Ab initio studies of spin-spiral waves and exchange interactions in 3d transition metal atomic chains

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The total energy of the transverse spin-spiral wave as a function of the wave vector for all 3d transition metal atomic chains has been calculated within ab initio density functional theory with generalized gradient approximation. It is predicted that at the equilibrium bond length, the V, Mn, and Fe chains have a stable spin-spiral structure, whilst the magnetic ground state of the Cr, Co and Ni chains remains to be collinear. Furthermore, all the exchange interaction parameters of the 3d transition metal chains are evaluated by using the calculated energy dispersion relations of the spin-spiral waves. Interestingly, it is found that the magnetic couplings in the V, Mn and Cr chains are frustrated (i.e., the second near neighbor exchange interaction is antiferromagnetic), and this leads to the formation of the stable spin-spiral structure in these chains. The spin-wave stiffness constant of these 3d metal chains is also evaluated and is found to be smaller than its counterpart in bulk and monolayer systems. The upper limit (in the order of 100 Kelvins) of the possible magnetic phase transition temperature in these atomic chains is also estimated within the mean field approximation. The electronic band structure of the spin-spiral structures have also been calculated. It is hoped that the interesting findings here of the stable spin-spiral structure and frustrated magnetic interaction in the 3d transition metal chains would stimulate further theoretical and experimental research in this field.

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I. INTRODUCTION

Noncollinear magnetism, especially the spin-spiral structures, has received much attention in recent decades, not only for possible magnetism-based technological applications[1-2] but also for fundamental physics[3-12]. In particular, it was recently reported that spin chirality in geometrically frustrated pyrochlore compounds could generate magnetic monopoles[13-14] and also large anomalous Hall effect[15]. It was also proposed recently that the spin-spiral structure could be the main source of the magnetoelectric effect observed recently in multiferroic oxides.[2-3] The spin-spiral structure, in which the magnetization rotates along a certain direction in a bulk material, was observed two decades ago in neutron diffraction experiments on fcc Fe and Fe$_{190}$Co$_x$ alloy precipitates in Cu.[16] This experimental finding has since stimulated many ab initio studies of the spin-spiral structures in bulk magnets.[12-14 20] Indeed, ab initio calculations[12 17 19] corroborated that stable spin-spiral states exist in fcc Fe. Furthermore, ab initio total energy calculations for the spin-spiral structures also helped to formulate an explanation of the anomalous magnetovolume properties of the Invar alloys (the Invar effect)[14].

Noncollinear magnetism in low-dimensional systems has also been studied both theoretically and experimentally in recent years.[1 21 23] For example, Mn monolayer on W(001) surface was recently investigated[7] jointly by spin-polarized scanning tunneling microscopy and also ab initio calculations, and it was concluded that a spin-spiral structure along the (110) direction exists in this monolayer system. A stable spin-spiral structure with propagation vector $q = (0,0,0.15)(2\pi/a)$ was also predicted to exist in the unsupported free-standing Fe(110) monolayer with the lattice constant of 3.16 Å[21,22]. Co/CoPt bilayers were also found to support noncollinear spiral structures by Brillouin light scattering[23]. Interestingly, very recent ab initio calculations show that in Mn chains on Ni(001), the magnetic structure could change from non-collinear to collinear ferrimagnetic, depending on whether the number of the Mn atoms is even or odd.[13]

Stimulated by possible unusual magnetism in one-dimensional (1-D) systems, we have recently carried out systematic ab initio studies of the collinear magnetic properties of linear and zigzag atomic chains of all 3d[24], 4d and 5d[25] transition metals. Although the ideal infinite freestanding 3d transition metal atomic chain is unstable and cannot be prepared experimentally, short suspended monostrand metal nanowires and atomic chains have been prepared in mechanical break junctions.[26-28] Furthermore, structurally stable Co atomic chains have been recently prepared on a vicinal surface of Pt(997) surface[29] or inside nanotubes.[30] Therefore, we have also performed ab initio calculations for the 3d transition metal linear atomic chains on the Cu(001) surface[31,32] in order to understand how the substrates would affect the magnetic properties of the nanowires.

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The purpose of the present work is to study possible spin-spiral structures in all 3d transition metal atomic chains by \textit{ab initio} calculation of the total energy of the spin-spiral state as a function of propagation wave vector \( \mathbf{q} \). Indeed, we find that the magnetic ground state in the V, Mn and Fe chains would be a spin-spiral state. Furthermore, we evaluate the exchange interaction parameters between the atoms and also spin-wave stiffness constants of all the atomic chains considered here from the calculated energy dispersion relations of the spin-spiral waves. The obtained exchange interaction parameters allow us to understand why the spin-spiral state is stable in the V, Mn and Fe chains but is not stable in the Cr, Co and Ni chains. Finally, we also estimated the upper limits of the magnetic phase transition temperature for all the atomic chains.

This paper is organized as follows. After a brief description of the computational details in Sec. II, we present all the calculated energy dispersion relations of the spin-spiral waves of the 3d atomic chains in Sec. III. These results show that a stable spin-spiral state exists in the V, Mn and Fe chains. Reported in Sec. IV are the obtained exchange interaction parameters which enable us to understand the stability of the obtained magnetic ground state in each atomic chain considered. In Sec. V, we present the calculated spin-wave stiffness constant and also the estimated magnetic phase transition temperatures for the 3d atomic chains. Finally, the band structures of the spin-spiral state of the V and Mn chains are displayed in Sec. VI, and a summary of this work is given in Sec. VII.

### II. THEORY AND COMPUTATIONAL METHOD

In the present first principles calculations, we use the accurate frozen-core full-potential projector augmented-wave (PAW) method \cite{blochl94, kresse99} as implemented in the Vienna \textit{ab initio} simulation package (VASP) \cite{vasp1, vasp2}. The calculations are based on density functional theory with the exchange and correlation effects being described by the generalized gradient approximation (GGA) \cite{perdew96}. A very large plane-wave cutoff energy of 500 eV is used. The shallow core 3p electrons of the 3d transition metals are treated as valence electrons. We adopt the standard supercell approach to model an isolated atomic chain. The nearest wire and wire distance adopted here is 20 Å. We start with the theoretical equilibrium bond lengths for collinear magnetic states from our previous study of 3d TM nanowires\cite{magnusson20}. However, in the fully unconstrained noncollinear magnetic calculations\cite{magnusson19}, for the spin spiral structures, we vary the bond length in order to study the bond length dependence of the stability of the spin spiral state. The Γ-centered Monkhorst-Pack scheme with a \( k \)-mesh of \( 1 \times 1 \times n \) (\( n = 100 \)) in the full Brillouin zone (BZ), in conjunction with the Fermi-Dirac-smearing method with \( \sigma = 0.02 \) eV, is used for the BZ integration.

| \( m_s \) (\( \mu_B \)/atom) | \( d \) (Å) | \( q \) (2\( \pi \)/d) | \( E(q) \) (meV/atom) |
|-----------------------------|-------------|----------------|----------------|
| V                           | 1.47        | 2.05           | 0.25           | -166.4        |
| Cr                          | 4.18        | 2.32           | 0.50           | -155.2        |
| Mn                          | 4.43        | 2.40           | 0.33           | -113.3        |
| Fe                          | 3.30        | 2.25           | 0.10           | -15.5         |
| Co                          | 2.18        | 2.15           | 0.00           | —             |
| Ni                          | 1.14        | 2.18           | 0.00           | —             |

We consider the transverse spin-spiral states where all the spins rotate in a plane perpendicular to the spiral propagation vector \( \mathbf{q} \). The total energies of the transverse spin-spirals as a function of the magnitude of spin-spiral wave vector \( q \) are calculated self-consistently by using the generalized Bloch condition approach \cite{magnusson19, magnusson20}. To study the exchange interactions, we apply the frozen-magnon approach and obtain the exchange interaction parameters by a Fourier transformation of the energy spectra of the spin-spiral waves.

### III. STABILITY OF SPIN-SPIRAL STATES

The calculated total energies \([E(q, \theta)]\) as a function of the spin-spiral propagation vector \( q \) of the 3d transition metal chains at several different bond lengths \( d \) are plotted in Fig. 1. Since we consider here the transverse spin-spiral waves only, the angle between the chain axis (i.e., \( z \)-axis) and the magnetization direction \( \theta = \pi/2 \), and hence we simply write \( E(q, \theta = \pi/2) = E(q) \). The spin-spiral structure at wavevector vector \( q = 0 \) corresponds to the collinear ferromagnetic (FM) state, whilst the state at \( q = 0.5 \) (2\( \pi \)/d) corresponds to the antiferromagnetic (AF) state. Therefore, as shown in Fig. 1 at \( q = 0 \) the lowest total energy state of the Cr (Mn) chain occurs at 2.80 (2.60) Å, but it appears at 2.32 (2.29) Å at \( q = 0.5 \) (2\( \pi \)/d), being in good agreement with our previous collinear magnetic calculations\cite{magnusson20}. Interestingly, Fig. 1 shows that both the FM and AF states in the V, Mn and Fe chains become unstable against formation of a spin-spiral structure. Furthermore, the lowest total energy of the spin-spiral state occurs at the bond length that is generally different from that of the collinear magnetic states. For example, the ground state of the Mn chain is the spin-spiral state with the equilibrium bond length of 2.40 Å, instead of 2.60 Å (the FM state) and 2.29 Å (the AF state)\cite{magnusson19}.

Nonetheless, there is no stable spin-spiral state in the Cr, Co and Ni chains. In the Cr chain, therefore, the AF state remains the stable state. In the Co and Ni chains, the FM state still has the lowest total energy (see Fig. 1). In fact, we could not even obtain a spin-spiral
solution for the Ni chain at the wave vector $q$ being larger than 0.3 ($2\pi/d$). This is because, as shown in Fig. 1, an increase in the number of valence electrons leads to an increased stabilization of the FM state whilst a decrease in the number of valence electrons tends to stabilize the AF state. This observation is further corroborated by the fact that in previous GGA calculations [40], the FM state wave vector increases (Fig. 1b). For comparison, we notice that in previous GGA calculations [40], the FM state could not be stabilized in bulk Cr metal, whilst, in contrast, that for the V and Mn chains is much shorter, being 4 and 3 bond lengths, respectively. However, the spin-spiral wave length $\lambda$ can depend on the bond length, and this dependence is especially pronounced for the V chain, as demonstrated in Fig. 1b. When the V chain is stretched to the bond length of 2.40 Å, the spiral propagation vector $q$ becomes $\sim$0.35 ($2\pi/d$), but when it is further stretched to $d = 2.55$ Å, $q$ is reduced to $\sim$0.20 ($2\pi/d$). A similar behavior of the spin-spiral wave vector can be found for the Fe chain, as shown Fig. 1b.

The energy of a spin-wave excitation (i.e., the magnon dispersion relation) is given as the derivative of the total energy of the spin-spiral state with respect to the magnon number [18, 20]

$$\varepsilon(q) = \hbar\omega(q) = 2\mu_B \frac{\Delta E(q, \theta)}{\Delta M} = \frac{4\mu_B}{m_{s0}}[E(q) - E(0)] \quad (1)$$

where $\Delta E(q, \theta) = E(q, \theta) - E(0, \theta) = E(q) - E(0)$ is the energy of a spin spiral of wave vector $q$ relative to the ferromagnetic state ($q = 0$), $\Delta M$ is the decrease of the magnetization per site projected onto the z-axis, and $m_{s0}$ is the spin magnetic moment per site at $q = 0$. The calculated magnon dispersion relations for the V, Cr, Mn, Fe, Co and Ni chains at the minimal energy bond length are plotted in Fig. 2.

Ab initio calculations of the excitation energy of the spin-spiral wave along some high-symmetry lines in the Brillouin zone in bulk bcc Cr [20], fcc Mn [20], bcc Fe [16–18, 20], fcc Co [16–18, 20], and fcc Ni [16–18, 20] metals have been reported before, and the stable spin-spiral structures were found in bcc Cr and fcc Mn. The stable spin-spiral wave with a wave length of $\sim$7 lattice constants was also found in a freestanding bcc Fe(110)
monolayer with lattice constant of 3.16 Å in two previous ab initio studies. Here we predict the existence of the stable spin-spiral structures in 1D freestanding transition metal (V, Mn and Fe) atomic chains for the first time.

IV. EXCHANGE INTERACTIONS

To a rather good approximation, we can map a metallic magnet onto an effective Heisenberg Hamiltonian with classical spins\(\mathbf{14,18}\)

\[
H_{\text{eff}} = -\frac{1}{2} \sum_{i,j} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j
\]

where \(J_{ij}\) is an exchange interaction parameter between atomic site \(i\) and site \(j\), and \(\mathbf{s}_i\) (\(\mathbf{s}_j\)) is the unit vector representing the direction of the local magnetic moment at site \(i\) (\(j\)). In the frozen magnon approach, the exchange interaction parameters \(J_{ij}\) are related to the magnon excitation energy \(\varepsilon(q)\) by a Fourier transformation

\[
J_{0j} = \frac{1}{N_q} \sum_{\mathbf{q}} e^{-i \mathbf{q} \cdot \mathbf{R}} J(q)
\]

where \(N_q\) is the number of \(q\) points in the Brillouin zone included in the summation and

\[
\varepsilon(q) = 4 \mu_B \frac{m_s}{m_s^0} [E(q) - E(0)] = -\frac{2\mu_B}{m_s^0} \sin(\theta)^2 J(q) = -\frac{2\mu_B}{m_s^0} J(q)
\]

Here, \(\theta\) is fixed to \(\pi/2\) for all the spin-spiral states and \(J(q)\) is the Fourier transform of the exchange parameters.

We therefore evaluate the exchange interactions in the 3d transition metal chains via Eqs. 3 and 4 by using the calculated magnon dispersion relations, as shown in Fig. 2.

The obtained exchange interaction parameters as a function of the interatomic distance are plotted in Fig. 3 and also listed in Table II. In the minimum energy bond lengths, as shown in Fig. 3a, the magnetic coupling between two first nearest neighbors in the V, Fe, Co and Ni chains is ferromagnetic \((J_{01} > 0)\), whilst it is antiferromagnetic \((J_{01} < 0)\) in the Cr and Mn chains. In the Co and Ni chains, the magnetic coupling between the second nearest neighbors remain ferromagnetic \((J_{02} > 0)\) and this explains why the ground state of these chains is ferromagnetic. In contrast, the magnetic coupling between the second nearest neighbors in the V, Mn and Fe chains is antiferromagnetic \((J_{02} < 0)\), i.e., the exchange interactions in these chains would be frustrated. As a result, noncollinear spin-spiral states in these chains may become energetically more favorable than either collinear ferromagnetic or antiferromagnetic state. Let us take the Mn chain as an example, and consider the atomic spin at the origin. This spin tends to couple antiferromagnetically both with its two nearest neighbors and also with its two second near neighbors because the first and second near neighbor exchange parameters \(J_{01}\) and \(J_{02}\) are negative (see Fig. 3a and Table II). However, this would make its two nearest neighbor spins ”frustrated” because they would have to couple ferromagnetically with one nearest neighbor on one side and antiferromagnetically with the other nearest neighbor on the opposite side. This frustrated magnetic coupling therefore would energetically favor a spin-spiral state. In fact, accord-

### Table II: Calculated exchange interaction parameters \((J_{0j})\) (meV) between two \(j\)th nearest neighbors \((j = 1, 2, 3, 4, 5)\) in the V, Cr, Mn, Fe, Co and Ni atomic chains.

|       | \(J_{01}\) | \(J_{02}\) | \(J_{03}\) | \(J_{04}\) | \(J_{05}\) |
|-------|------------|------------|------------|------------|------------|
| V     | 4.2        | -22.8      | -0.2       | 2.6        | -2.4       |
| Cr    | -65.0      | 17.6       | -7.2       | 4.0        | -2.6       |
| Mn    | -78.4      | -43.2      | 9.8        | -3.0       | 1.2        |
| Fe    | 158.2      | -57.8      | 4.4        | 2.6        | -3.2       |
| Co    | 156.4      | 13.0       | -22.8      | 16.6       | -11.8      |
| Ni    | 109.0      | 6.6        | 20.0       | -24.6      | 7.4        |
ing to the mean field theory for an 1-D classical Heisenberg spin chain with the negligible small magnetic coupling between third near neighbors and beyond (see, e.g., Ref. 12, in the frustrated magnetic coupling situation \(J_{02} < 0\), the system would be ferromagnetic \((q = 0)\) if \(J_{01} > 4|J_{02}|\), and would be antiferromagnetic \((q = \pi/2)\) if \(J_{01} < -4|J_{02}|\). Table I shows clearly that the condition \(J_{01} < -4|J_{02}|\) is met for the Co and Ni chains, giving rise to the ferromagnetic ground state, and that the condition \(J_{01} < 4|J_{02}|\) is fulfilled for the Co and Ni chains, giving rise to the antiferromagnetic ground state. Interestingly, a stable spin-spiral structure with the spiral propagation vector \(q\) given by \(\cos(qd) = -J_1/4J_2\) would occur if \(J_{02} < 0\) and \(4J_{02} < J_{01} < 4|J_{02}|\). Using the exchange coupling parameters listed in Table I, we would obtain the spiral propagation vector \(q = 0.24, 0.32\) and 0.13 \((2\pi/d)\), respectively, for the V, Mn and Fe chains. These estimated \(q\) values agree very well with that obtained by the fully selfconsistent total energy calculations (Table I).

Figure 1 shows that the stability of spin-spiral state in the V, Mn and Fe chains depends pronouncedly on bond length \(d\). Therefore, we also calculate the exchange interaction parameters for these chains with several other bond lengths and the results are plotted in Fig. 3(b). The equilibrium bond length for the FM V and Mn chains is 2.60 Å. The equilibrium bond lengths for the AF Mn and Fe chains are 2.29 Å and 2.15 Å, respectively. It is clear from Fig. 3 that the calculated exchange interaction parameters can be sensitive to the bond length. For example, the magnitude of the nearest neighbor exchange interaction \(J_{01}\) in the V atomic chain is dramatically increased from 2.1 meV to 40 meV as the bondlength is increased from 2.05 Å to 2.60 Å. A similar behavior is found for the Fe chain (Fig. 3). Interestingly, in contrast, the magnitude of the nearest neighbor exchange interaction \(J_{01}\) in the Mn chain is significantly reduced as the bond length is increased. Nevertheless, the exchange interaction parameters for the second near-neighbor and beyond are less affected by the bond length (see Fig. 3).

Ab initio evaluation of the exchange interaction parameters in bulk ferromagnets Fe, Co and Ni have been reported many times before. For example, the nearest neighbor exchange interaction \(J_{01}\) in fcc Fe was determined to be 39.0 meV\(^4\) and 57.3 meV\(^4\), respectively. The nearest neighbor exchange interaction \(J_{01}\) in fcc Co was estimated to be 29.5 meV\(^4\). In bulk fcc Ni, the \(J_{01}\) was calculated to be 5.6 meV\(^4\). In the freestanding square Fe and Co monolayers with the Cu(001) lattice constant, the nearest neighbor exchange interaction \(J_{01}\) is 92.5 and 77.6 meV\(^4\), respectively. These indicate that in 2D systems, in general, the exchange interactions are significantly enhanced as compared with their bulk counterparts, mainly because of reduced coordination numbers. Table II show that the nearest neighbor exchange parameters \(J_{01}\) in the Fe, Co and Ni chains, are much larger than in their bulk counterparts. This may be attributed, at least partially, to the fact that the nearest bond length in the atomic chains is significantly shorter than in their bulk counterparts\(^24\). Our calculated \(J_{01}\) values in the Fe and Co chains are also significantly larger than the corresponding \(J_{01}\) values in the freestanding Fe and Co monolayers\(^11\). Interestingly, in the Fe atomic chains deposited on the Cu(111) surface, the effective exchange interaction parameter \(J_{eff}\) was determined to be around 136 meV\(^4\), being comparable with the corresponding \(J_{01}\) value of the freestanding Fe chain listed in Table II.

V. SPIN-WAVE STIFFNESS AND CRITICAL TEMPERATURE

The calculated energy dispersion relations of the spin-spiral waves \(\varepsilon(q)\) for the 3d transition metal chains at the ground state bond length are displayed in Fig. 2. In the range of small \(q\), \(\varepsilon(q) = Dq^2\), where the spin-wave stiffness constant \(D\) relates the spin-wave energy \(\hbar\omega(q)\) to the wave vector \(q\) in the long wavelength limit. The spin-wave stiffness constant \(D\) of an atomic chain can be estimated by fitting an even order polynomial to the corresponding spin-wave spectrum shown in Fig. 2. The spin-wave stiffness constant \(D\) obtained in this way for the 3d metal chains are listed in Table III. A negative value of \(D\) means that the FM state is not stable against a spin-spiral wave excitation. Table III shows that the spin-wave stiffness constant \(D\) in the V, Cr, Mn and Fe chains is negative. Only in the Co and Ni chains, the \(D\) is positive.

In principle, one can also calculate the spin-wave stiffness constant \(D\) via\(^16\)

\[
D = \frac{2\mu_B}{m_{s0}} \frac{d^2E(q)}{dq^2} = \frac{\mu_B}{3m_{s0}} \sum_j J_{0j} R_{0j}^2
\]

where \(J_{0j}\) are the exchange interaction parameters and \(R_{0j} = |\mathbf{R}_0 - \mathbf{R}_j|\) is the distance between site 0 and site \(j\). In practice, Eq. 5 cannot be used directly to obtain reliable values for the spin-wave stiffness constant, because the numerical uncertainties at the long distances are amplified by the factor \(R_{0j}^2\). Here we use this expression to understand the calculated \(Ds\) listed in Table III. For example, the magnitude of the spin-stiffness constant \(D\) of the V chain is much larger than that of the Cr chain because the V chain has a much smaller spin magnetic moment (see Table I) and also a negative second near neighbor antiferromagnetic exchange parameter (see Table II). Furthermore, even though \(J_{01}\) is positive in the V and Fe chains, the \(D\) is negative, because the V and Fe chains have \(J_{02} < 0\) and \(J_{01} < 4|J_{02}|\).

For comparison, the spin-wave stiffness constants \(Ds\) for the three-dimensional (3D) and two-dimensional (2D) Fe, Co and Ni systems from previous ab initio calculations and experimental measurements, are also listed in Table III. It is clear from Table III that the spin-wave stiffness constant tends to become smaller as the dimensionality of the system gets reduced. This may be expected (see Eq. 5) because the number of near neighbors
TABLE III: Calculated spin wave stiffness constant $D$ (meVÅ$^2$) and magnetic transition temperature $T_C$ of the 3d metal chains. Also listed are the $D$s and $T_C$s for the 3D and 2D metal systems from previous $ab$ initio calculations and experimental measurements, for comparison.

| Chain  | 3D   | 2D   | 1D   | 3D   | 2D   | 1D   |
|--------|------|------|------|------|------|------|
| V      | -    | -    | -424 | -    | -    | 94   |
| Cr     | -    | -    | -106 | 311$^a$ | -    | 414  |
| Mn     | -    | -    | -504 | -    | -    | 274  |
| Fe     | 250$^a$, 330$^b$ | 164$^c$ | -78  | 1414$^d$, 1043$^d$ | 1265$^e$ | 410  |
| Co     | 663$^a$, 510$^b$ | 570$^c$, 427$^c$ | 616 | 1645$^c$, 1388$^d$ | 1300$^e$ | 606  |
| Ni     | 756$^a$, 555$^d$ | -    | 655 | 397$^a$, 627$^d$ | -    | 458  |

$^a$Theoretical calculations (Ref. [18]).
$^b$Neutron-scattering measurement extrapolated to $0$ K (Ref. [24]).
$^c$Theoretical calculations (Ref. [13]).
$^d$Brillouin light scattering measurement (Ref. [48]).
$^e$Neutron-scattering measurement (Ref. [19]).
$^f$Neutron-scattering measurement (Ref. [49]).

The more accurate expression for the critical temperature within the random phase approximation (RPA) also exists

$$\frac{1}{k_B T_C^{RPA}} = \frac{6\mu_B}{M N_q} \sum_{\mathbf{q}} \frac{1}{\varepsilon(\mathbf{q}) + \Delta} \tag{9}$$

where $\Delta$ is the magnetic anisotropy energy. The RPA expression generally gives the critical temperatures for bulk ferromagnets Fe, Co and Ni being in better agreement with experiments than the MF expression[18]. Furthermore, the critical temperatures with the MF approximation are usually significantly higher than that from the RPA calculations[11,18]. Using our calculated spin-wave dispersion relations (Fig. 2) and also the $\Delta$ values from Ref. [24] we obtain $T_C^{RPA} = 230$ K for the Co chain and $T_C^{RPA} = 229$ for the Ni Chain. Therefore, the estimated critical temperatures listed in Table III should be considered only as the upper limits. Finally, we note that in 1-D isotropic Heisenberg model with finite-range exchange interactions, there is no spontaneous magnetization at any nonzero temperature because fluctuations become important[52]. Nonetheless, this discouraging conclusion has to be revised in the presence of a magnetic anisotropy and long range interactions. Indeed, ferromagnetism in 1-D monatomic Co metal chain on a Pt substrate has been recently reported[29]. A detailed discussion on possible finite temperature spontaneous magnetization in 1-D systems has been given in Ref. [53].

VI. ELECTRONIC BAND STRUCTURE

In order to study how the spin-spiral structure affect the electronic band structure[39] and also to help getting further insight into the spin-spiral instability at the microscopic level, the electronic band structures of the V and Mn chains at several spin-spiral wave vectors $q$ are displayed in Figs. 4 and 5 respectively. The ferromagnetic ($q = 0$) band structures are presented in Figs. 4 and 5. Because of the linear chain symmetry, the bands may be grouped into three sets, namely, the nondegenerate $s$– and $d_{z^2}$-dominant bands, doubly degenerate $(d_{xz}, d_{yz})$ bands, and $(d_{x^2–y^2}, d_{xy})$ dominant bands, see Figs. 4a and 5a. 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 $\gamma$ bonds. The $d_{xz}$, and $d_{yz}$, bands, on the other hand, are more dispersive due to the stronger overlap of the $d_{xz}$ and $d_{yz}$ orbitals along the chain, which gives rise to the $\pi$ bonds. The $s$– and $d_{z^2}$-dominant bands are most dispersive since these orbitals form strong $\sigma$ bonds along the chain.

Two main changes could appear in a ferromagnetic band structure when a spin-spiral wave is introduced,
FIG. 4: (color online) Band structures of the V chain in different spiral propagation vector \( q \) along \( \Gamma \) to \( Z \) direction. Figure (a), \( q = 0 \) \((2\pi/d)\), that indicates a spin-polarized ferromagnetic band structure whilst figure (f), \( q = 0.5 \) \((2\pi/d)\), indicates an AF band structure.

FIG. 5: (color online) Band structures of Mn in different spiral propagation vector \( q \) along \( \Gamma \) to \( Z \) direction. Figure (a), \( q = 0 \) \((2\pi/d)\), that indicates a spin-polarized ferromagnetic band structure whilst figure (f), \( q = 0.5 \) \((2\pi/d)\), indicates an AF band structure.

VII. CONCLUSIONS

We have calculated the total energy of the transverse spin-spiral wave as a function of the wave vector for all 3d transition metal atomic chains within \textit{ab initio} density functional theory with generalized gradient approximation. As a result, we predict that at the equilibrium bond length, the V, Mn, and Fe chains have a stable spin spiral structure. Furthermore, all the exchange interaction parameters of the 3d transition metal chains are evaluated by using the calculated energy dispersion relations of the spin-spiral waves. Interestingly, we find that the magnetic couplings in the V, Mn and Cr chains are frustrated (i.e., the second near neighbor exchange interaction is antiferromagnetic), and this leads to the formation of the stable spin-spiral structure in these chains. The spin-wave stiffness constant of these 3d is also evaluated and compared with its counterpart in bulk and monolayer systems. We have also estimated the upper limit of the possible magnetic phase transition temperature in these atomic chains within the mean field approximation. The electronic band structure of the spin-spiral structures have also been calculated. We hope that our findings of the stable spin-spiral structure and frustrated magnetic interaction in the 3d transition metal chains would stimulate further theoretical and experimental research in this field. Indeed, after learning our \textit{ab initio} results, Sandvik recently studied a spin-1/2 Heisenberg chain with both frustration and long-range interactions by exact diagonalization.\cite{54} He found a first-order transition between a Neel state and a valence-bond-solid with coexisting critical \( k = \pi/2 \) spin correlations.\cite{54}
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