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Pressure-induced ferromagnetic half-metallicity in cobaltocene

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Abstract – The electronic and magnetic properties in organometallic compound cobaltocene under pressure have been investigated by the first-principles calculations based on the van der Waals density functional theory. At ambient pressure, cobaltocene lies in the paramagnetic state, which is consistent with the experimental measurements. With increasing pressure, the paramagnetic phase evolves into the ferromagnetic semiconducting phase. When pressure exceeds 60 GPa, the closing of gap between valent and conducting bands results in the ferromagnetic half-metallicity in cobaltocene. The formation of the metallic state can be understood in terms of the orientation and hybridization of Co d_{xz} , d_{yz} and C p_z orbitals. We also find that the ferromagnetic half-metallicity arises at much lower pressure upon doping rhodocene into cobaltocene. Our results provide a new route to realize the half-metallicity in cobaltocene and similar metallocene compounds.

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Introduction. – Half-metal, which acts as a conductor and an insulator to electrons in two spin channels, has attracted great interest due to its potential application in spintronics. As representatives of half-metallic materials, Heusler alloys [1–5] and manganese perovskites [6–8] have been studied extensively. Recently, the half-metallicity in organic materials has become another hot research topic [9–11]. Metallocene belongs to an important class of organometallic compounds, which consists of two cyclopentadienyl (Cp) anions bound to a metal center with a general formula $(C_5H_5)_2M$ (M denoting the metal center). Based on the density functional theory (DFT), the first-principles calculations predicted that the one-dimensional $(VCp)_\infty$ wire [12] and the multidecker sandwich cluster $V_n(FeCp_2)_{n+1}$ [12,13] are the ferromagnetic (FM) half-metal and semiconductor, respectively. These studies suggest that metallocene containing transition metal and its derivatives can serve as the important structural subunit for FM semiconductor, half-metal and single-molecule magnet.

Pressure is an effective way to tune the physical properties of various kinds of materials. For instance, applying pressure can drive a phase transition from the striped antiferromagnetic (AFM) state to the superconducting phase in iron-based superconductors [14]. It has been found that the superconducting critical temperature is changed by pressure for cuprate and iron-based superconductors [15–18]. Significant effects of pressure were also found out for organic compounds. A pressure-induced FM to AFM transition was observed in the β -phase par-nitrophenyl nitronyl nitroxide [19]. In an organic radical ferromagnet 2,5-difluorophenyl- α -nitronyl nitroxide, pressure was found to induce an increase of the magnetic dimension and FM transition temperature [20]. Recently, experiments showed that pressure causes an intriguing Mott transition in κ -(ET)₄Hg_{2.89}Br₈ with a finite doping level [21]. However, there were very few theoretical or experimental reports on the effect of pressure on the electronic structure and magnetism of metallocene. It is very interesting to know how magnetic couplings and magnetic state change with pressure in metallocene. Moreover, it is not clear what is the doping effect of

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nonmagnetic and magnetic dopants on its electronic and magnetic properties.

In this work, we perform a systematic study on the effect of pressure and doping on the electronic and magnetic properties of cobaltocene. The results presented below show that FM coupling is favorable in the compressed cobaltocene, and the FM half-metallicity can be realized when pressure exceeds a critical value. For the rhodocene doped cases, the FM half-metallicity arises at much lower pressure.

Computational details. – Our calculations were performed by using the plane-wave basis sets and pseudopotential method, and the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) formula [22] and projector augmented-wave (PAW) pseudopotentials [23] were adopted, as implemented in Vienna *ab initio* simulation package (VASP) [24,25]. The plane-wave basis cutoff was set to 342.4 eV, the Gaussian broadening technique was used and a mesh of $4 \times 6 \times 8$ k-points was sampled for the Brillouin zone integration. The convergence thresholds of the total energy, force on each atom are 10^{-5} eV and 0.005 eV/Å, respectively.

As cobaltocene is a typical molecular crystal, van der Waals (vdW) interaction is an important aspect of physics. In our calculations, vdW interaction correction was contained into the total energy which takes the form of $E_{DFT-disp} = E_{KS-DFT} + E_{disp}$. E_{KS-DFT} is the conventional Kohn-Sham DFT energy, and E_{disp} is the vdW correction term which is computed using the DFT-D2 method of Grimme [26] in the VASP code.

Results and analysis. –

Paramagnetic phase at ambient pressure. Cobaltocene is a type of organometallic compound with the formula $(C_5H_5)_2Co$, consisting of two Cp rings bound on two sides of a cobalt atom with the sandwich structure. The electron configuration of the cobalt ion is $3d^7$. The crystal lattice of cobaltocene is monoclinic with $P2_1/a$, and each unit cell contains two molecules which are vertical to each other in an *ab*-plane. The crystal geometry is shown in fig. 1(a).

Magnetic susceptibility measurements [27] and molecular calculations [28] showed that each cobalt ion has a magnetic moment close to $1 \mu_B$, but cobaltocene lies in the paramagnetic ground state. One reasonable explanation is that the Co magnetic moments are shielded by Cp rings from their neighbors, leading to a vanishingly small magnetic interaction among cobaltocene molecules. Since it is difficult to simulate the paramagnetic state in the DFT calculation, here, we use an indirect method to illustrate the ground state of cobaltocene. Fixed at the experimental lattice parameters, the spin polarization calculations are performed for three magnetic orderings including FM, intralayer AFM and interlayer AFM, which are shown in figs. 1(b)–(d). The calculated results show that the energy of the FM state is 0.3 meV and 0.08 meV lower than

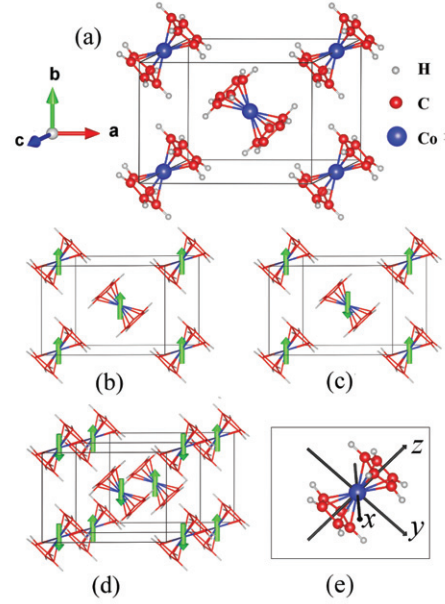


Fig. 1: (Color online) (a) Cobaltocene crystal structure in a monoclinic unit cell composed of two cobaltocene molecules; (b),(c),(d) show the schematic diagram of the FM, intralayer-AFM and interlayer-AFM orders. The up and down directions of green arrows represent the up spins and down spins of Co atoms. The $1 \times 1 \times 2$ supercell shown in (d) is the magnetic cell for the interlayer-AFM order. (e) *xyz* coordinate system used in the description of five 3d orbitals and three 2p orbitals.

those of the interlayer- and intralayer-AFM states, which suggests that at finite temperatures, the moment directions can vary randomly from molecule to molecule due to negligible magnetic coupling, resulting in the paramagnetic phase. In addition, the dispersion energy, which can be read out from the VASP output file, was found to be close to a constant (18.88528 eV) for the three magnetic orderings.

The intralayer-AFM ordering is a checkerboard-like AFM ordering, close to paramagnetism due to the net zero moment and high magnetic symmetry [29]. We perform a full structure optimization of cobaltocene in the intralayer-AFM ordered phase, and the obtained lattice parameters are $a = 10.321$ Å, $b = 7.924$ Å, $c = 5.703$ Å, and $\beta = 122.728^\circ$, in perfect agreement with the experimental parameters [30] $a = 10.376$ Å, $b = 7.754$ Å, $c = 5.779$ Å, and $\beta = 122.057^\circ$. The agreement demonstrates the applicability of C, H and Co pseudopotentials and reasonability of computational details in our calculation, providing a basis of reliability for exploring the structure of cobaltocene under pressure.

Pressure-induced FM semiconducting and half-metallic phases. To simulate the cases under pressure, the volume of the cobaltocene cell is decreased gradually from the experimental value to 85.7%, 72.9%, 61.4%, and 51.2% through scaling the lattice constants by the ratios 0.95, 0.9, 0.85, and 0.80. The corresponding pressure increases

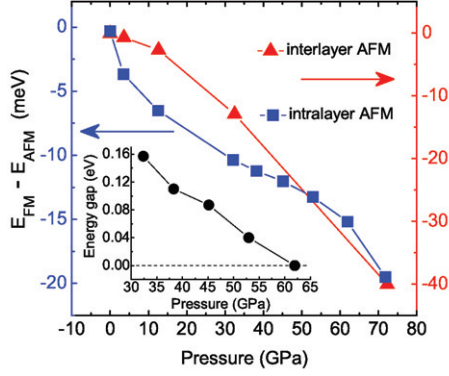


Fig. 2: (Color online) Energy difference $E_{FM} - E_{AFM}$ as a function of pressure. The blue squares and red triangles correspond to the intralayer-AFM and interlayer-AFM phases, respectively. The inset figure shows the pressure dependence of the energy gap between valent and conducting bands.

from 3.6 GPa to 12.6 GPa, 32.5 GPa, and 72.1 GPa (the deviation of pressure is less than 0.1 GPa within the above three magnetic orders). The energies in the FM and AFM (either intralayer-AFM or interlayer-AFM) states are denoted as E_{FM} and E_{AFM} , respectively. In fig. 2, we show the pressure dependence of the energy difference $E_{FM} - E_{AFM}$. The negative value of the energy difference indicates that the FM state is more stable than the two AFM states. Thus, we can conclude that the FM state is the ground state of cobaltocene under pressure. With increasing pressure, the absolute value of the energy difference becomes larger, suggesting that FM magnetic exchange interactions are enhanced by pressure.

To quantify the magnetic interactions in cobaltocene under pressure, we assume that the energy differences between FM and AFM states are produced mainly by the interactions between Co spins and express the total energy in the Heisenberg model,

$$H = J_1 \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{\ll ij \gg} \vec{S}_i \cdot \vec{S}_j, \quad (1)$$

where J_1 and J_2 denote the magnetic couplings between nearest-neighbor (NN) Co atoms along the c -axis and next-nearest-neighbor (NNN) Co atoms on the ab -plane. $\langle ij \rangle$ and $\ll ij \gg$ stand for the summations over NN and NNN Co sites. J_1 and J_2 , extracted from the total energies in the FM and AFM states, are listed in table 1. As can be seen, the magnetic couplings J_1 and J_2 take negative values and become more negative with increasing pressure, which explicitly indicates that the FM couplings between NN and NNN Co atoms are favorable in cobaltocene under pressure. In table 1, we also present J_1 and J_2 obtained from the calculations without vdW correction. Notice that although the magnetic couplings are changed when the vdW correction is not taken into account, they show the similar trend of enhancement of

Table 1: The magnetic couplings J_1 and J_2 at different unit cell volumes with and without vdW correction. The units of volume, pressure (P) and magnetic coupling are $\text{\AA}^3$, GPa and meV/S^2 , respectively. Here, S is the total spin of the Co atom.

Volume	With vdW			Without vdW		
	P	J_1	J_2	P	J_1	J_2
392	0.4	-0.08	-0.01	-0.7	0.61	0.05
336	3.6	-0.24	-0.38	2.4	0.66	-0.07
286	12.6	-0.76	-0.77	10.4	-0.50	-0.80
241	32.5	-3.26	-1.31	28.5	-3.91	-1.51
201	72.1	-10.04	-2.29	65.6	-11.60	-2.84

FM coupling as pressure is increased. At the experimental volume ($392 \text{\AA}^3$), the small magnetic couplings from the calculations with vdW correction, which provides a natural explanation of the experimentally observed paramagnetic behavior, demonstrate that the vdW interaction plays an important role in cobaltocene.

At ambient pressure, cobaltocene in the FM state is a semiconductor with an energy gap of 0.18 eV. With increasing pressure, the energy gap is monotonically reduced, as shown in the inset of fig. 2. When pressure exceeds 60 GPa, the energy gap is gradually closed, resulting in the FM half-metallic state. Figure 3(a) shows the calculated total density of states (DOS) at the pressure of 72.1 GPa. Clearly, the spin-up channel is metallic with the DOS value of 3.05 states/eV per cell, while the spin-down channel is semiconducting with a gap of 2.6 eV. There are two Co atoms in a unit cell, one at center and the other at the edge, as shown in fig. 1(a). The projected DOS of five $3d$ orbitals for the Co at the edge are presented in fig. 3(b) in terms of the rectangular coordinates system, in which the yz -plane is parallel to the ab crystal plane and the z -axis deviates from the a -axis by 45° . The relative position of cobaltocene molecule in the coordination system is shown in fig. 1(e).

The electron configuration of the Co atom in the cobaltocene molecule is $d^7 (e_{2g}^4 a_{1g}^2 e_{1g}^1)$ confirmed by the experimental study in ref. [27]. The five $3d$ orbitals are divided into three components in a ligand field splitting imposed by two Cp rings. Two degenerate e_{2g} levels and one a_{1g} level are occupied, and one single unpaired electron resides in the e_{1g}^* level to form $1 \mu_B$ magnetic moment around the Co atom. In our calculations based on the cobaltocene crystal, the above features are fully reflected by the projected DOS in fig. 3(b). The $d_{x^2-y^2}$ and d_{z^2} states are almost degenerate and have the lowest energy centered at -3.0 eV below the Fermi level; the d_{xy} states come second with a little higher energy; the orbitals d_{xz} and d_{yz} locate around the Fermi level.

In the xyz coordinate system, the orbitals d_{xz} and d_{yz} point to carbon atom in Cp rings, and have a strong hybridization with the p_z orbital of the C atom. By comparing fig. 3(c) with fig. 3(b), we can find that the

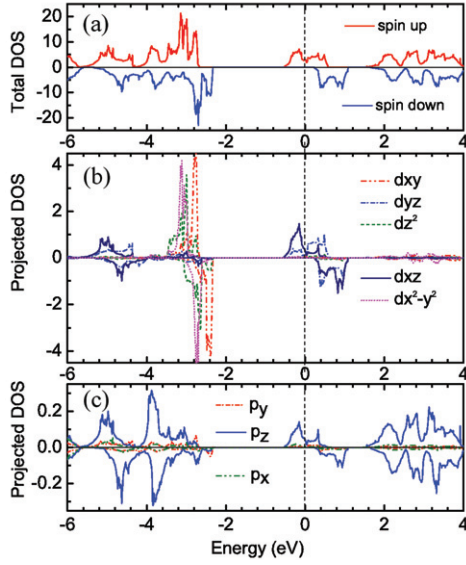


Fig. 3: (Color online) Cobaltocene in the FM ground state under the pressure of 72.1 GPa: (a) total density of states for spin-up and spin-down channels; (b) projected density of states onto the five Co 3d orbitals of one Co atom; (c) projected density of states onto the three C 2p orbitals of one C atom. The xyz coordination system is shown fig. 1(e). Positive and negative values of DOS correspond to spin-up and spin-down channels, respectively. The Fermi level is set to be zero.

distribution of C p_z states is consistent with Co d_{xz} and d_{yz} states around -5.0 eV and the Fermi level. With increasing pressure, the distance between the Co and Cp ring is shortened and the hybridization of C p_z and Co d_{xz} , d_{yz} states gets stronger, which leads to more delocalized Co d_{xz} , d_{yz} states and results in the transition from semiconductor to metal. The moment around the Co atom remains close to $1.0 \mu_B$ with pressure reaching to 100 GPa, indicating that half-metallicity in cobaltocene is robust under high pressure. This unique feature is very different from the magnetism in covalent compounds such as iron arsenide compounds [31,32] in which the moment is quenched under less than 10 GPa.

We have also performed the GGA+ U calculations to explore the effect of electron correlation on the magnetic couplings and electronic structure. At the experimental volume ($392 \text{ \AA}^3$) and $U = 4 \text{ eV}$, J_1 and J_2 are -0.425 meV/S^2 and -0.0875 meV/S^2 , respectively, suggesting an enhancement of FM couplings by the Hubbard U . However, the electronic structure at $U = 4 \text{ eV}$ shows that almost degenerate $d_{x^2-y^2}$ and d_{z^2} orbitals are split and the DOS of d_{xy} and $d_{x^2-y^2}$ orbitals have a substantial overlap. This situation is not in agreement with the experimental observation [27]. In a recent study [13], the DFT calculations without U correction were shown to reproduce well the experimental values of C-C and C-H bond lengths, metal-ligand distances, binding energy and ionization energy of scandocene, titanocene, vanadocene, and manganocene. These facts suggest that the DFT

without U correction is applicable for the transition metal metallocene.

Rhodocene-doping-induced FM half-metallicity under lower pressure. In order to realize the FM half-metallicity in cobaltocene, we also study the influence of doping on the electronic structure. Considering that iron, nickel and rhodium are the nearest-neighbor elements for cobalt in the periodic table of elements, ferrocene, nickelocene and rhodocene are chosen as dopants to replace some amount of cobaltocene. In the following calculations, the cell volume is fixed at 61.4% of the experimental value, and the corresponding pressure is about 32.5 GPa.

The unit cells in figs. 1(a) and (d) are used in the calculations for the 50% and 25% doped systems, where one cobaltocene molecule is substituted by the dopant. Our calculations show that the ferrocene-doped cobaltocene with 25% or 50% dopant concentration is still semiconducting with a 0.18 eV gap. For nickelocene-doped cobaltocene with 50% concentration, we calculate the total energies in the cases that the moments of Ni and Co atoms are parallel and anti-parallel. In the anti-parallel case, namely the AFM state, the energy is 6 meV per Ni atom lower than the parallel case. Hence, nickelocene doping is not favorable for the formation of FM half-metallicity in cobaltocene.

Rhodium sits below cobalt in the element table, so we can expect that rhodocene and cobaltocene have similar magnetic properties. In the 50% rhodocene-doped system, the energy of the FM state is 12.8 meV per Rh atom lower than the one of the AFM state. In the 25% doped case, although the Rh moment is set to be anti-parallel to three Co moments at the beginning of the calculation, the relaxed direction of the Rh moment becomes parallel to the Co moments. These results demonstrate that the FM phase is the ground state of rhodocene-doped cobaltocene. In addition, we notice that the Rh moment is $0.48 \mu_B$ and $0.27 \mu_B$ in the 50% and 25% doped systems, much less than $0.85 \mu_B$ of the Co atom in the two cases. The Bader charge analysis indicates that the charge deviations of rhodocene and cobaltocene to 59 electrons in the neutral case are 0.11 and 0.15 in the 50% and 25% doped systems, respectively. This demonstrates that there is no obvious charge transfer between rhodocene and cobaltocene molecules.

Figure 4 shows the projected DOS of Co 3d and Rh 4d orbitals for one Co and one Rh atom in the 25% doped system. Rh 4d states are mainly located in the range from -4.5 to -3.5 eV and Co 3d states are centered at -2.5 eV. Compared to the Co 3d states, the Rh 4d states have a wider energy spread and less spin polarization, which is associated to the more delocalized charge distribution and smaller magnetic moment around Rh atom. As a result of Rh-induced stronger hybridization with C atom, rhodocene-doped cobaltocene is a FM half-metal at about 32.5 GPa, much lower than ~ 60 GPa in the single scheme of applying pressure in the above section.

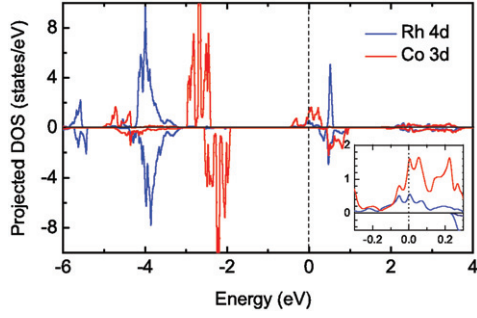


Fig. 4: (Color online) Projected DOS onto the Co 3d orbitals and Rh 4d orbitals for one atom. Positive and negative values of DOS correspond to spin-up and spin-down channels, respectively. The inset figure displays the enlarged view around the Fermi level.

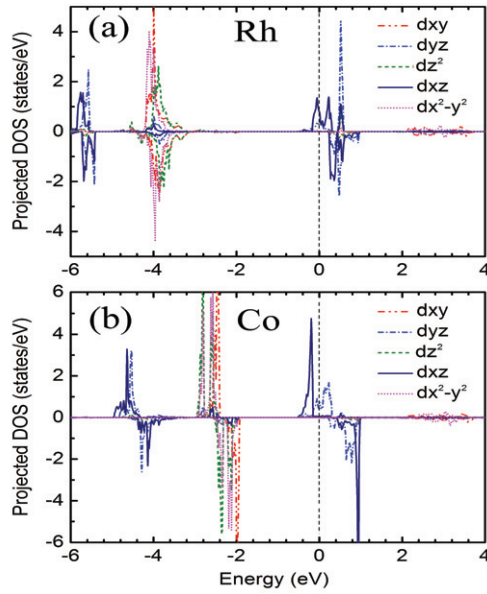


Fig. 5: (Color online) Projected DOS onto the five Co 3d orbitals and five Rh 4d orbitals in the 50% rhodocene-doped system. Positive and negative values of DOS correspond to spin-up and spin-down channels, respectively. The Fermi energy is set to be zero.

The projected DOS for the five partial Co 3d and Rh 4d orbitals are shown in fig. 5. Similar to the Co atom, the Rh 4d orbitals are split into e_{2g} ($d_{x^2-y^2}$ and d_{z^2}), a_{1g} (d_{xy}), and e_{1g}^* (d_{xz} and d_{yz}) levels, which can be attributed to the similar crystal field of Co and Rh atoms. One can notice that the projected DOS of the Rh atom around the Fermi level are much lower the ones of the Co atom, indicating that the Rh 4d orbitals deviate the d^7 ($e_{2g}^4 a_{1g}^2 e_{1g}^{*1}$) electron configuration. A comparison of the projected DOS in fig. 5(b) and fig. 3(b) shows that the doping of rhodocene into cobaltocene results in a pronounced redistribution of electronic states of the Co atom around the Fermi level, which is produced by the deformation of the cobaltocene molecule in the doped system due to the size difference of the two kinds of molecules.

Conclusions. — In summary, we have investigated systematically the pressure effect on the electronic and magnetic properties of pure cobaltocene and rhodocene-doped cobaltocene by the first-principle calculations. Our results indicate that the FM ordering is favored in the compressed system, and FM exchange interactions are enhanced with increasing pressure. When pressure exceeds 60 GPa, cobaltocene undergoes a phase transition from FM semiconductor to half-metal. When rhodocene is doped into cobaltocene, the half-metallicity can be realized at much lower pressure. Another unique feature of cobaltocene is that the moment of $1.0 \mu_B$ is kept under high pressure up to 100 GPa. The special electronic and magnetic properties of cobaltocene and similar organometallic compounds under pressure provide valuable information for designing organic spintronic materials.

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