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Magnetic properties of Co nanochains

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Using the full potential linearized augmented plane wave method, spin and orbital magnetic moments along with the magnetocrystalline anisotropy energies (MAE) of linear shape Co nanochains consisting of two to seven atoms were explored. The MAE and orbital magnetic moments are strongly oscillatory against the size of nanochains. The magnetic circular dichroism sum rules were validated, but the relationship between MAE and the anisotropy of orbital moments was denied for these ultrasmall nanoentities due to large spin-flip contribution to MAE.

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Magnetic nanowires fabricated on stepped surfaces[1] and in pinholes[2] have many significant applications such as spin filtering and high density magnetic recording. Monatomic chains of Co and Mn, the smallest possible nano-entities, were successfully fabricated through either self-assembled growth on Pt(997) (Ref. 3) or tip manipulation in scanning tunneling microscope[4] (STM) experiments. In the ultrasmall scale, magnetic properties display many peculiar behaviors that challenge theoretical explanations and predictions, especially for the size and shape dependence of magnetic anisotropy energy (MAE) that is crucial for the stability of magnetism in one-dimensional (1D) systems.

Due to the intrinsic complexity in the treatment of spin-orbit coupling and computational demand, very few first-principles calculations for the determination of MAE in nanowires and nanoclusters have been presented so far. For instance, tight-binding Hubbard model calculations revealed that the MAE of unsupported small Fe clusters is strongly dependent on the bond length and *d*-band filling[6]. Lazarovits *et al.* calculated magnetic properties of small Fe, Co, and Ni clusters on top of Ag(100) with the Korringa-Kohn-Rostoker (KKR) Green's-function method[7] and found that MAE for individual atoms strongly depends on the position. We recently reported the MAE of Co monatomic wires for both free-standing and on top of Cu(001) and Pt(001) substrate materials[8] and explained the MAE from the electronic origin. Here, we report results of magnetic properties of finite Co monatomic chains consist of two to seven atoms. The main purpose is to address three aspects for nanomagnetism: (1) the magnitude of MAE in the reduced size and extreme shape; (2) the applicability of magnetic circular dichroism (MCD) sum rules for ultrasmall systems; the possibility to establish simple correlation between MAE and other accessible properties, such as the anisotropy of orbital magnetic moments. Answers for these questions through model calculations will lay a foundation for further theoretical and experimental work in nanomagnetism.

The thin film version of the full potential linearized augmented plane wave (FLAPW) method[9,10] used here has no shape approximation in the charge, potential, and wave-function expansions. The generalized gradient approximation [(GGA), PBE-96 formalism] (Ref. 11) was adopted to describe the exchange correlation interaction. Spherical harmonics with a maximum angular quantum number of $l_{max}=8$ were used to expand the charge, potential, and wave function in the muffin-tin region. Energy cutoffs of 225 Ry and 16 Ry were used for the plane-wave star function and basis expansions in the interstitial region. The core electrons are treated fully relativistically. The spin-orbit coupling (SOC) for valence states was treated second variationally. The torque approach[12] was adopted to evaluate MAE, which was proven to be highly reliable and efficient for low-dimensional systems.

In the present calculations, monatomic chains are aligned along the *z* axis, and the periodic boundary condition in the *x*-*y* plane (lateral direction) is imposed for computational purposes. A square unit cell with a lattice a constant of 13 a.u. in the lateral plane, as compared through calculations with larger lattice sizes (up to 20 a.u.) and varying *k* points (Γ point only or multiple meshes), is sufficient to minimize the interaction between adjacent chains. In the geometry

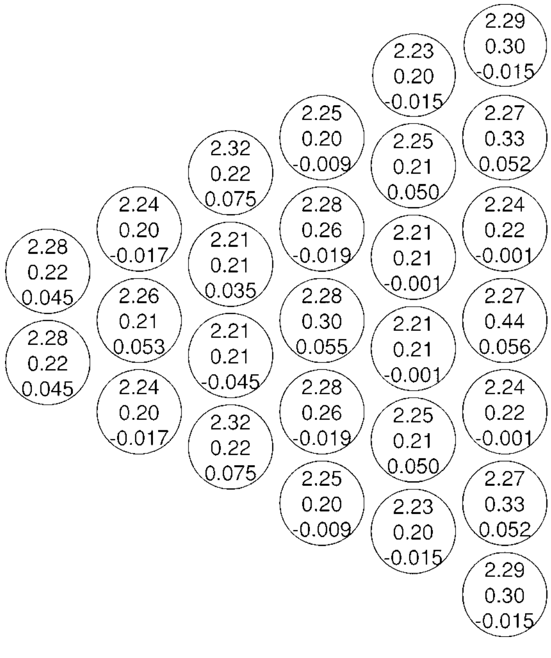

FIG. 1. The calculated $\langle S_z \rangle$, $\langle L_z \rangle$, and $\langle T_z \rangle$ for each atom in Co monatomic chains.

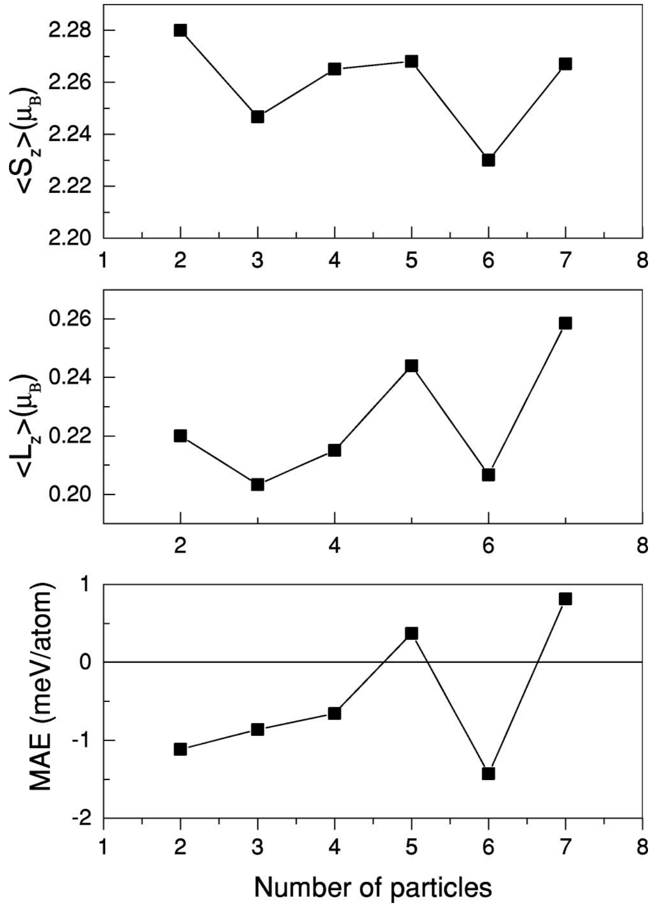

FIG. 2. Size dependence of averaged (a) $\langle S_z \rangle$, (b) $\langle L_z \rangle$, and (c) MAE. The averaged quantities are obtained by simply dividing the total value quantity with the number of particles.

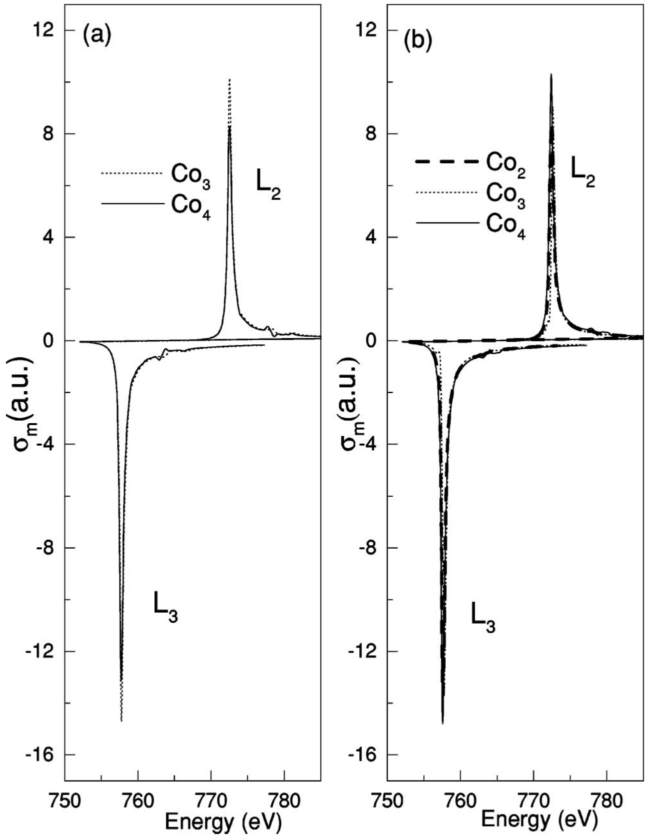

FIG. 3. MCD spectra of (a) the central atoms in Co_3 and Co_4, and (b) the edge atoms in Co_2, Co_3, and Co_4.

studied here, the dependence of energy E on the polar angle θ can be expressed in the two lowest order terms as

$$E = E_0 + E_1 \sin^2\theta + E_2 \sin^4\theta. \qquad (1)$$

With this convention, the MAE defined as MAE equal to $E_x - E_z = E_1 + E_2$ can be obtained as the torque at $\theta = 45°$. Positive (negative) MAE means that the magnetization is along with (perpendicular to) the axis of the monatomic chain (i.e., the z axis here). Although the present calculations were performed for free-standing monatomic chains for a conceptual demonstration, it is necessary to explore the effect of substrate materials in the near future for practical application. In this spirit, the Co interatomic distance in each chain is chosen not through total energy minimization process, but to be fixed at 4.82 a.u., which matches the Cu(001) lattice parameter.[13] We checked the MAE of the Co trimer, varying the interatomic distance between 4.62 and 5.2 a.u., and found no significant change in the MAE. This indicates that the choice in the interatomic distance will not affect discussions elaborated below.

In Fig. 1 the atom-resolved spin and orbital magnetic moments, along with the magnetic dipole moments $\langle T_z \rangle$, are presented. One can see that the magnetic moments are strongly enhanced compared to the corresponding values in the bulk Co and even in a free-standing Co monolayer due to the drastic reduction in the coordinate numbers (to one or two only).[14] Surprisingly, the spin magnetic moments are rather uniformly distributed from the edge to the central Co atoms. The maximum is no longer necessary to occur on the edge sites. By contrast, the orbital magnetic moments show rather strong size and position dependencies. For instance, $\langle L_z \rangle$ at the center in Co_7 is about 40% smaller than that at the second atom from the edge. Figures 2(a) and 2(b) demonstrate the size dependence of the average spin and orbital magnetic moments.[5] Clearly, much longer Co chains are needed to recover the $<L_z>$ of infinite 1D wire[8] ($\langle L_z \rangle = 0.28\ \mu_B$, $\langle S_z \rangle = 2.23\ \mu_B$).

The size dependence of the MAE per atom is plotted in Fig. 2(c) and one can see strong oscillations of MAE. For instance, perpendicular magnetization was found from Co_2 to Co_4, but Co_5 shows parallel magnetization to the chain axis. On the other hand, Co_6 displays strong perpendicular magnetization, whereas Co_7 again manifests parallel magnetization as does Co_5. In our previous calculations and also as was reconfirmed with square unit cells here, the MAE of an infinite 1D Co monatomic wire with the same interatomic distance was found to be -1.15 meV/atom. This again implies that the Co_7 is still too short to imitate an infinite system. Note the calculated results of MAE for neither Co wires nor Co short chains are larger than those for Co thin films.[15] This indicates that one cannot acheive a stable magnetic state in Co nanostructures at the ambient temperature by merely

TABLE I. Sum rule errors R_i in Co_2, Co_3, and Co_4.

System	R_1	R_2
Co_2		0.11
Co_3	0.05	0.06
Co_4	0.04	0.06

TABLE II. Calculated MAE(meV) and $\langle L_z\rangle - \langle L_x\rangle$ in (μ_B).

System	E_{MAE}(meV)	$\langle L_z\rangle - \langle L_x\rangle$	$E_{MAE}(\downarrow\downarrow)$	$E_{MAE}(\downarrow\uparrow)$
Co_2	–2.23	0.05	−0.919	−1.217
Co_3	−2.590	0.06	−1.314	−1.155
Co_4	−2.62	−0.02	0.336	−2.67
Co_5	1.86	−0.18	4.38	−2.09
Co_6	−8.59	0.18	−5.59	−2.47
Co_7	5.70	−0.43	10.18	−3.62

changing its size and shape. Instead, it was found to be possible to obtain large MAE by either placing Co on a Pt surface[3,16] or, furthermore, by mixing with Pt.[17]

It is well known from the second-order perturbation theory that the MAE can be related to the anisotropy of orbital moments, namely, $\langle L_z\rangle - \langle L_x\rangle$, when the spin orbit interaction through the spin flip process is ignored.[18] The importance of this relationship stems from the possibility of measuring MAE through magnetic circular dichroism (MCD) sum rules. To validate this approach, it is important to check (1) the validity of the MCD sum rules[19,20] and (2) the proportionality between MAE and $\langle L_z\rangle - \langle L_x\rangle$ through direct calculations.

MCD has been established as a powerful tool for the determination of $\langle S_z\rangle$ and $\langle L_z\rangle$. The MCD sum rules[21,22] for *d* states, in the combined format, can be expressed as

$$\frac{I_m}{I_s} = \frac{\langle L_z\rangle}{2\langle S_e\rangle}, \quad \langle S_e\rangle = (\langle S_z\rangle + 7\langle T_z\rangle)/3, \tag{2}$$

where

$$I_m = \int_{L_2+L_3} \sigma_m dE, \quad I_s = \int (\sigma_{m,L_3} - 2\sigma_{m,L_2}) dE. \tag{3}$$

Here σ_m is the difference of the absorption cross section between the left and right circularly polarized incident light. The MCD spectra of L_2 and L_3 edges for Co_2, Co_3, and Co_4 are plotted in Fig. 3 with the panel (a) for central atoms in Co_3 and Co_4, while panel (b) is for the edge atoms in Co_2, Co_3, and Co_4. Overall, they show a single peak profile, but some small structures can be found for Co_4 in the region 6–7 eV above the main peaks. Differences in peak intensities and positions are also noticeable. The sum rule error, defined as $R_i = (I_m/I_s)/(\langle L_z\rangle/2\langle S_e\rangle) - 1$, is reasonably small as displayed in Table I for each atom. Here, R_1 denotes the sum rule error of the central atoms in Co_3 and Co_4, while R_2 is for the edge atoms in Co_2, Co_3, and Co_4. Interestingly, it is worthwhile to point out that the magnetic dipole moment $\langle T_z\rangle$ part is vital for the validity of sum rules. For most atoms, the $7\langle T_z\rangle$ term is larger than 10% of $\langle S_z\rangle$. The quantitative determination of $\langle L_z\rangle$ and $\langle S_z\rangle$ thus may rely on an interplay between theory and experiment since $\langle T_z\rangle$ and the number of holes are generally unknown in MCD measurements.

In Table II we present the calculated total anisotropy of orbital moments along with the total MAE, which is split further into contributions from different spin parts. It was found that the majority spin channel ($\uparrow\uparrow$) gives positive contributions in all cases, but with a much smaller magnitude (by a factor of 7–10) compared to MAE ($\downarrow\downarrow$) or MAE ($\downarrow\uparrow$), except for Co_4. As listed in Table II, there is indeed an accordance between MAE ($\downarrow\downarrow$) and $\langle L_z\rangle - \langle L_x\rangle$, although the latter was calculated with all spin contributions. In general, however, the overall results indicate that there is no clear proportionality or even sign correlation between MAE and $\langle L_z\rangle - \langle L_x\rangle$ for these ultrasmall entities. The reason for this failure is clear since MAE ($\downarrow\uparrow$) is comparable to MAE ($\downarrow\downarrow$) but the contributions to $\langle L_z\rangle - \langle L_x\rangle$ through the spin flip channel are two orders of magnitude smaller than those arising from the non-spin-flip interaction.

In summary, FLAPW calculations revealed peculiar size and site dependencies of magnetic properties in ultrasmall Co monatomic chains with two to seven atoms. Despite the drastic size reduction and shape change, no obvious MAE enhancement is found in Co chains from those for Co thin films. It was obtained that the magnetic property of a finite Co monatomic chain consist of seven atoms is still far away from that of an infinite chain. The combined form of MCD sum rules is validated within a 10% deviation. A simple correlation between the MAE and orbital anisotropy $\langle L_z\rangle - \langle L_x\rangle$ cannot, however, be established by the virtue of the fact that the spin orbit coupling via the spin flip process plays a substantial role in the calculations of MAE.

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