

The structural, electronic, and magnetic properties of Fe–Ir, Co–Ir and Ni–Ir linear and zigzag nanowires: First-principles calculations

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ABSTRACT

The magnetic and electronic properties of both linear and zigzag bimetallic chains of Fe–Ir, Co–Ir and Ni–Ir have been calculated based on density functional theory and using the generalized gradient approximation. It is found that all considered zigzag chains form a twisted two-legged ladder, look like a corner-sharing triangle ribbon, and have a lower total energy than the corresponding linear chains. All the Fe–Ir, Co–Ir and Ni–Ir linear and zigzag chains have stable or metastable ferromagnetic (FM) states. The bond lengths in bimetallic Fe–Ir, Co–Ir and Ni–Ir at ferromagnetic state are larger than those in the corresponding structures at nonmagnetic state. Interestingly, the Ni–Ir zigzag nanowire has two energy minimum states, both ferromagnetic and nonmagnetic (NM), indicating a possible stable condition for mechanically controllable break-junction experiments.

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1. Introduction

Magnetism in nanostructures has been a very active research area in the last few decades [1–4] because of its novel fundamental physics and fascinating potential applications. Among these nanostructures, the infinite one-dimensional (1D) structure might be the simplest and most important one and, thus, has attracted considerable attention [5–8]. A great deal of theoretical research has been done on both finite and infinite chains of atoms. Theoretical studies using either semi-empirical tight-binding or *ab initio* density functional theory for many infinite and finite chains have been reported. For example, linear chains of Co [9–13], Fe [11,14], and Ni [15,16], as well as zigzag chains of Fe [14] have been reported. Recently, the magnetic properties of transition metal infinite linear chains of Fe, Co, Ni have been calculated [10–14,17]. Possible magnetism in *s*- and *sp*-electron element linear and zigzag chains has also been studied theoretically [18]. Furthermore, some theoretical studies even cover a large range of transition metal elements *3d* [14,19,20], *4d* [15,21,22], and *5d* [22,23] on the structural, electronic and magnetic properties of transition metal (TM) linear chains.

Experimentally, modern methods of preparing metal nanowires have made it possible to investigate the influence of dimensionality on the magnetic properties. For example, Gambardella et al. [4] recently succeeded in preparing a high density of parallel atomic chains along steps by growing Co on a high-purity Pt (997) vicinal surface and then observed 1D magnetism in a narrow temperature range of 10–20 K.

Despite these experimental and theoretical being concerned with electronic and magnetic properties, Seivane et al. [16] and Suárez et al. [24] in their study of linear and zigzag monatomic chains point out that the stability of an infinite chain is a necessary condition for the finite size chain in the mechanically controllable break-junction experiments [16]. Moreover, Thiess et al. [25] report a very important and interesting issue of why it is hard to prepare a long chain in these experiments.

Bimetallic Fe–Pt face-centered tetragonal (fct) nanorods were recently fabricated by electron beam-induced deposition using an ultrahigh vacuum scanning electron microscope [26]. The line width of the well-aligned ferromagnetic Fe–Pt nanorod is about 26 (nm). However, there are only a few theoretical calculations regarding these bimetallic nanowires, such as Ni–Pd and Ni–Pt [27]. In our previous theoretical study of *3d* [19], *4d* and *5d* [22] transition metal freestanding nanowires, we found that the freestanding Pt nanowires are nonmagnetic while Ir is magnetic for both linear and zigzag structure. Therefore, in this study we perform a systematic *ab initio* study of the structural, magnetic and electronic properties of Fe–Ir, Co–Ir and Ni–Ir linear and zigzag nanowires. Although we study only freestanding Fe–Ir, Co–Ir and Ni–Ir bimetallic linear and zigzag nanowires, the underlying physical trends may also hold for monatomic chain deposited on weakly interacting substrates.

2. Theory and computational method

In the present first principles calculations, we use the accurate frozen-core full-potential projector augmented-wave (PAW) method [28], as implemented in the Vienna *ab initio* simulation package (VASP) [29,30]. The calculations are based on density

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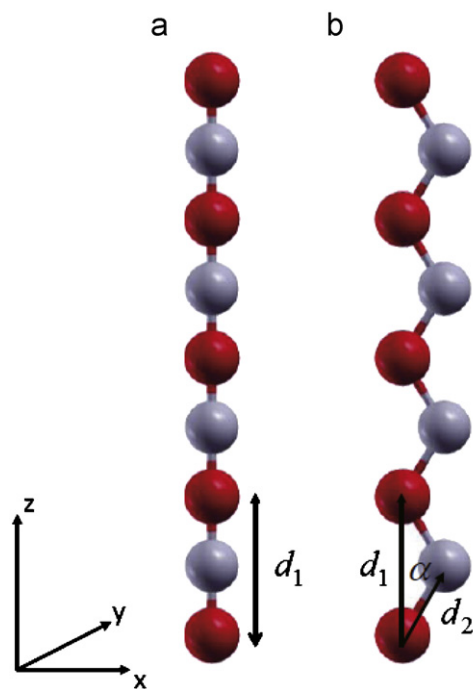


Fig. 1. Schematic structure for (a) the linear and (b) zigzag atomic chains. The interatomic distance d_1 is defined as the distance (in Å) between the same kind of ions whilst d_2 (in Å) for zigzag structure is the distance between different kinds of ions.

functional theory with the exchange and correlation effects being described by the generalized gradient approximation (GGA) [31], and with the first inner p orbitals treated as valence electrons. We use a standard supercell approach with two different kinds of atoms in a supercell to model isolated linear and zigzag atomic chain. The interatomic distance d_1 (Å) and d_2 (Å) for linear and zigzag chains, see Fig. 1, was obtained from the minimum of the total energy (eV/atom) as a function of interatomic distance (d_1). The nearest wire and wire distance in this study is 20 Å, which is wide enough to decouple the near neighbor interactions. A very large plane-wave cutoff energy of at least 400 eV is used in this study. For the freestanding bimetallic atomic chain, the Γ -centered Monkhorst–Pack scheme with a k -mesh of $1 \times 1 \times n$ ($n=60$) in the full Brillouin zone (BZ), in conjunction with the Fermi–Dirac smearing method with $\sigma = 0.04$ eV, is used to generate k -points for the BZ integration. The number of k -mesh, n , is tested with $n=30, 40, 50, 60, 70, 80$, and 100. At $n=60$, the total energy is converged to less than 0.1 meV.

3. Structural and magnetic properties

In this study, the bond length, d_1 , denotes the distance between the same kind of ions and d_2 the distance between different kinds of ions; see Fig. 1. To obtain the equilibrium bond length, we calculate the total energy (eV) as a function of interatomic distance d_1 (in Å) for both linear and zigzag nanowires; see Fig. 2(a)–(c). The equilibrium bond length was obtained from the minimum total energy for both linear and zigzag atomic chains. The calculated equilibrium bond lengths (d_1 and d_2) and spin magnetic moments (m_s) of the Fe–Ir, Co–Ir and Ni–Ir linear and zigzag nanowires are listed in Table 1 and Fig. 2. For comparison, we also list the equilibrium bond length of pure Fe, Co, Ni, and Ir linear and zigzag nanowires obtained from previous theoretical results of 3d [19], 4d, and 5d [22] transition metal linear and zigzag nanowires given in Table 1. In my previous study of pure Fe, Co, Ni and Ir nanowires, the

equilibrium bond length for linear nanowires was also calculated from the minimization of the total energy while the equilibrium structure of the zigzag nanowires was obtained from the structure optimization. For the pure Fe, Co, Ni, and Ir linear chains, the equilibrium bond lengths for FM states are 4.50, 4.30, 4.36, and 4.56 (Å), respectively. These values are double those reported in my previous results because the definition of the structure parameter d_1 is different; see Fig. 1. The equilibrium bond lengths of the nonmagnetic state of pure Fe, Co, Ni, and Ir linear atomic chain are 3.88, 4.04, 4.26, and 4.56 (Å), respectively.

In bimetallic linear nanowires, the equilibrium bond lengths for ferromagnetic state of linear Fe–Ir, Co–Ir, and Ni–Ir are 4.38, 4.33, and 4.45 (Å), respectively. While for the nonmagnetic state, the corresponding equilibrium bond lengths are 4.26, 4.28, and 4.39 (Å), see Fig. 2 and Table 1. Clearly, the bond length in a ferromagnetic state is larger than in a nonmagnetic state due to larger kinetic energy in a magnetic state. Furthermore, for the bimetallic Fe–Ir, Co–Ir, and Ni–Ir linear chains, the bond lengths for magnetic and nonmagnetic states are in between the corresponding pure system. The magnetization energy, which is defined as the total energy difference between magnetic and nonmagnetic states, i.e. $E^{FM} - E^{NM}$, of pure Fe, Co, Ni, and Ir linear nanowires are -0.53 (eV/mag. atom), -0.39 (eV/mag. atom), -0.15 (eV/mag. atom), and -0.03 (eV/mag. atom), respectively, while for Fe–Ir, Co–Ir, and Ni–Ir linear chain are -0.50 (eV/mag. atom), -0.07 , and -0.15 (eV/mag. atom). Very interestingly, both linear and zigzag nanowires of Fe, Co, Ni, Ir, Fe–Ir, Co–Ir, and Ni–Ir have stable or metastable ferromagnetic and nonmagnetic states; see Fig. 2(a)–(c), and the FM states are more stable than the nonmagnetic states. The magnetization energy for the zigzag Fe–Ir, Co–Ir and Ni–Ir are -0.57 , -0.29 and -0.08 (eV/mag. atom).

Clearly from Fig. 2(a)–(c), we found that the nonmagnetic Fe–Ir, Co–Ir, and Ni–Ir NM zigzag atomic chains, as well as the ferromagnetic Ni–Ir zigzag chains have two energy minimum states. The first energy minimum is a global energy minimum state located at a small interatomic distance with bond angle α around 60° , which looks like a corner-sharing triangular ribbon. To simplify, we label it the ZZ_g state in this article. The other energy local minimum state is at a larger interatomic distance with a small bond angle α around 30° , which physically appears to have a zigzag geometric, and we label it the ZZ_l state.

The existence of an energy second minimum state is at least a necessary condition for the formation of a finite-sized chain in mechanically controllable break-junction experiments [16]. The calculated structure parameters of Fe, Co, Ni, Ir, Fe–Ir, Co–Ir, and Ni–Ir zigzag nanowires are listed in Table 1. In the zigzag chains, the bond angle in a ferromagnetic state is larger than in a nonmagnetic state. At larger interatomic distances, see Fig. 2(g)–(i), the bond angle of zigzag nanowires becomes zero and the results of magnetic and nonmagnetic states reduce to those of the corresponding linear nanowires.

The calculated magnetic moments (μ_B /atom) of linear and zigzag nanowires as a function of interatomic distance d_1 (Å) are displayed in Fig. 2(d)–(f), and also listed in Table 1. The magnetic moments for Fe, Co, Ni, Ir, Fe–Ir, Co–Ir, and Ni–Ir linear chains are 3.41, 2.24, 1.11, 0.66, 1.61, 1.06, and 1.06 (μ_B /atom), respectively. In the bimetallic zigzag nanowires, Fe–Ir, Co–Ir, and Ni–Ir are magnetic at almost all considered interatomic distances; see Fig. 2(d)–(f). In general, due to the increase of coordination number, the magnetization becomes smaller in zigzag nanowires; see Fig. 2 and Table 1.

4. Density of states

The plot in Fig. 3 shows the site-decomposed and spin-decomposed ferromagnetic densities of states (DOSS) of the linear (left panel) and zigzag (right panel) nanowires. The densities of

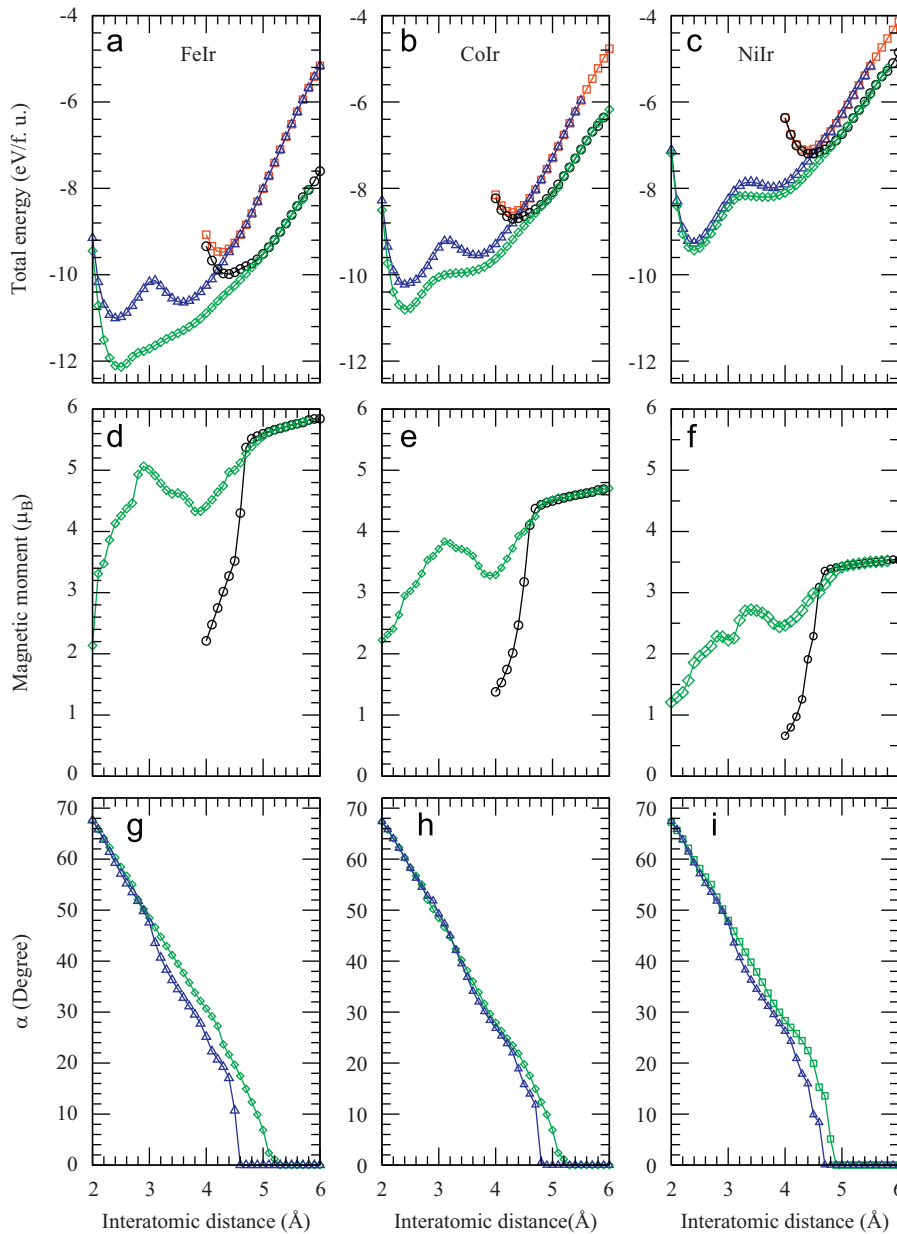


Fig. 2. Total energy per formula unit (eV/f.u.), upper panel; magnetic moment per atom (μ_B /atom), middle panel; and bond angle α (in degree), bottom panel of the Fe–Ir (right), Co–Ir (middle), and Ni–Pt (left) linear and zigzag atomic chains.

the spin down are multiplied by -1 for easy comparison. For the Fe-site, Co-site, Ni-site and Ir-site, only d -dominant states are plotted, see Fig. 3. First, following from our previous studies of the freestanding linear and zigzag TM nanowires, in the absence of the SOC and because of the linear chain symmetry, the dominant bands may be divided into three groups, namely, nondegenerate s - and d_{z^2} -dominant bands, double degenerate (d_{xz} , d_{yz}) and ($d_{x^2-y^2}$, d_{xy}) dominant bands. The ($d_{x^2-y^2}$, d_{xy}) bands are narrow because the $d_{x^2-y^2}$ and d_{xy} orbitals are perpendicular to the chain, thus forming weak δ bonds. The (d_{xz} , d_{yz}) bands, on the other hand, are more dispersive due to the greater overlap of the d_{xz} and d_{yz} orbitals along the chain, which gives rise to the π bonds. The s - and d_{z^2} dominant bands are most dispersive since these orbitals form strong σ bonds along the chain.

These characteristic bands of the bimetallic nanowires are similar; for example, the clear shape of the spin-up state around -0.8 eV for linear Fe–Ir, Co–Ir, and Ni–Ir, in Fig. 3(a), (c) and (e), is mainly due to the Ir spin-up $d_{x^2-y^2}$ and d_{xy} bands. These Ir d bands

are exchange split and give rise to a spin magnetic moment; see Fig. 3. However, the $d_{x^2-y^2}$ and d_{xy} bands of the 3d TM Fe, Co and Ni split more and give a great contribution to magnetization. In the zigzag chains, the number of bands becomes doubled in the zigzag chains because of the doubling of the number of atoms due to the breaking of rotational symmetric. However, the energy bands are also highly spin split, see Fig. 3(b), (d) and (f), and the split of the spin-up and spin-down bands may be correlated with the spin magnetic moment. The DOSs of linear nanowires have larger spin-up and spin-down band-split than the corresponding ones in zigzag nanowires, indicating larger magnetic moments in linear nanowires. In the bimetallic linear Fe–Ir chain, see Fig. 3(a), the bands are the most split and the Fe–Ir linear chain has the largest magnetic moments. On the other hand, the exchange split of the d orbitals is proportional to the spin magnetic moments.

The electric and spin current transports are determined by the characteristics of the band structure near the Fermi level (E_F). Therefore, it would be useful to examine the DOSs of both the

Table 1

Equilibrium bond lengths d_1 , d_2 (in Å), bond angle α (in degree) and magnetic moment m per magnetic atom (μ_B /atom) for linear and zigzag nanowires. ZZ_g(ZZ_l) denotes the zigzag chain at α around 60°(30°).

	Structure	States	d_1 (Å)	d_2 (Å)	α	m (μ_B /atom)	
Fe ^a	Linear	NM	3.88				
		FM	4.50			3.41	
	ZZ _g	NM	2.27	2.10	57.2		
		FM	2.43	2.24	57.2	3.01	
Co ^a	Linear	NM	4.04				
		FM	4.30			2.24	
	ZZ _g	NM	2.26	2.23	59.6		
		FM	2.32	2.22	58.5	2.05	
Ni ^a	Linear	NM	4.26				
		FM	4.36			1.11	
	ZZ _g	NM	2.07	3.28	71.6		
		FM	2.29	2.28	59.8	0.87	
Ir ^b	Linear	NM	4.56				
		FM	4.56			0.66	
	ZZ _g	NM	2.45	2.53	61.0		
		FM	2.44	2.56	61.5	0.63	
ZZ _l	FM	4.00	2.27	28.4	0.29		
	Fe–Ir	Linear	NM	4.26			
			FM	4.38			1.61
		ZZ _g	NM	2.41	2.34	59.0	
FM			2.47	2.40	59.0	2.11	
ZZ _l	NM	3.58	2.14	33.2			
	Co–Ir	Linear	NM	4.28			
			FM	4.33			1.06
		ZZ _g	NM	2.39	2.38	59.9	
FM			2.43	2.38	59.3	1.48	
ZZ _l	NM	3.66	2.15	31.7			
	Ni–Ir	Linear	NM	4.39			
			FM	4.45			1.06
		ZZ _g	NM	2.39	2.42	60.4	
FM			2.40	2.42	60.3	0.93	
ZZ _l	NM	3.79	2.19	30.1			
	FM	3.65	2.23	35.1	1.32		

^a Theoretical calculations (Ref. [19]).

^b Theoretical calculations (Ref. [22]).

linear and zigzag atomic chains in the vicinity of the E_F . The spin polarization P is a useful quantity for the spin current transports and is defined as

$$P = \frac{N_{\uparrow}(E_F) - N_{\downarrow}(E_F)}{N_{\uparrow}(E_F) + N_{\downarrow}(E_F)} \quad (1)$$

where $N_{\uparrow}(E_F)$ and $N_{\downarrow}(E_F)$ are the spin-up and spin-down DOS at the E_F , respectively. In our previous study of pure Fe, Co, and Ni linear atomic chain [19], Fe, Co and Ni are highly spin-polarized and the spin polarizations are around -0.961 , -0.920 , and -0.951 , respectively, whilst the spin polarization of Ir linear chain is -0.47 [22]. The spin polarizations of zigzag chain of Fe, Co, Ni and Ir become -0.643 , -0.884 , -0.890 , and -0.28 , respectively. Also, our calculated spin polarizations of bulk FM bcc Fe, fcc Co, and fcc Ni are -0.55 , -0.77 , and -0.81 , being considerably smaller than the spin polarization of the corresponding linear chains. In this study of bimetallic linear and zigzag chains, the spin polarizations for the linear Fe–Ir, Co–Ir and Ni–Ir chain are -0.031 , -0.364 and -0.644 , respectively, while for the zigzag chain are -0.652 , -0.850 and -0.817 .

5. Conclusions

Based on the density functional theory and using the generalized gradient approximation, the magnetic and electronic

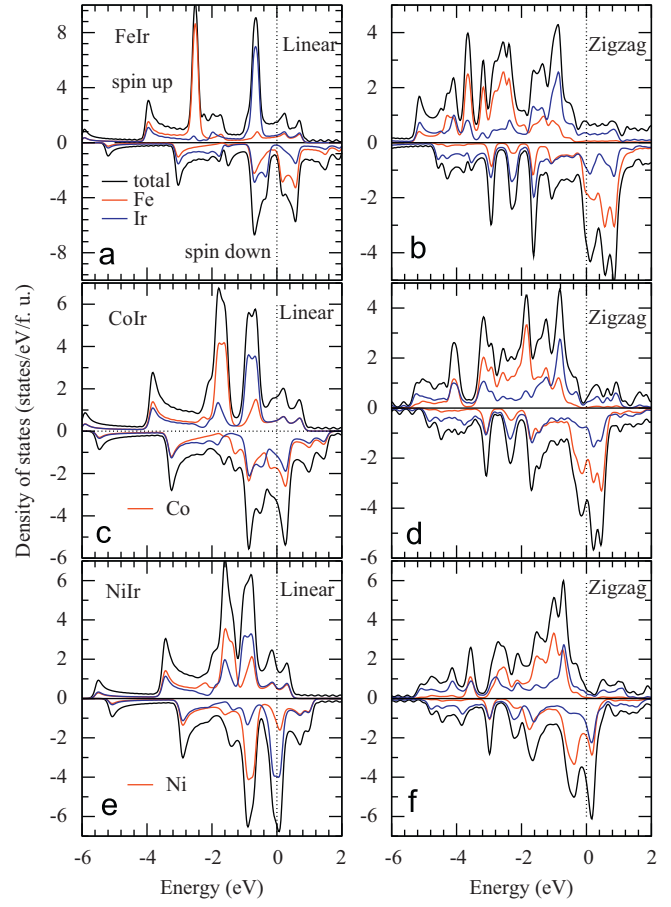


Fig. 3. Total, Fe-site, Co-site, Ni-site, and Ir-site-decomposed and spin-decomposed densities of states of the linear (left panel) and zigzag (right panel) ferromagnetic nanowires. For the Fe-site, Co-site, Ni-site, and Ir-site, only d -dominant states are plotted. The Fermi level (dot vertical lines) is at the zero energy.

properties of both linear and zigzag bimetallic chains of Fe–Ir, Co–Ir and Ni–Ir have been reported. We found that the zigzag structure is more stable than the linear structure and the ferromagnetic state is also more stable than the nonmagnetic state. These freestanding bimetallic linear and zigzag chains are magnetic in all considered bond lengths. The Ni–Ir zigzag nanowire has two energy minimum state of both ferromagnetic and nonmagnetic state, indicating a possible stable condition for mechanically controllable break-junction experiments.

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References

- [1] H.J. Elmers, J. Hauschild, H. Höche, U. Gradmann, H. Bethge, D. Heuer, U. Köhler, Phys. Rev. Lett. 73 (1994) 898.
- [2] S. Heinze, M. Bode, A. Kubetzka, O. Pietzsch, X. Nie, S. Blügel, R. Wiesendanger, Science 288 (2000) 1805.
- [3] O. Pietzsch, A. Kubetzka, M. Bode, R. Wiesendanger, Phys. Rev. Lett. 84 (2000) 5212.

- [4] P. Gambardella, A. Dallmeyer, K. Maiti, M.C. Malagoli, W. Eberhardt, K. Kern, C. Carbone, *Nature* 416 (2002) 301.
- [5] D. Li, B.R. Cuenya, J. Pearson, S.D. Bader, W. Kuene, *Phys. Rev. B* 64 (2001) 144410.
- [6] S.B. Suh, B.H. Hong, P. Tarakeshwar, S.J. Youn, S. Jeong, K.S. Kim, *Phys. Rev. B* 67 (2003) 241402(R).
- [7] G. Rubio, N. Agrait, S. Vieira, *Phys. Rev. Lett.* 76 (1996) 2302.
- [8] V. Rodrigues, J. Bettini, P.C. Silva, D. Ugarte, *Phys. Rev. Lett.* 91 (2003) 096801.
- [9] A. Dallmeyer, C. Carbone, W. Eberhardt, C. Pampuch, O. Rader, W. Gudat, P. Gambardella, K. Kern, *Phys. Rev. B* 61 (2000) R5133.
- [10] J. Hong, R.Q. Wu, *Phys. Rev. B* 67 (2003) 020406(R).
- [11] C. Ederer, M. Komelj, M. Fahnle, *Phys. Rev. B* 68 (2003) 052402.
- [12] B. Lazarovits, L. Szunyogh, P. Weinberger, *Phys. Rev. B* 67 (2003) 024415.
- [13] M. Komelj, C. Ederer, J.W. Davenport, M. Fahnle, *Phys. Rev. B* 66 (2002) 140407(R).
- [14] D. Spisak, J. Hafner, *Phys. Rev. B* 65 (2002) 235405.
- [15] D. Spisak, J. Hafner, *Phys. Rev. B* 67 (2003) 214416.
- [16] L. Fernández-Seírvane, V.M. García-Suárez, J. Ferrer, *Phys. Rev. B* 75 (2007) 075415.
- [17] T. Nautiyal, T.H. Rho, K.S. Kim, *Phys. Rev. B* 69 (2004) 193404.
- [18] Z.-Z. Zhu, J.-C. Zheng, G.Y. Guo, *Chem. Phys. Lett.* 472 (2009) 99.
- [19] J.C. Tung, G.Y. Guo, *Phys. Rev. B* 76 (2007) 094413.
- [20] C. Ataca, S. Cahangirov, E. Durgun, Y.-R. Jang, S. Ciraci, *Phys. Rev. B* 77 (2008) 214413.
- [21] A. Smogunov, A. Dal Corso, A. Delin, R. Weht, E. Tosatti, *Nat. Nanotechnol.* 3 (2008) 22.
- [22] J.C. Tung, G.Y. Guo, *Phys. Rev. B* 81 (2010) 094422.
- [23] A. Delin, E. Tosatti, *Phys. Rev. B* 68 (2003) 144434.
- [24] V.M. García-Suárez, D.Z. Manrique, C.J. Lambert, J. Ferrer, *Phys. Rev. B* 79 (2009) 060408.
- [25] A. Thiess, Y. Mokrousov, S. Heinze, S. Blugel, *Phys. Rev. Lett.* 103 (2009) 217201.
- [26] R.C. Che, M. Takeguchi, *Appl. Phys. Lett.* 87 (2005) 223109.
- [27] X.-L. Che, J.-H. Li, B.-X. Liu, *Commun. Theor. Phys.* 52 (2009) 123–127.
- [28] P.E. Blöchl, *Phys. Rev. B* 50 (1994) 17953; G. Kresse, D. Joubert, *Phys. Rev. B* 59 (1999) 1758.
- [29] G. Kresse, J. Hafner, *Phys. Rev. B* 48 (1993) 13115.
- [30] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* 6 (1996) 15.
- [31] Y. Wang, J.P. Perdew, *Phys. Rev. B* 44 (1991) 13298; J.P. Perdew, Y. Wang, *Phys. Rev. B* 45 (1992) 13244.