

CO Molecules adsorption on Co nanoclusters : A First-principles study

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1. Introduction

Magnetic nanostructures have attracted a great deal of interest because of their potential applications in magnetic sensors and high density magnetic recording media.[1] Nanostructures nowadays have been produced by using co-deposition technique of metallic clusters together with insulating matrix gas molecules. The tunneling magnetoresistance (TMR) of granular films made from Co clusters embedded in molecular matrix CH₄, C₂H₄, and CO₂ increases with increasing interaction between the Co clusters and the matrix.[2] The interaction between the Co clusters and the molecules however is not strong enough for chemical binding. In order to eventually obtain a large TMR in the Co granular systems, CO molecule matrix is introduced. It is well known that CO molecules strongly interact with transition metal (TM) atoms. The Co clusters coated with CO molecules have large TMR of about 50 % at T = 1.7 K.[3] Moreover CO adsorption on Co clusters causes magnetization quenching.[4]

Because the value of TMR depend on the interaction between Co clusters and CO molecules, theoretical study is requested to find stable adsorption geometries. Our purpose is to consider possible structures for CO adsorption on Co clusters and to understand large TMR and the magnetism.

2. Model and computational method

We have used a small Co cluster with icosahedral structure and large Co clusters with fcc polyhedral structure as substrate. The Co nanoclusters have globular fcc structure with the diameter of 5.01, 7.09, 8.68, and 10.02 Å. The Co-Co bond length is 2.506 Å as like as that of the fcc bulk Co. Several adsorbing configurations such as Co atom top, bridge, square facet, and triangle facet on the substrate are considered. The stable adsorption geometries are determined by minimizing the total energies of clusters.

We have performed *ab initio* spin-polarized total energy calculations within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof 1996 for the exchange-correlation energy.[5] We solved the self-consistent Kohn-Sham equations by direct diagonalization of the Hamiltonian in atomic orbitals basis set consisting of finite-range numerical pseudoatomic wave functions. Norm conserving Troullier-Martins pseudopotentials factorized in the Kleinman-Bylander form were used to consider core electrons. The Γ -point is considered for Brillouin zone integrations. The geometry is optimized until the atomic force is less than 0.04 eV/Å using the conjugate gradient method.

3. Results and discussion

We have examined the adsorption of CO on Co₁₃ cluster with fcc polyhedral structure. Figure 1 shows three adsorption types. The CO molecule adsorbs to the carbon atom end on Co substrate. We find that CO molecule is most stably adsorbed on Co square facet as shown in Fig. 2(c). The calculated Co-C bond length of 2.03 Å is consistent with the distance in bulk CoC. The gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) decreases to 0.17 eV from the value of 0.24 eV for pure Co₁₃ cluster. The magnetic moments of surface Co atoms decrease by CO adsorption. We find the Fermi level is shifted down and the charge transfer occurs from Co atom to CO molecule. The spin polarization for Co₁₃/CO adsorbed on Co square facet increases to 71.9 % compared with 65.3 % for pure Co₁₃ cluster. The value of TMR depends on the spin polarization of the tunneling electrons according to Julliere model. The calculated TMR at independent temperature is 34 % by

the definition $P^2 / (1+P^2)$, where P indicates spin polarization. This value is comparable with the corresponding experimental value of 39 %. The calculated binding energy of Co_{13}/CO adsorbed on square facet is larger than that for Co_{13}/CO adsorbed on top and bridge. This result implies that the value of TMR depends on the interaction between Co substrate and CO adsorbate.

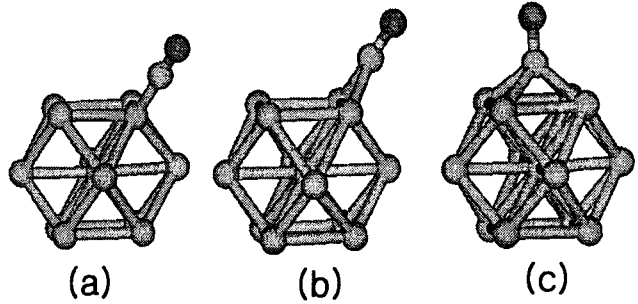


Fig. 1. Co/CO clusters adsorbed on (a) top of Co atom (b) bridge (c) square facet.

The magnetic moments for Co atom and CO molecule in Co_n/CO ($n=13, 19, 43,$ and 55) systems are shown in Table

1. The CO molecules are adsorbed on one plane of Co clusters. The local magnetic moments of Co atoms directly bonded with CO molecules in $\text{Co}_{55}/(\text{CO})_4$ are $1.82 \mu_B$ for onefold, $1.31 \mu_B$ for twofold, $0.54 \mu_B$ for threefold coordination. The magnetic moments of surface Co atoms bonded with CO molecules decrease with increasing coordination number. We find that the magnetic moment for core in Co_n/CO is slightly perturbed according to comparison with values for pure Co_n . The CO molecule has antiferromagnetic coupling with surface Co atoms.

	Co_{13}/CO	$\text{Co}_{19}/(\text{CO})_3$	$\text{Co}_{43}/(\text{CO})_4$	$\text{Co}_{55}/(\text{CO})_4$
μ_c (μ_B/atom)	1.99 [2.01]	1.94 [1.98]	1.72 [1.67]	1.65 [1.67]
μ_s (μ_B/atom)	2.05 (1)	1.97 (1), 1.54 (2)	1.96 (1)	1.82 (1), 1.31 (2), 0.54 (3)
μ_{CO} ($\mu_B/\text{molecule}$)	-0.14	-0.11	-0.38	-0.07

Table 1. Magnetic moments for center (μ_c) and surface (μ_s) Co atoms in Co_n/CO ($n=13, 19, 43,$ and 55). The values in bracket indicate the magnetic moment of center Co atom in pure Co_n . The values in parentheses denote the coordination number between surface Co atom and CO molecules.

In conclusion, we found the influence of CO adsorption causes Fermi level shift and reduction of the magnetic moment for Co cluster surface. The Co clusters coated with CO molecules increase spin polarization due to charge transfers from Co atom to CO molecule and have a large tunnelling magnetoresistance (TMR) comparable with the experimental value.

4. Reference

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