Possible ferromagnetism in *s*- and *sp*-electron element nanowires

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ABSTRACT

We present a general physical picture for the one-dimensional nanomagnetism of elements with only *s*- or *sp*-valence electrons based on the atomic orbital interactions, first-principles calculations and Stoner criterion combined. It is shown that *s*- and *sp*-electron atoms, such as Na, Mg, Al, and Si, can exhibit magnetism in the geometry of linear chains. The *s*-electron elements show magnetism when the bonds are compressed, and, in contrast, the *sp*-elements exhibit magnetism when the bonds are elongated. The underlying mechanism has been understood by a general physical picture, that is, the exchanges among electronic states of multiple subbands around the Fermi level.

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1. Introduction

The monatomic chains, being an ultimate one-dimensional (1-D) structure, are a testing ground for the theories and concepts developed for the three-dimensional (3-D) systems. It is of fundamental importance to understand the electronic and magnetic properties in the lower dimensionality, as well as the atomic structures in a truly 1-D nanowire. In recent years, the nanoscale magnetism has been a very active research topic [1–8] because of its novel fundamental physics and important potential applications. The novel experiments on 1-D magnetic systems have opened a new vista in nanomagnetism and nanospintronics [9–11]. Particularly important are the spin-dependent quantum transport properties, the ballistic anomalous magnetoresistance and the spin and magnetization tunneling [12,13]. These studies have stimulated extensive theoretical investigations, and many new magnetic phenomena have been predicted which do not exist in higher dimensions.

Transition metals, because of their partly filled *d* orbitals, have a strong tendency to magnetize. While the monatomic 3*d*, 4*d*, and 5*d* transitional-metal chains are under extensive theoretical and experimental investigations [4,7,14], the magnetism of other elements (especially with only *s*- or *sp*-valence electrons) in one-dimensional case are not well studied. On the basis of the stabilized-jellium model and Stoner criteria, the 3-D nanowires of simple (nonmagnetic) metals have been predicted to undergo a transition to a spin-polarized magnetic state at critical radii [8]. First-principles density functional calculations on the spontaneous magnetization of aluminum nanowires, both unsupported and supported on the NaCl(100) surface, have also been reported

[15]. They have confirmed that unsupported 1-D Al linear chain can show magnetization when elongated beyond the equilibrium length. The ferromagnetic instabilities in atomically thin lithium and sodium wires are also investigated by the density functional theory [16]. Despite of the above mentioned theoretical research, current understanding on novel magnetic properties of nanowires and how magnetism of elements with only *s*- or *sp*-electrons arises is still incomplete. The purpose of the present work is to present a physical picture which can be used to understand the magnetic behavior in many atomic chains of elements with only *s*- or *sp*-electrons based on systematic first-principles calculations and analysis of atomic orbital interactions as well as considerations of the Stoner criterion [8] and Lieb–Mattis theorem [17]. The calculation predicts that *s*-electron elements in linear atomic chains show magnetism when the bonds are compressed, while the *sp*-elements exhibit magnetism when the bonds are stretched. The results can be understood by a general physical picture based on atomic orbital interactions.

2. Computational details

For the first-principles calculations, the accurate projector augmented wave (PAW) method as implemented in the Vienna *ab initio* simulation package (VASP) [18,19] has been employed. The calculations are based on density functional theory (DFT) with the exchange and correlation being described by the generalized gradient approximation (GGA) [20]. Brillouin-zone integrations are approximated by using special *k*-point sampling of the Monkhorst–Pack scheme [21] with a $1 \times 1 \times 50$ grid for the linear chains (*z* direction is chosen as chain axis), in conjunction with the Fermi–Dirac-smearing method with $\sigma = 0.01$ eV. The convergences of total energy with respect to the *k*-points sampling and the plane-wave energy cut-off have been both examined. The free-standing atomic

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chains are simulated by a two-dimensional array of infinite long, straight wires. The nearest wire–wire distance between the neighboring chains is, at least, 15 Å, which should be wide enough to decouple the neighboring wires. In order to double check the accuracy of magnetic moment of atomic chains, we have also performed full potential augmented plane-wave calculations using WIEN2K code [22].

3. Results and discussion

We first discuss the magnetic properties of linear atomic chains of elements with only *s*-valence electrons. The atomic spin magnetic moments of Na (with valence 3*s*¹) and Mg (3*s*²) linear chains as a function of bond length in the ferromagnetic (FM) state are displayed in Fig. 1a and b. The vertical line points out the bond length (*d_m*) where the magnetism of the chains emerges. The positions of equilibrium bond length (*d₀*) are also shown in the figures. The results show that both the Na and Mg linear chains show no magnetism at their equilibrium positions. However, they exhibit FM magnetism when the bonds are compressed. The amounts of bond compression needed in order to exhibit magnetism for Na linear chain is much larger than that of Mg chain, with a compression of 1.52 Å and 0.28 Å for Na and Mg chains, respectively (see Table 1). The emergence of magnetism for the *s*-electron elements in the 1-D linear chain can be predicted by a general physical picture based on the atomic orbital interactions. The picture is then verified by our first-principles calculations and also corroborated by the Stoner criterion and Lieb–Mattis theorem. Fig. 2a and b are the wavefunctions at the Γ -point for the atomic chains with only *s*-electrons at the equilibrium and compressed bond length, respectively. According to the Bloch theorem, we have $\Psi_{\Gamma} = \sum_n e^{ik\vec{R}_n} \chi_n = \sum_n e^0 \chi_n = \sum_n \chi_n$, with χ_n is the *s*-atomic orbital at each lattice site. We could first suppose that, at the equilibrium bond length, only *s*-electrons contribute to the electronic conduction in the chain, i.e., only *s*-band across the Fermi level (this is consistent with the first-principles calculations which will be shown later). The density of states (DOS) at the Fermi level may not be large enough to make the nonmagnetic state unstable at this

Table 1

Geometry parameters for the linear chains. *d₀* is the equilibrium bond length, and *d_m* is the critical bond length where the magnetism emerged.

Linear chains	<i>d₀</i>	<i>d_m</i>	<i>d_m</i> – <i>d₀</i>	
Na	3.34	1.82	–1.52	Bond compression
Mg	3.08	2.80	–0.28	
Al	2.42	2.50	+0.08	Bond elongation
Si	2.20	2.96	+0.76

Fig. 2. The schematic wavefunctions for the *s*- or *sp*-electron atoms linear chains, (a) at Γ -point for the equilibrium bond length; (b) at Γ -point for the compressed bond; (c) at Z -point (0,0,0.5) for the equilibrium state.

equilibrium state (as the case in Fig. 1a). However, when the linear chain is sufficiently compressed, as seen in Fig. 2b, the π -bonding

Fig. 1. The spin magnetic moment per atom as a function of bond length for the atomic linear chains. (a) for Na, (b) for Mg, (c) for Al, and (d) for Si linear chains, respectively. The Stoner parameters $I \cdot \text{DOS}(E_F)$ as a function of bond length are also shown.

p_x (and p_y) electrons can also contribute to the electronic conduction of the chain, that is, p -electron bands should then also cross the Fermi level and contribute to the $\text{DOS}(E_F)$ (this is again consistent with the first-principles band structure calculations which will be shown later). As long as the chain is compressed with enough extent, the total DOS at Fermi level will then be large enough for the system to fulfill the Stoner criterion for magnetism, i.e., $I \cdot \text{DOS}(E_{F_NM}) > 1$, with I is the Stoner parameter [23,24] calculated from bulk materials. The $I \cdot \text{DOS}(E_{F_NM})$, with the DOS calculated from the nonmagnetic (NM) state, as a function of bond length for Na and Mg chains are also displayed in Fig. 1a and b. The figures indicate that the appearance of ferromagnetism in these metallic systems can be understood on the basis of the Stoner criterion. In one word, as seen from the atomic orbital interactions and the Stoner theory, theoretically, s -electron elements can show magnetism in the linear chain geometry when the chain is compressed to a short enough bond length. The picture is general, although it may be of significance only theoretically for some elements, for example, the bond compression of 1.52 Å (which is as large as 46% of the bond length by our *ab initio* calculation) for the Na chain in order to have magnetism seems not to be possible practically.

We now present the band structures of 1-D linear chains of elements with only s -electrons. Plotted in the Fig. 3 are the band structures of Na and Mg linear chains at the equilibrium and the compressed bond lengths obtained from spin-polarized density functional calculations. Both the Na and Mg linear chains at equilibrium state show nonmagnetism, with only s -band crosses the Fermi level for Na chain and a filled s -band for Mg chain, respectively. For the compressed bonds, see right panels of Fig. 3, both Na and Mg linear chains can then get magnetization. The π -bonding p_x (and p_y) electrons are now contributing to the electronic conduction of the chains, as explained/predicted theoretically in the previous paragraph. The Stoner parameter $I \cdot \text{DOS}(E_{F_NM})$ as a function of bond length plotted in Fig. 1 shows that magnetism appears almost exactly when the Stoner criterion is fulfilled. The present picture indicates that the magnetism of s -electron element chains originates from both s - and p -electron bands rather than pure s -electron band. The contribution of both s - and p -electrons

to the Fermi surface leads to the splitting of bands into the spin-up and spin-down ones. In other words, the magnetism arises due to the exchanges of electronic states of multiple subbands. For example, with decrease of bond length, the $p_x(p_y)$ -band near Γ point moves down and even below the Fermi level after certain critical bond length (d_m), while the s -band and p_z -band near Z point lifts up, resulting in more than one bands to cross the Fermi level. These results are in consistent with the Lieb–Mattis theorem [17], which formally prohibits ferromagnetic ground states for strictly one-dimensional systems in the absence of spin- or moment-dependent forces. The theorem is strictly valid for single band systems, but no longer applicable when two or more transverse subbands are occupied. Therefore, the present picture for the ferromagnetism instability for s -electron element chains does not in violation of the Lieb–Mattis theorem.

We further discuss the magnetism of linear chains of elements with sp -valence electrons. The spin magnetic moment per atom as a function of bond length for Al (with valence $3s^23p^1$) and Si ($3s^23p^2$) linear chains in the FM state, as well as the calculated Stoner parameters $I \cdot \text{DOS}(E_{F_NM})$ as a function of bond length, are displayed in Fig. 1c and d. Again, both the Al and Si linear chains show nonmagnetism at their equilibrium bond length. However, they both exhibit FM magnetism when the bonds are elongated. The amounts of bond elongation needed for exhibiting magnetism for Si is much larger than that of Al chain, with elongation of 0.76 Å and 0.08 Å for Si and Al chains, respectively (see also Table 1). To make the Al chain FM, one only needs to elongate it slightly (0.08 Å). This is possible in break-junction experiments. Same as the s -electron atoms, the magnetism of sp -electron chains appears when the Stoner criterion is fulfilled. At the equilibrium bond length, both systems show Stoner parameters $I \cdot \text{DOS}(E_{F_NM}) < 1$. With the elongation of bond length, the Stoner parameter increases and finally the condition $I \cdot \text{DOS}(E_{F_NM}) > 1$ is reached, as shown in the Fig. 1c and d. The calculated spin-polarized band structures of the Al and Si chains at the equilibrium and elongated bond lengths are shown in Fig. 4. A picture of atomic orbital interactions can also be provided. Instead of using the Γ -point, the Z-point, i.e. (0,0,0.5) in the Brillouin-zone, is now used to explain more efficiently the picture. The wavefunction at Z-point are presented in Fig. 2c. According to the Bloch theorem, we have $\Psi_Z = \sum_n e^{ik \cdot \vec{R}_n} \chi_n = \sum_n (-1)^n \chi_n$, with χ_n are the s - and p -atomic orbitals at each lattice site. The picture of atomic orbital interactions

Fig. 3. Spin-polarized band structures, (a) and (b) for the equilibrium and compressed bond length of Na linear chains, respectively; (c) and (d) for the Mg chains. The Fermi level is set to be 0 eV, shown by dot line, the solid lines are for spin-up and dash lines are for spin-down bands, respectively. The components of s , $p_x(p_y)$, and p_z are indicated by open square (red), open circle (green), and solid circle (blue), respectively. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Spin-polarized band structures, (a) and (b) for the equilibrium and elongated bond length of Al linear chains, respectively; (c) and (d) for the Si-chains. The symbols are the same as in Fig. 3.

around the Fermi surface for Al and Si linear chains is somewhat different from the Na and Mg ones. At the equilibrium bond length, for the Al chain, part of p_x (and p_y) π -bonding band near Γ -point are occupied in addition to a fully occupied band (see Fig. 4) due to 3-valence electrons per Al atom. The $\text{DOS}(E_F)$ is now not large enough to make the nonmagnetic state unstable. When the bond is elongated, the strength of s -state anti-bonding at Z-point is weakened, see Fig. 2c, which lowers the corresponding s -anti-bonding band near the Z-point, as shown in the Fig. 4b. As long as the bond is sufficiently elongated the s -anti-bonding electrons near Z-point will eventually contribute to the electronic conductance of chain (i.e., band crossing the E_F) and increase the DOS at the Fermi level, and then make the nonmagnetic state unstable, that is, the Stoner condition $I \cdot \text{DOS}(E_{F_NM}) > 1$ will be fulfilled. For the Si-chain, both the part of p_x (and p_y) π -bands near Γ -point and part of s -anti-bonding band near Z-point are occupied since each Si atom has 4-valence electrons. When the bond is elongated, the strength of anti-bonding interactions near Z-point decreases (see Fig. 2c). Consequently, the conduction bands near Z-point are lowered which makes the p_x (and p_y) π -bands as well as other bands more flat (the flattening of bands will increase the DOS). The magnetism of Si-chain can finally appear as long as the bond is elongated with enough extent, in other words, the Stoner condition $I \cdot \text{DOS}(E_{F_NM}) > 1$ will eventually be fulfilled. Again, the ferromagnetism instability for sp -electron element chains does not violate the Lieb–Mattis theorem. In short, theoretically but maybe not practically, both the sp - and s -electrons elements in the linear chain geometry should show ferromagnetism, when the chain is compressed or elongated to an enough short or long bond length.

In more detail, the calculated spin-polarization P for Na, Mg, Al and Si linear chains as well as the number of conduction bands that cross the Fermi level are listed in Table 2. The spin-polarization P 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 . The most useful materials for spintronic applications are the half-metallic materials in which one spin channel is metallic and the other spin channel is insulating. The spin-polarization for these half-materials is either 1.0 or -1.0 , and the electric conduction would be fully spin-polarized. From Table 2, it is interesting to see that Al chain with $d = 2.54 \text{ \AA}$ is half-metallic. Therefore, with a small bond length elongation of $0.04 \text{ \AA}$ (since $d_0 = 2.50 \text{ \AA}$), the Al chain can be half-metallic. It is also clear that FM Na and Mg chains have much higher spin-polarizations than Al and Si chains at the selected bond length, except for the Al chain with $d = 2.54 \text{ \AA}$. Furthermore, we present in Fig. 5 the contour plots of the total charge density and the spin charge density for Al linear chain, again as a representative, at the elongated bond length of $2.54 \text{ \AA}$. The spin density is defined as $\rho(\vec{r}) = \rho_{\uparrow}(\vec{r}) - \rho_{\downarrow}(\vec{r})$, i.e., the difference between spin-up and spin-down electron charge densities. A significantly covalent bonding between Al atoms in the 1-D chain geometry is visible in the total charge density plot. The spin density plot indicates that the major spin component is in perpendicular to

Fig. 5. (a) Total charge density and (b) spin charge density of Al linear chain. The Al atom is indicated as small green sphere. For (b), solid line is for $\rho_{\uparrow}(\vec{r}) - \rho_{\downarrow}(\vec{r}) \geq 0$, while dash line is for $\rho_{\uparrow}(\vec{r}) - \rho_{\downarrow}(\vec{r}) < 0$. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

the chain, while the minor spin component is in between the atoms along the chain direction.

The strictly 1-D atomic chains are somewhat artificial in equilibrium or in elongated (compressed) states. Allowing linear chains to relax, the zigzag geometries of all the chains studied are energetically more stable than the linear ones. For the Na zigzag chain, the stabilization energy, which is defined as the cohesive energy difference between zigzag and linear chains, is 0.13 eV/atom . For the Mg zigzag chain, the stabilization energy is 0.26 eV/atom . The Al and Si chains show two energy minima in the zigzag geometry. The stabilization energies are 0.78 and 0.07 eV/atom for Al, and 0.73 and 0.45 eV/atom for Si, respectively. Such a structural instability of linear atomic chain has been discussed previously in the transition metal chains [14]. Since it should be hard to achieve for unsupported chains, we have also calculated the magnetic properties of 1-D Mg zigzag chain (as a representative) supported by the NaCl(100) surface. For the unsupported Mg chain, it shows a magnetization of $0.16\mu_B$ at the equilibrium zigzag geometry. Our result shows that magnetization of Mg zigzag chain keeps unchanged when supported by NaCl(100) surface, due to the weak interaction between Mg chain and the substrate. More detail will be presented elsewhere.

4. Conclusions

In summary, atoms with only s - or sp -valence electrons, like Na, Mg, Al, and Si, are shown to exhibit magnetism in the geometry of one-dimensional chains, with the chain is either compressed or elongated. We have presented a general physical picture for understanding such a 1-D nanomagnetism of elements with only s - or sp -electrons, based on the atomic orbital interactions, the

Table 2

Spin polarization P at some selected bond length d . The $n_{\uparrow}$ and $n_{\downarrow}$ are the number of spin-up and spin-down bands that cross the Fermi level, respectively.

Linear chains	d	Magnetization μ_B	$(n_{\uparrow}, n_{\downarrow})$	P
Na	1.82	0.12	(3, 1)	0.759
Mg	2.60	0.24	(3, 1)	0.801
Al	2.54	1.00	(3, 0)	1.0
Al	2.60	1.00	(3, 1)	0.220
Si	2.98	1.35	(3, 1)	-0.200

first-principles calculations, the Stoner criteria, and the Lieb–Mattis theorem combined. For the linear chains, all elements studied show no magnetism at their equilibrium states. However, linear chain of *s*-electron atoms show magnetism when the bonds are compressed, while the *sp*-elements exhibit magnetism when the bonds are elongated. This rule originates from the exchange of electronic states of subbands of atomic chains as a function of bond length, which can be justified by simple atomic orbital interactions, as shown in the text, thus expects to be hold for many other elements with only *s*- or *sp*-valence electrons. In fact, we have calculated several atomic linear chains consists of elements other than those mentioned above, such as carbon and gold, and find that our rule holds for these elements.

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