Nanowires for spintronics: A study of transition-metal elements of groups 8–10

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We have investigated systematically the changes in the electronic structure and magnetic moment of transition-metal elements of groups 8–10 (Fe, Ru, Os; Co, Rh, Ir; Ni, Pd, Pt) as their dimensionality is reduced. Many interesting results are predicted. The importance of spin-orbit interaction for 4-*d* and 5-*d* elements is exemplified: by predicting correct magnetic ground state for the linear chains (LC's) of Pt. Interestingly, all these systems, except Ir, are predicted to be magnetic in one dimension (LC's). We also show that only one type of carriers are available for conduction in LC's of Fe, Co, Ni, and Pd, suggesting suitability of nanowires of these for spintronics. Our results are in very good agreement with available experimental data.

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As nanotechnology has become a fast growing and highly promising field, descend from the bulk to lower dimensions is witnessing a variety of novel and exotic properties displayed by the materials. Two-dimensional (2D) materials like monolayers (ML's) and thin films often exhibit interesting properties with a wide range of applications.[1] Experimental evidences show that ML's of nonmagnetic substances on suitable substrates may exhibit magnetism.[1,2] On the other hand, the metallic and magnetic nanowires may become important for electronic/optoelectronic devices, quantum devices, magnetic storage, nanoprobes, and spintronics. Linear atomic chains are the ultimate 1D material. The existence of such linear chains (LC's), though mostly transient in nature, has been demonstrated experimentally.[3–6] To predict properties at lower dimensions, we explore the behavior of the materials as their dimensionality changes from 3 to 2 to 1, and find that most of these elements exhibit magnetic ground state in 1D while some of these are found to have only one type of carriers making these potential candidates for the emerging area of spintronics which is expected to lead to new generation of highly efficient devices.

In our previous study,[7] we found that none of the noble elements Cu, Ag, and Au exhibits magnetism as dimensionality is reduced. Transition metals (TM's) on the other hand, because of their partly filled *d* orbitals, have a strong tendency to magnetize. Bulk Fe, Co, and Ni are well known for their ferromagnetic ordering. It has been suggested experimentally that small Rh clusters may possess a permanent magnetic moment μ,[8] though bulk Rh is nonmagnetic. Very recently, experiments have shown magnetic nature of LC's of Co, Pd, and Pt.[6] Thus, the TM elements are interesting subjects to study changes of their electronic structure, with dimensionality. In particular, it would be of interest to explore if magnetism is favored in these, especially in the systems of 4-*d* and 5-*d* elements, at lower dimensions. We report the effect of dimensionality on the electronic structure of TM elements of groups 8–10 (3-*d* elements: Fe, Co, and Ni; 4-*d* elements: Ru, Rh, and Pd; and 5-*d* elements: Os, Ir, and Pt). The calculations were performed using the full potential linear augmented plane wave method as is implemented in the WIEN97 code.[9] As the generalized gradient approximation (GGA) has an improvement over local-density approximation (LDA) in describing TM magnetism and structural properties,[10] the exchange and correlation are treated in the GGA using Perdew-Wang '91.[11] Brillouin-zone integrations for density of states (DOS) are performed using the tetrahedron method with Blöchl corrections.[12]

Inclusion of relativistic effects has been found to be crucial in the study of Au systems.[7,13] Scalar-relativistic (SR) effects are included for the valence states in all the calculations presented here. The relativistic effect due to spin-orbit (SO) interaction is important for 5-*d* TM's, and also, to a lesser extent though, for 4-*d* TM's. Hence we also performed calculations including SO interaction, using a second variational method, for all the systems of 4-*d* and 5-*d* elements under study. These will be referred to as fully relativistic (FR). Core states have been treated fully relativistically in SR as well as FR calculations. We considered the most basic cases when the material is in its ideal 3D state (the bulk), ideal 2D state (an unsupported ML), and ideal 1D state (a free standing LC). We have chosen the (111) plane of fcc, energetically most favored with the densest packing of atoms, as a representative of the 2D structure for all the elements, while for 1D we chose the ideal monatomic LC.

We studied the cohesive energy E_c as a function of lattice constant x. The calculated binding energy (BE) per bond, $E(x)$ ($=E_c$/coordination number), was fitted with the universal BE curve.[14] The force (bond strength) is obtained from the slope of the BE curve at the inflexion point. The SR as well as FR values for d and E_c from this work are listed in Table I along with other calculations[15–18] and available experimental results.[5,19] Our calculations for both d and E_c agree well with the available experimental data. The agreement for the E_c of 3-*d* metals Fe, Co, and Ni has significantly improved, in comparison to previous calculations. The decrease in coordination number manifests itself in lowering the nearest-neighbor distance and E shows a rise with decrease in dimensions. The d for Ir and Pt LC's (2.30 and 2.40 Å, respectively) is in good agreement with the observed values (2.2 ± 0.2 and 2.4 ± 0.2 Å, respectively[5]). These are consistent with the very recent calculations by Delin and Tosatti.[18] Our E_c values for LC's are in consistently good agreement with the GGA results of Bahn and Jacobsen[16] for Ni, Pd, and Pt. However, the LDA values[17] are somewhat

TABLE I. The equilibrium bond length d (in Å), cohesive energy E_c (in eV), and magnetic dipole moment μ (in μ_B) for group 8–10 transition elements in different dimensionalities.[a]

		3-*d*			4-*d*			5-*d*		
		Fe	Co	Ni	Ru	Rh	Pd	Os	Ir	Pt
d	$3D^{x/r}$	2.49[2.50]	2.51[2.51]	2.49[2.51]	2.71[2.75]	2.69[2.75]	2.75[2.82]	2.74[2.79]	2.71[2.81]	2.77[2.86]
	3D	2.48	2.51	2.47	2.71*(2.71)	2.73*(2.72)	2.81*(2.81)	2.75*(2.75)	2.78*(2.76)	2.86*(2.83)
	2D	2.41	2.35	2.35	2.55*(2.54)	2.57*(2.58)	2.64*(2.63)	2.58*(2.56)	2.58*(2.57)	2.62*(2.61)
	1D	2.28	2.18	2.18	2.24*(2.23)	2.27*(2.27)	2.44*(2.45)	2.28*(2.26)	2.30*(2.29)	2.40*(2.38)
	$1D^r$							2.30*(2.31)	2.34*(2.31)	2.48*(2.42)
E_c	$3D^{x/r}$	4.28[5.2]	4.39[5.4]	4.44[5.4]	6.74[6.4]	5.75[5.5]	3.89[3.7]	8.17[7.2]	6.94[6.2]	5.84[5.0]
	3D	4.76	5.25	4.73	6.59*(6.58)	5.90*(5.87)	3.62*(3.58)	7.69*(7.38)	7.34*(7.02)	5.48*(5.25)
	2D	3.25	3.84	3.52	4.62*(4.55)	4.23*(4.15)	2.52*(2.46)	6.10*(5.48)	5.97*(5.30)	4.95*(4.39)
	1D	1.53	2.03	1.89	2.79*(2.71)	2.60*(2.51)	1.07*(1.00)	3.61*(2.85)	4.08*(3.27)	3.32*(2.77)
μ	$3D^{x/r}$	2.22[2.44]	1.72[1.68]	0.61[0.67]	0	0	0	0	0	0
	3D	2.28	1.69	0.64	0	0	0	0	0	0
	2D	2.47	1.85	0.86	0.81*(0.84)	1.01*(1.01)	0.00*(0.19)	0.00*(0.38)	0.12*(0.42)	0.00*(0.12)
	1D	2.98	2.08	1.10	0.79*(0.92)	0.22*(0.16)	0.53*(0.60)	0.40*(1.10)	0.00*(0.73)	0.43*(0.00)
	$1D^r$							0.3*(1.3)	0.0*(0.8)	0.6*(0.0)

[a]All the calculations are using GGA. The numbers with asterisk are the FR values. All other calculated results are SR values. $3D^{x/r}$ denotes the values for 3D from experiment (Ref. 19) and theory (Ref. 15, in brackets). $1D^r$ denotes values from Ref. 18. The experimental values of d (Ref. 5) for 1D systems are 2.2 ± 0.2 Å (Ir) and 2.4 ± 0.2 Å (Pt). The SR calculated values (Ref. 16): for the d/E_c of 3D systems are 2.49 Å/5.16 eV (Ni), 2.82 Å/3.78 eV (Pd), 2.83 Å/5.58 eV (Pt); for the d/E_c of 1D systems are 2.16 Å/2.23 eV (Ni), 2.52 Å/1.20 eV (Pd), and 2.41 Å/2.83 eV (Pt). The LDA values (Ref. 17) for d/E_c of 1D linear chains are 2.21 Å/4.58 eV (Ru), 2.25 Å/3.27 eV (Rh), 2.37 Å/1.73 eV (Pd). The FR value for difference in the energies of 3D and 1D for Os, Ir, and Pt is 5.5, 4.5, and 4.0 eV, respectively, from Ref. 18.

high as compared to the GGA values. In view of (i) LDA having the tendency for overestimating the cohesive energies, (ii) GGA being more suited to describe the electronic properties of transition elements,[10] and (iii) an overall good agreement for our E_c values for the bulk with experiment, we believe that our GGA results are more realistic for LC's.[20]

The formation of an LC depends on the relative bond strength, i.e., the difficulty in breaking the bonds in the chain and in the regions it emanates from. As a first approximation we can regard the maximal force F as a measure of the force necessary to break the LC. The F for the ML's and bulk may also be viewed in the same light.[16] We find that the value of F also shows a bigger jump in going from 2D to 1D than in going from 3D to 2D. The ratio of the F for the LC's and ML's to that for the bulk is displayed in Fig. 1. The break-force ratios for ML's have much smaller value, lying in the range 0.8–1.8, with most of the values lying around a flat line showing no special preferences. On the other hand, the break-force values for the chains are about 1.4–3.6 times higher than the bulk value, with some of the cases showing fairly high values. We note that the ratio in the case of Co, Ru, Rh, Os, Ir, and Pt (and also Au[7]) is much higher, suggesting relative stability of monatomic LC's of these elements, in agreement with experimental observations[4–6] for LC's of Co, Ir, Pt, and Au. Hence, our elementary calculations of break force are consistent with experiments, and we feel that with the advancements in technology, experimental realization of Ru, Rh, and Os LC's is not a far-fetched possibility, though realization of such LC's requires a particular setting for each material offering a new challenge.[6]

Figure 2 shows the total DOS for the energy-minimized structures of these elements in 2D and 1D. The partial DOS (not displayed) shows that major contribution for the central peak comes from d states for all the cases, while that outside its shoulders is due to s-d hybridization. Comparing the DOS for the 3D, 2D, and 1D cases of each individual element, we find that the main difference that comes into picture on lowering the dimensionality is the reduction in the bandwidth. The bands become sharper, a manifestation of the reduced d and coordination, as we descend in dimensionality. For the cases with magnetic ground state, the exchange splitting increases en route, as indicated by the DOS curves.

We find that our calculations[21] yield the correct magnetic or nonmagnetic ground state for each 3D case. Pd is non-

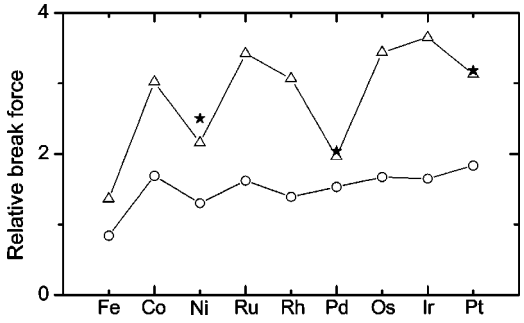

FIG. 1. The break force ratio with respect to the bulk for ML's (in circle) and linear chains (in triangle) of different TM elements of groups 8–10. The points marked with an asterisk are the data for LC's from Bahn and Jacobsen.[16]

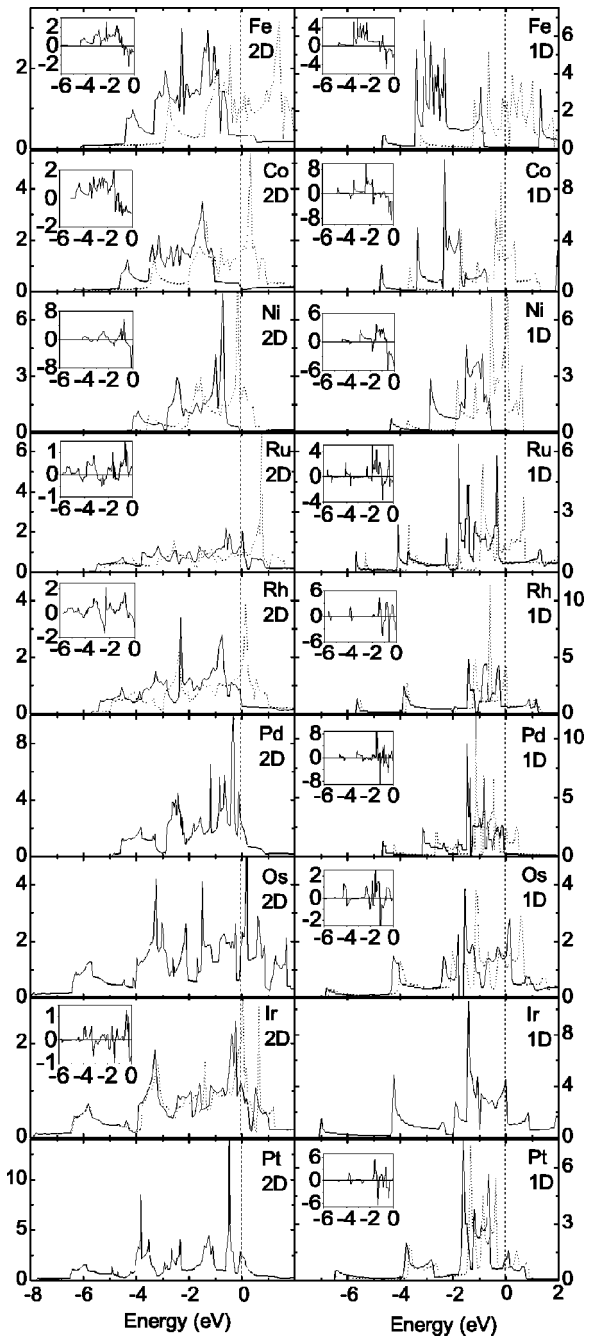

FIG. 2. DOS (in states per cell, for nonmagnetic cases, and in states per cell per spin, for magnetic cases) for the 2D and 1D structures of the TM elements of groups 8–10. The inset, indicating the spin polarization, shows excess of majority and minority carriers for magnetic cases. Fermi energy is at 0 eV.

magnetic, but ''almost'' ferromagnetic, i.e., it can be ferromagnetic with perturbation, in agreement with the experiments. The calculated μ for bulk Fe, Co, and Ni ($2.28\mu_B$, $1.69\mu_B$, and $0.64\mu_B$, respectively) are in good agreement with the corresponding experimental values ($2.22\mu_B$, $1.72\mu_B$, and $0.61\mu_B$, respectively[19]). As we go to 2D, these μ rise to $2.47\mu_B$, $1.85\mu_B$, and $0.86\mu_B$, respectively, while for 1D chains, they are still higher as $2.98\mu_B$, $2.08\mu_B$, and $1.10\mu_B$, respectively. This is in good qualitative agreement with Stern Gerlach deflection measurements[22] demonstrating enhancement of magnetism in clusters of Fe, Co, and Ni. The ML's of Fe, Co, and Ni on Ag(001) also show large μ.[23] In view of this enhancement, magnetic ordering is expected for almost all the ML's. However, we find that ML's of Pd, Os, and Pt are nonmagnetic. Although the SR calculations predict magnetic ordering for these ML's, inclusion of SO interaction makes the magnetic ordering vanish. This is in agreement with earlier study[23] where ML's of almost all these elements exhibited magnetism, while Pd and Pt ML's stayed nonmagnetic on substrates such as Ag(111), Ag(001), and Au(001), and an Os ML stayed nonmagnetic on Ag(111) and Au(001).

Our calculations predict magnetic ordering for the LC's of Ru, Rh, and Pd, the μ being $\sim 0.79\mu_B$, $0.22\mu_B$, and $0.53\mu_B$, respectively. Pd LC's have already been experimentally demonstrated as magnetic.[6] We show that SO interactions are important for the 4-*d* TM's also, the effect getting more accentuated as we go to lower dimensions. For the LC's of the 5-*d* elements, the effect of SO interaction is significant and can destroy the stability of the magnetic or nonmagnetic ground state. We find that SR calculations for Os LC's yield a large μ ($1.10\mu_B$) at the equilibrium d, while the FR calculations yield a much lower value of $0.31\mu_B$. Furthermore, for Ir LC's, SR calculations yield a sizable μ, which is totally washed out on performing the FR calculations. On the other hand, Pt chains are nonmagnetic with SR calculations, while inclusion of SO interaction results into a magnetic state ($0.43\mu_B$). The transition from magnetic/nonmagnetic to nonmagnetic/magnetic ground state may be attributed to the shifting of *d*-band edges with respect to Fermi level when SR and FR calculations are performed. Very recently, experiments have established ferromagnetic nature of Pt LC's.[6] Thus the FR calculations help bring forth the correct magnetic phase for the Pt wires, exemplifying the need for inclusion of SO interaction while studying 5-*d* systems. Our FR calculations show that the energy difference between the nonmagnetic and ferromagnetic phases is extremely small (a few meV) for the LC's of these 4-*d* and 5-*d* elements. This emphasizes the need for inclusion of SO interaction and of using a very accurate band structure method, like FPLAPW method (where no approximations are made on the shape of the potential) for studying such sensitive cases of 4-*d* and 5-*d* elements.[24]

An interesting feature to note in the DOS curves for LC's of Fe, Co, Ni, and Pd is that the majority states are completely filled and it is only the minority carriers that are available for conduction at the Fermi energy E_f. Experimentally,[6] very clear peaks at $0.5G_0$ have been observed only recently in the conductance of Co and Pd chains, compatible with a fully polarized conduction channel for these. This suggests that nanowires of Fe, Co, Ni, and Pd would make a good case for generation of devices based on spin-dependent transport for the so-called spintronics.[25]

In conclusion, the equilibrium bond length/energy tends to decrease/increase and the bands become sharper, as the dimensionality reduces. A simple calculation of break force suggests relative stability of Co, Ru, Rh, Os, Ir, and Pt LC's. Since Co, Ir, and Pt LC's have already been realized experi-

mentally, we feel that with the advancement in technology, Ru, Rh, and Os LC's are also likely to be realized soon. Fe, Co, and Ni show enhanced μ as dimensionality is lowered; this trend has already been witnessed in their clusters. ML's of all these elements, except Pd, Os, and Pt, order magnetically. The inclusion of SO interaction makes significant contributions to the electronic energy bands and the cohesive energy for 4-*d* and 5-*d* TM elements, the effects getting more pronounced as the dimensionality decreases. For some of the cases the magnetic properties using SR calculations are dramatically different from those using SO interaction, e.g., SR calculations for LC's of Ir (Pt) suggest presence (absence) of magnetic ordering, while FR calculations suggest the contrary. Magnetic nature of Pt chains has been witnessed[6] justifying the crucial role that SO interaction plays in deciding properties of such low-dimensional systems. It is worth noting that the difference for E_c of the magnetic and nonmagnetic phases in some of the cases is very small, ~ 5 meV, emphasizing the need for very accurate band structure methods together with the inclusion of SO interaction. It is interesting to note that for Fe, Co, Ni, and Pd LC's, only one kind of carriers are available for conduction at E_f, suggesting the applicability of nanowires of these for spintronics. Only recently, experiments have established availability of only one kind of carriers in Co and Pd LC's. We expect more experimental results to follow in near future on the lines predicted by our calculations.

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