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Effect of dimensionality on transition-metal elements of groups 3–7

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We report theoretically on the effect of dimensionality on elementary low-dimensional systems of transition metals of groups 3–7 (Sc, Y; Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Mn, Tc, Re). This work completes the exploration on elementary low-dimensional systems of all transition metals, those of groups 8 to 12 being reported earlier. In contrast to the elementary low-dimensional systems of late transition metals, magnetic moment per atom (μ) predicted for some cases of early transition metals is very large. An interesting trend is observed for magnetic ordering as we go from group 3 to 7. The elementary low-dimensional systems of groups 3 and 4 prefer ferromagnetic ordering, with only Hf preferring to stay nonmagnetic as in bulk. Antiferromagnetic ordering is preferred by elementary low-dimensional systems of transition metals of groups 5 to 7. The maximum μ for ferromagnetic elementary low-dimensional systems (1.8 μ_B for Sc linear chains) is much smaller than that for antiferromagnetic systems ($\sim$3.4 μ_B for linear chains of Cr and Mn). The antiferromagnetic ordering in two-dimensional systems is invariably accompanied by lattice expansion with respect to bulk. Our results are in accordance with available experimental and theoretical results. Magnetic linear chains of Sc, Ti, Zr (ferromagnetic in nature), and Cr, Re (antiferromagnetic in nature) are predicted to offer relative ease of formation experimentally and could be useful from an application point of view.

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I. INTRODUCTION

Appearance of magnetism at low dimensions,[1–6] for some of those materials which are nonmagnetic in bulk, could lead to a real technological breakthrough, and a high economic impact is foreseen because of the possibility of their incorporation into a future generation of information storage devices. This possibility is higher in the case of low-dimensional systems of 4*d* and 5*d* transition metals, because of their partly occupied *d* orbitals. Linear chains constitute the most elementary one-dimensional (1D) structure. Much theoretical work has been done on linear chains of Au and Ag, and some on linear chains of late transition metals.[1,2,7–9] We recently focused on the late transition metals of groups 8 to 12 (Fe, Ru, Os; Co, Rh, Ir; Ni, Pd, Pt; Cu, Ag, Au; Zn, Cd, Hg) and studied[2,8,9] the effect of dimensionality on these. Many interesting features were predicted and discussed, in agreement with available experimental observations. Elementary systems of early transition metals remain relatively much less explored. This work presenting the effect of the dimensionality on early transition metals of groups 3 to 7 (Sc, Y; Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Mn, Tc, Re), is a sequel to our previous study.[2,8,9] Through this, we have made an attempt to complete the exploration of the electronic structure of elementary low-dimensional systems of all the transition metals. In the course of the progress of our calculations, Spišák *et al.*[1] have reported a study on metal linear chains including those of Y, Zr, Nb, Mo, Tc, Hf, Ta, W, and Re, and Zhu *et al.*[10] on Ti atomic chains. Experimentally no work on linear chains of the early transition metals has been reported. However, recently continuous Nb wires, about 7–15 nm in diameter, have been fabricated by sputter-coating fluorinated carbon nanotubes[11] and Mo nanowires of millimeter-scale length have been produced using electrochemical step edge decoration.[12] Very recently highly conductive nanowires of Ti have been fabricated using sapphire single crystal,[13] and conductive W nanowires have been produced on substrate of Si and SiO_2 by means of focused ion beams.[14]

II. COMPUTATIONAL DETAILS

We studied these early transition metals in the three-dimensional (3D) state (bulk); ideal two-dimensional (2D) state (an unsupported monolayer); and an ideal 1D state (a free standing linear chain). For 3D systems, we used the experimental crystal structure [hexagonal closed packed (HCP) for Sc, Y, Ti, Zr, Hf, Tc, and Re; body centered cubic (BCC) for V, Nb, Ta, Mo, and W] except for Cr and Mn. Bulk Cr and Mn have complex antiferromagnetic (AFM) structures and noncollinear effects play an important role in predicting the true ground state. However, it has been reported[15] that the equilibrium lattice constant and calculated cohesive energy/atom for bulk Cr in the AFM phase differ from those in hypothetical nonmagnetic (NM) phase by only 0.001 Å and 2 meV, respectively. Overlooking these small differences, we calculated 3D Cr in the NM phase with BCC structure. The AFM ordering of the observed ground-state phase of Mn has not received much attention since it is exceedingly complex. For this study, where there is more emphasis on the low-dimensional phase, we calculated bulk Mn in the hypothetical simple BCC structure. The results are presented at equilibrium lattice constant for each case. Using energy minimization, we found that while for HCP metals, the base plane was energetically most stable in 2D, for BCC metals the (110) plane was favored over hexagonal packing.

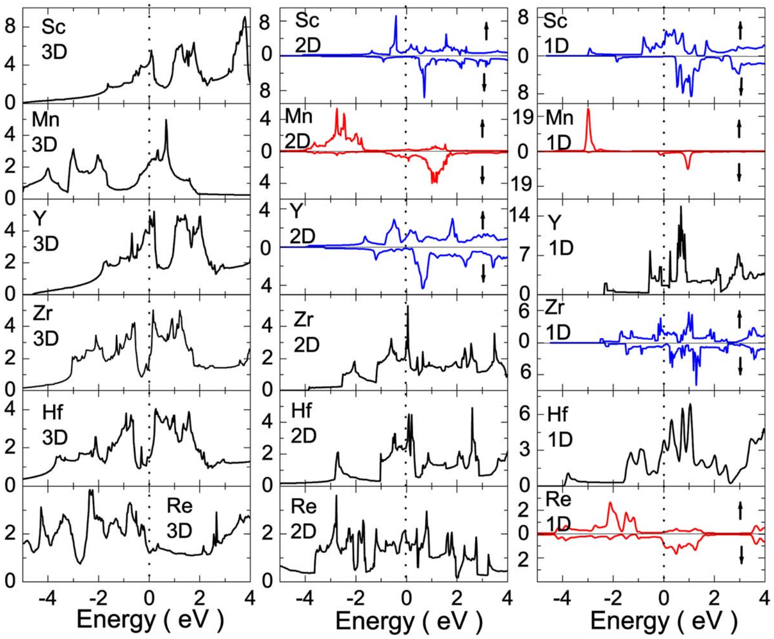

FIG. 1. (Color online) Density of states (in states/eV/atom for NM and states/eV/atom/spin for FM and AFM cases) for elementary low dimensional systems of 3-*d* (Sc and Mn), 4-*d* (Y and Zr), and 5-*d* (Hf and Re) transition metals. The Fermi level is at 0 eV. Online NM, FM, and AFM cases are shown with black, blue, and red color, respectively, in all the figures.

We considered NM, ferromagnetic (FM), and AFM phases for the low-dimensional systems. In this work, we have considered the most basic structures and have confined to the simplest AFM ordering: e.g., in linear chains, direction of spin is reverse at the alternate sites, and for the monolayers, we have considered row-wise AFM ordering. Nevertheless noncollinear aspects of magnetism[16] are very important, particularly for systems of Cr and Mn. A great deal of research has been reported by the group of Blügel related to magnetism in transition metal systems and, particularly,[17–19] on the noncollinear properties of Mn and Cr monolayers on various substrates.

We employed an all electron full potential linearized augmented plane wave method[20] with the exchange and correlation treated in the generalized gradient approximation. A large number of *k* points was used (300 for 2D and 78 for 1D in the irreducible Brillouin zone) and the convergence with respect to number of *k* points and energies was thoroughly checked. Other details may be found in our earlier work.[2,8,9] We carried out scalar relativistic calculations for all, while relativistic calculations, where spin-orbit interaction was included using the second variational approach, were also performed for systems of 4-*d* and 5-*d* elements. The results presented by us for 4-*d* and 5-*d* elements are from relativistic calculations with spin-orbit interaction while those for 3-*d* elements are from scalar relativistic calculations. Our results are in agreement with previous calculations.[1,10,21] To the best of our knowledge, spin-orbit interaction is not included in the previous theoretical studies listed here. We find that its inclusion plays an important role in modifying the electronic structure in some cases, as it also did in case of Ir and Pt linear chains earlier[2,4] bringing the results in agreement with experiment.[6]

III. RESULTS AND DISCUSSIONS

We present (Fig. 1) the total density of states (DOS) for elementary low-dimensional systems of two elements each from 3-*d* elements [Sc (FM in both 2D and 1D) and Mn (AFM in both 2D and 1D)], 4-*d* elements [Y (FM in 2D and NM in 1D) and Zr (NM in 2D and FM in 1D)], and 5-*d* elements [Hf (NM in both 2D and 1D) and Re (NM in 2D and AFM in 1D)], as representative cases. The calculated DOS for 3D cases is in good agreement with previous work.[22] Increasing sharpness of DOS in going from 3D to 2D to 1D reflects the effect of dimensionality. It shows that *d* bands become flatter on decreasing the dimensionality which is consistent with the decrease in the coordination number. In the early transition metals, only one type of carriers are available for conduction in elementary low-dimensional systems of Sc only, in contrast to the late transition metals of which linear chains of Fe, Co, Ni, and Pd were found suitable for spintronics theoretically[2] as well as experimentally.[6]

Our bulk equilibrium-nearest neighbor distance (d_{nn}) and cohesive energy/atom (E_c) are in very close agreement with experimental values.[23] The calculated d_{nn} in different dimensionalities are plotted in Fig. 2. For most of the elements, the d_{nn} decreases with the dimensionality indicating stronger in-

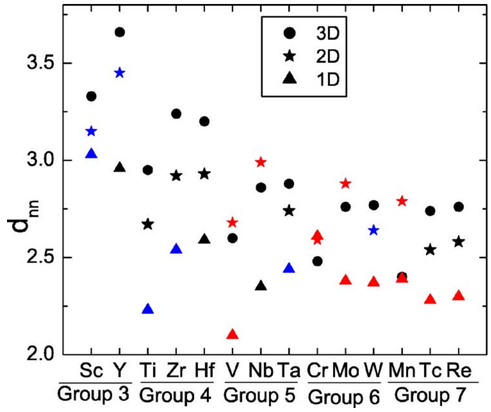

FIG. 2. (Color online) Nearest neighbor distance (Å) for bulk and elementary low dimensional systems of early transition metals.

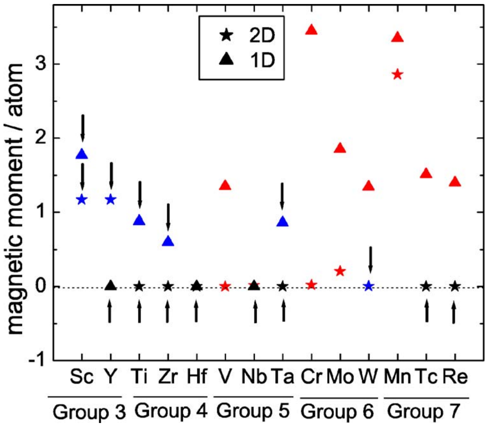

FIG. 3. (Color online) Magnetic moment (μ_B) for elementary low dimensional systems of early transition metals. Upward (downward) arrows indicate NM (FM) cases while symbols without arrows are for AFM cases.

teratomic interactions on going toward nanoscale system, in agreement with experimental observations.[24] Unlike other transition metals, the d_{nn} for linear chains of Cr, and for monolayers of V, Cr, Mn, Nb, and Mo is greater than that for the bulk. This is an uncommon feature observed only for Hg linear chains, amongst late transition metals,[9] resulting in vanishing of the *s*-*p* band overlap robbing Hg of metallic property in 1D. We note that all the present cases with lattice expansion exhibit AFM ordering. Such an expansion of lattice constant has been experimentally observed for one monolayer of Cr on Au(100) (Ref. 25) in qualitative agreement with our results. Furthermore, experiments show[26] that sparse monolayer atoms of Mn on a Cu (001) substrate undergo size enhancement with large magnetic moment per atom (μ) which is in agreement with our Mn 2D results where d_{nn} increases from bulk (2.40 Å) to monolayer (2.79 Å) with large predicted μ of 2.86 μ_B.

Since the surface to volume ratio α increases on lowering the dimensions, the decrease in E_c for these transition metals (not shown) is in consonance with $E_c = E_b(1-0.75\alpha)$ from a recent model[27] for fully free standing nanocrystals with E_b as the bulk cohesive energy. Empirical results, obtained using a liquid drop model,[28] and experimental data[29] on E_c, determined by measuring the oxidation enthalpy, of Mo and W nanoparticles also indicate the same. Our results [d_{nn}=2.23 Å, E_c=1.99 eV] for Ti linear chains are in good agreement with very recent pseudopotential results[10] [d_{nn}=2.10 Å, E_c=1.99 eV]. The d_{nn} and E_c for 2D (1D) decrease by ~6% (~18%) and ~33% (~67%), respectively, with respect to that of bulk, the changes being much more pronounced in case of 1D. On reducing dimensionality from 3D to 2D and 1D, E_c/bond increases in general indicating stronger bonds in low dimensions.

Figure 3 displays the nature of preferred magnetic ordering for the elementary low-dimensional systems along with the predicted μ values. We find that Cr and Mn retain the tendency of AFM ordering at low dimensions too, as is the case for their bulk. An interesting trend of FM ordering being favored in systems of group 3 and 4, with Hf maintaining NM nature as in bulk, is observed. Thereafter, it is the AFM ordering that is favored in general. The μ values for FM systems are, in general, much lower as compared to those for AFM systems some of which promise very high μ value. FM linear chains of Sc, Ti, Zr, and Ta have predicted μ values of 1.77, 0.88, 0.60, and 0.86 μ_B, respectively, while linear chains of Cr, Mn, Mo, Tc, W, and Re favor an AFM state with μ of ±3.45, ±3.35, ±1.85, ±1.51, ±1.34, and ±1.40 μ_B, respectively. The monolayers of Sc and *Y* are predicted to have FM ordering with $\mu \sim 1$ μ_B/atom while the monolayers of Mn are predicted to favor AFM coupling with large $\mu \sim \pm 2.86$ μ_B. As already mentioned earlier, the equilibrium d_{nn} for all the AFM 2D cases is larger than the bulk value. Monolayers of V, Cr, Nb, Mo (AFM in nature), and of W (FM in nature) are predicted to possess negligibly small μ. Our calculations show that the V linear chain prefers the AFM ordering by a very small margin of 8 meV/atom with respect to the FM ordering. Out of the 14 transition metals (28 elementary low-dimensional systems) considered in this work, besides Hf, linear chains of only Y and Nb, and monolayers of only Ti, Zr, Ta, Tc, and Re do not show a preference for magnetic ordering. Hence low dimensionality is conducive to development of magnetic ordering in most of the cases. The preference for magnetic ordering along with narrowing of the bands with reduction in dimensionality in many transition metals is reminiscent of earlier results, e.g., lattice expansion renders bulk Pd magnetic[30] or band broadening prevents the 4*d* and 5*d* bulk metals from being magnetic.[31]

Our results for predicted AFM ordering for monolayers of V and Mn are in agreement with experimental results that report AFM coupling with low magnetic moment in V monolayers on Fe(001),[5] and AFM ordering of Mn monolayer on W(110) (Ref. 32) with a large μ ($\sim \pm 3.3$ μ_B). The difference in numerical values of μ for the monolayers between those from our work and the experiments[5,32] is explained by the different environments involved. Also our result for magnetism of free standing monolayers of Mn is in agreement with results from Blügel's group for one monolayer of Mn on Fe(111) (Ref. 17) and on Cu(111) (Refs. 18 and 19) showing a row-wise antiferromagnetic nature. The AFM state for the Cr monolayer from our results is also in qualitative agreement with results from Kurz *et al.*[18] According to their theoretical study, the Cr monolayer on Fe(111) (Ref. 17) and Cu(111) (Ref. 18) substrates shows AFM ordering, though preferring noncollinear 120° Néel structure to the row-wise AFM structure. Our equilibrium lattice constant (a_0) for Mo monolayers is in agreement with previous theoretical study[33] suggesting the AFM state for Mo monolayers with a_0 lying between 5.15 and 5.55 a.u. For the magnetic ordering, all the available results for linear chains from a previous calculation[1] are consistent with ours: e.g., linear chains of Y, Nb, Hf, are NM; those of Zr, Ta are FM; linear chains of Mo, Tc, W, and Re prefer AFM ordering. The FM Ti linear chains have μ of 0.88 μ_B in agreement with very recent value of 0.61 μ_B from the all-electron method.[21] Very recently AFM nature has been confirmed for the linear chain of 10 Mn atoms,[34] which is in consonance with our results. The AFM ordering of Cr linear chains from our calculations is in qualitative agreement with the experimental observations on the complex [$(CH_3)_4N$]$CrCl_3$ consisting of a linear one-dimen-

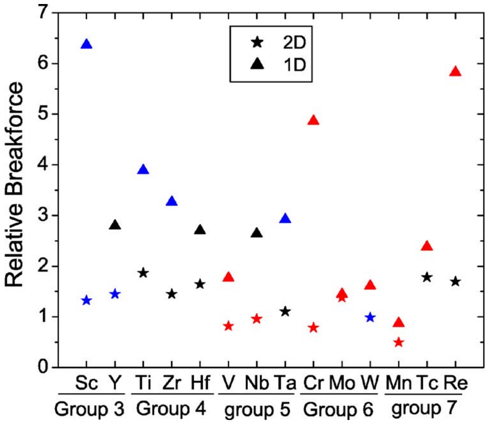

FIG. 4. (Color online) Relative break force with respect to bulk for elementary low dimensional systems of early transition metals.

sional chain of Cr atoms with three bridging chlorine atoms between them. The compound shows one-dimensional magnetic behavior with AFM nature due to cation-cation exchange interaction via nearest-neighbor Cr ions in the chain.[35]

Estimated relative break force[2,36] (the ratio of the forces required to break a single bond for the nanostructure with respect to that for the bulk bonds), a measure of the ease of formation from bulk, for these linear chains and monolayers is shown in Fig. 4. Our results show that formation of linear chains of Sc, Ti, Cr, Re, Zr, Y, Nb, Tc, Hf, and Ta is favored, more so for the former four, with a large predicted value. The conspicuously low value for Mn linear chains can be ignored given that the actual crystal structure and ordering were not taken into account. We estimated the lifetime for the nanowires of these transition metals using a recent model proposed by Burki *et al.*[37] for the kinematics of thin nanowires. Using Debye frequency[23] and surface tension value,[38] we estimated[37] the activation energy $\Delta E=0.6(\hbar^2\sigma/m_e)^{1/2}$ and lifetime $\tau=\upsilon_D^{-1}\exp(\Delta E/T)$. It is interesting to note that the predicted lifetime value for Mn, NW is lowest, in agreement with the very low break force value predicted by our calculations. The calculated activation energies when compared with our E_c values show qualitatively the same trend (not presented here) for the linear chains of the 3-*d* transition metals. Combining the break force information with the predicted magnetic moment, we observe that amongst FM linear chains Sc, Ti, and Zr, and amongst AFM linear chains Re and Cr, with μ values as 1.8, 1.0, 0.6, ±1.4, and ±3.5 μ_B, respectively, offer themselves as suitable candidates for formation and consequently for applications as magnetic nanowires.

IV. CONCLUSIONS

This study on monolayers and linear chains of transition metals of groups 3 to 7 shows that low dimensionality, in general, is conducive to magnetic ordering for the elementary low-dimensional systems of early transition metals. An interesting trend is observed in this respect as we go from group 3 to 7. Elementary low-dimensional systems of groups 3 and 4 prefer FM ordering, with the μ decreasing steadily till we reach Hf which prefers to stay NM as in bulk. Thereafter, most of the cases prefer AFM ordering with fairly large μ values, the maximum being ~3.4 μ_B for Cr and Mn linear chains, and 2.86 μ_B for Mn monolayers. In the groups 5 to 7, only W monolayers and Ta linear chains prefer FM ordering while linear chains of Nb and monolayers of Ta, Tc, and Re fail to show a preference for magnetic ordering. The d_{nn}, in general, decreases with dimensionality in agreement with the experiments. However, certain elementary low-dimensional systems (monolayers of V, Nb, Cr, Mo, and Mn; and Cr linear chains) exhibit expansion with respect to bulk and favor AFM ordering. Interestingly, the maximum predicted μ for elementary low-dimensional systems of late transition metals was ~3 μ_B while μ for linear chains of Cr, and Mn, is larger. Our results, e.g., on lattice expansion, magnetic ordering, and magnetic moment per atom, are in qualitative agreement with available experimental and theoretical results. Combining the break force information with the predicted magnetic moment, we observe that among FM linear chains Sc, Ti, and Zr, and among AFM linear chains Re and Cr, should offer ease of formation experimentally, e.g., in mechanically controlled break junction experiments, and should prove suitable from an application point of view.

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