACs in TM@Au, the easy magnetization axis remains along the z axis, but its MAE changes from 6.24 to 4.63 meV. When encapsu-

lated by a Au nanotube, the easy magnetization axis of the Ni atom chain changes from being along the z axis to being perpendicular to the z axis and the MAE decreases to −2.53 meV. The MAEs for Fe, Co and Ni MACs encapsulated by a Au nanotube are very large compared with those of bulk Fe, Co and Ni.[32] Given the high stability of the TM@Au, this makes it possible for them to be used in practical applications in ultrahigh density magnetic storages.

Table 3. The MAEs of the free-standing MACs ($MAE^{(a)}$) (in units of meV), MAEs of the MACs in TM@Au ($MAE^{(b)}$) (in units of meV), and MAEs of the TM@Au ($MAE^{(c)}$) (in units of meV).

TM	$MAE^{(a)}$	$MAE^{(b)}$	$MAE^{(c)}$
Fe	2.89	–2.58	–4.42
Co	0.26	–0.21	–5.53
Ni	6.24	4.63	–2.51

In the magnetic system, the spin magnetic moment of an atom is caused by the spin polarization. The spin magnetic moments of the TM atoms in TM@Au can be understood by analyzing the calculated spin-polarized density of states (DOS) For Fe@Au the DOS of the s and p states show that their contribution to the spin magnetic moment could be ignored. Therefore, only the DOS of d states in Fe and Au atoms in Fe@Au are shown in Fig. 2. The magnetic moment is mainly determined by Fe 3d states. For the Fe atom, the DOS of d orbits of spin up (d↑) is mainly localized below the Fermi level, while part of the DOS of d orbits of spin down (d↓) is above the Fermi level. This means that almost all of the orbits of d↑ are occupied and only a part of the orbits of d↓ are occupied.

The integrals over the DOS of d↑ and d↓ below the Fermi level are equal to the numbers of electrons occupying the states of d↑ and d↓, respectively, and the calculated values are 4.43 and 1.55. This can explain the result of the spin magnetic moment of a Fe atom in Fe@Au (3.00 μ_B). The detail of the spin occupying distribution in Fe@Au can be seen in the band structure in Fig. 2.

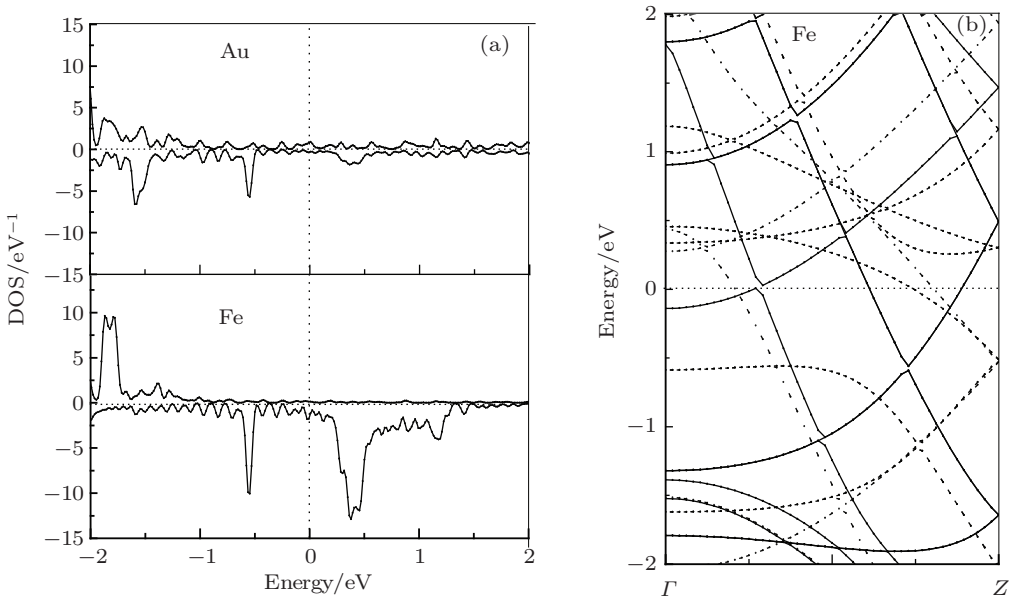


Fig. 2. (a) DOS of d states in Fe@Au and (b) band structure of Fe@Au. The Fermi level (the dotted line) is at zero energy. For the band structure, the straight lines and dot lines are channels of spin up and spin down, respectively.

Similar to Fe@Au, only the DOS of d states of Ni and Au atoms in Ni@Au are shown in Fig. 3. We can see that the spin polarization is slight in Ni@Au, and the magnetic moment is mainly determined by the Ni 3d states. For the Ni atom, almost all the DOS of d↑ is below the Fermi level and a small part of the DOS of d↓ is above the Fermi level. The calculated integrals over the DOS of d↑ and d↓ states below the Fermi level are 4.30 and 3.78, respectively, which can explain the result of the spin magnetic moment of the Ni atom in Ni@Au (0.55 μ_B). The band structure in Ni@Au is also shown in Fig. 3, and the above analysis can also be understood from the energy band.

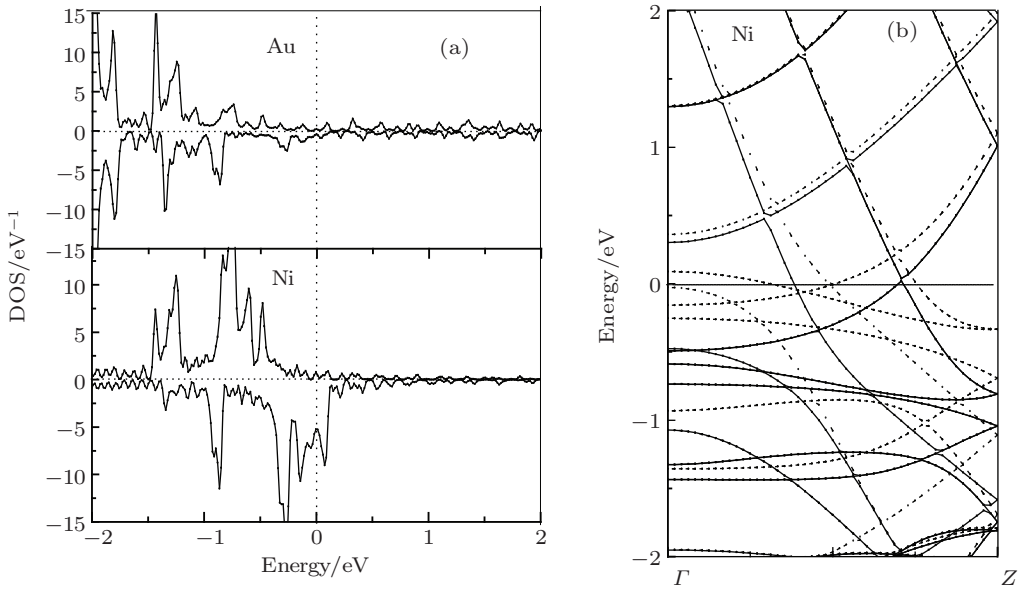


Fig. 3. (a) DOS of d states of Ni@Au; (b) band structure of Ni@Au. The Fermi level (the dotted line) is at zero energy. For the band structure, the straight lines and dot lines are channels of spin up and spin down, respectively.

4. Conclusions

The structural and magnetic properties of Fe and Ni atomic chains doped in Au nanotubes were carefully investigated using the DFT method. Our results show that the ground states of the Fe@Au and Ni@Au systems are all ferromagnetic stable, and that Fe@Au could keep the spin magnetic properties of a free-standing Fe monoatomic chain. In addition, the magnetic stability of the Fe@Au system is further verified by its relatively large magnetocrystalline anisotropy energy. Thus, this system may be viewed as a new candidate for use in electronic devices.

References

[1] Tseng G Y and Ellenbogen J C 2001 *Science* **294** 1293

[2] Huang Y, Duan X, Cui Y, Lauhon L J, Kim K H and Lieber C M 2001 *Science* **294** 1313

[3] Mokrousov Y, Bihlmayer G, Heinze S and Blugel S 2006 *Phys. Rev. Lett.* **96** 147201

[4] Tung J C and Guo G Y 2007 *Phys. Rev.* B **76** 094413

[5] Delin A and Tosatti E 2003 *Phys. Rev.* B **68** 144434

[6] Delin A and Tosatti E 2004 *J. Phys.*: *Condens. Matter* **16** 8061

[7] Tung J C and Guo G 2011 *Comp. Phys. Commun.* **182** 84

[8] Zhou Y G, J Xiao-Dong, Wang Z G, Xiao H Y, Gao F and Zu X T 2010 *Phys. Chem. Chem. Phys.* **12** 7558

[9] Yang C K, Zhao J and Lu J P 2003 *Phys. Rev. Lett.* **90** 257203

[10] Xiang H J, Yang J, Hou J G and Zhu Q 2005 *New J. Phys.* **7** 39

[11] Yang S B, Kong B S, Kim D W, Baek Y K and Jung H T 2010 *J. Phys. Chem.* C **114** 9296

[12] Wang Y, Wu Q, Wu Y M, He X J and Li L W 2012 *Chin. Phys.* B **21** 014212

[13] Xie Y and Zhang J M 2011 *Chin. Phys.* B **20** 127302

[14] Peng Z H, Gong X Y, Peng Y F, Guo Y C and Ning Y T 2012 *Chin. Phys.* B **21** 78102

[15] Valle M D, Tejedor C and Cuniberti G 2006 *Phys. Rev.* B **74** 045408

[16] Wang J, Jo C and Wu R 2008 *Appl. Phys. Lett.* **92** 032507

[17] Fabiano E, Constantin L A and Sala F D 2011 *J. Chem. Phys.* **134** 194112

[18] Ouyang F P, Peng S L, Chen L N, Sun S Y and Xu H 2011 *Chin. Phys.* B **20** 027102

[19] Wang Y J, Wang L D, Yang M and Yan C 2011 *Chin. Phys.* B **20** 117304

[20] Oshima Y and Onga A 2003 *Phys. Rev. Lett.* **91** 205503

[21] An W, Pei Y and Zeng X C 2008 *Nano Lett.* **8** 195

[22] Mokrousov Y, Bihlmayer G and Blügel S 2005 *Phys. Rev.* B **72** 045402

[23] Zhu LY, Wang J L and Ding F 2009 *J. Chem. Phys.* **130** 064706

[24] Blöchl P E 1994 *Phys. Rev.* B **50** 17953

[25] Kresse G and Furthmüller J 1996 *Comput. Mater. Sci.* **6** 15

[26] Kresse G and Joubert D 1999 *Phys. Rev.* B **59** 1758

[27] Wang Y and Perdew J P 1991 *Phys. Rev.* B **44** 13298

[28] Perdew J P and Wang Y 1992 *Phys. Rev.* B **45** 13244

[29] Perdew J P, Burke K and Ernzerhof K 1996 *Phys. Rev. Lett.* **77** 3865

[30] Methfessel M and Paxton A T 1989 *Phys. Rev.* B **40** 3616

[31] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188

[32] Eriksson O, Johansson B, Albers R C and Boring A M 1990 *Phys. Rev.* B **42** 2707