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Spin polarization in diamagnetic tris(8-hydroxyquinoline) cobalt induced by nonmagnetic metal Al

Huimin Yuan [a,b], Feng Jiang [a], Wanfeng Xie [a], Xijian Zhang [a], Zhiyong Pang [a,*], Shenghao Han [a,c,*]

[a] School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China
[b] College of Physics and Electronic Engineering, Qilu Normal University, Jinan 250013, PR China
[c] School of Space Science and Physics, Shandong University, Weihai 264209, PR China

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ABSTRACT

First-principles calculations based on spin density-functional theory (DFT) have been performed to study the magnetic properties of Al-doped tris(8-hydroxyquinoline) cobalt (CoQ_3). The results show that pure CoQ_3 molecule is nonmagnetic and the Co atom carries no magnetic moment. The Al dopants give birth to spontaneous spin polarization in CoQ_3 molecules, which localized mainly on the 3*d* orbitals of Co atom. The origin of magnetic moments is due to the charge transfers from Al atom to CoQ_3 molecule.

1. Introduction

Tris(8-hydroxyquinoline) aluminum (AlQ_3) has been widely employed as an active material in OLEDs given its high thermal stability, excellent electron-transporting ability, and high luminescence efficiency [1–3]. In view of its weak spin–orbit coupling and hyperfine interaction, extremely long spin lifetime and excellent electron-transporting ability [4,5], AlQ_3 has also attracted significant attention in the new emerged research field of organic spintronics which exploit the spin-polarized electron currents in organic semiconductors for the fabrication of new device structures that can serve as sensors, memory or logic elements [6,7]. In 2004, Xiong et al. observed a large magnetoresistance of 40% in an AlQ_3-based organic spin-valve [8]. Since then, great progresses have been made in the research on the spin injection, transport, and detection of AlQ_3-based devices [9–11].

For the organic spintronic devices, the properties of metal/organic interfaces are vitally important for spin injection and detection. Considerable efforts have been made to investigate the structures, chemical reactions, morphologies, adsorptions, energy level alignments, interface states, processes of spin injections, spin propagations, electronic and magnetic properties of metal/organic interfaces in organic spintronic devices. Because the metal/organic interface is an extremely thin two-dimensional (2D) system, it is challenging experimentally to achieve the accurate bonding information between the metal atoms and the molecules as well as their spintronic properties which are cruelly important for the understanding of the spin injection process in organic spintronic devices. This problem can be partially solved by using metal-doped organic films, which expand the metal/organic interfaces along the normal directions. Baik et al. reported room temperature ferromagnetism in Co-doped AlQ_3 thin films [11,12]. Obviously, the ferromagnetism in Co-doped AlQ_3, if be affirmed, has great significance for the efficient spin injection from Co into AlQ_3. Moreover, it also provides a new type of organic magnet which combines magnetic ordering with semiconducting functionality and optoelectronic properties. However, because Co metal has been used as a source material in the experiments, it is challenging to distinguish the ferromagnetism of Co–AlQ_3 complex from that of metal aggregates experimentally. This makes the magnetism in the Co/AlQ_3 system confused and hinders the development of AlQ_3-based magnetic materials and spintronic devices which contain Co/AlQ_3 interface. From this point of view, it is of great significance to design a system which contains Co, Al, 8-hydroxyquinoline and, above all, no magnetic metal aggregates to achieve a better understanding of the magnetism in the Co–AlQ_3 system.

* Corresponding authors at: School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China (S. Han).
E-mail addresses: pang@sdu.edu.cn (Z. Pang), hansh@sdu.edu.cn (S. Han).

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In this paper, a (Co, Al, 8-hydroxyquinoline) system by doping nonmagnetic metal Al into a diamagnetic small molecule tris(8-hydroxyquinoline) cobalt (CoQ_3) is studied using first principles. Spontaneous spin polarization arose in diamagnetic CoQ_3 after Al doping.

2. Theoretical methods

The density functional theory (DFT) calculations were carried out using the projector augmented wave method in the Vienna *ab initio* simulation package (VASP) [13,14]. The generalized gradient approximation (GGA) implemented in Perdew–Wang 91 (PW91) scheme [15,16] was adopted for the exchange–correlation potential. The cut-off energy was 400 eV and the valence configuration of Co element was set as $3d^8 4s^1$. For the Brillouin zone sampling, $1 \times 1 \times 1$ Monkhorst-Pack k mesh was used for the isolated molecular CoQ_3 and doped CoQ_3. The structure relaxations were carried out until all the atomic forces on each ion were less than 0.02 eV/Å.

3. Results and discussion

First, the electronic structure and the magnetic property of pure CoQ_3 isolated molecule were investigated. Similar to AlQ_3, FeQ_3 and GaQ_3 [17–20], CoQ_3 molecule is composed of a metal atom in the center and three 8-hydroxyquinoline ligands (Fig. 1(a)). A CoQ_3 molecule was put in a large enough cubic cell, the vacuum layer of 20 Å was used to avoid interactions with the images reproduced by periodic boundary conditions. Fig. 1(b) and (c) shows the total density of states (DOS) and the C, N, and Co atoms projected DOSs of the isolated CoQ_3 molecule. The total DOS of isolate CoQ_3 molecule shows (Fig. 1(b)) no spin polarization emerges around the Fermi energy level. In CoQ_3 molecule, the Co atom donates three electrons to the N and O atoms, the Co^{3+} ion has a $3d^6$ configuration. Under the influence of the N and O atoms, the *d* orbital of Co ion splits into a triply degenerate t_{2g} level and a doubly degenerate e_g level. For octahedral field, the t_{2g} levels are expected to be lower than the e_g levels [21]. Depending on the relative values of the crystal-field splitting energy and the mean spin-pairing energy, there are two possible arrangements as shown in Fig. 2: (1) all the six electrons occupy the low t_{2g} energy orbital, leading to a low-spin state (LS), $t_{2g}^6 e_g^0$, and a moment of 0 μ_B/Co; (2) four of the electrons occupy the t_{2g} orbital, and two in the high e_g orbital, leading to a high-spin state (HS), $t_{2g}{}^4 e_g{}^2$, and a moment of 4.0 μ_B/Co [22,23]. We can draw the conclusion that the Co^{3+} ion adopts the $t_{2g}^6 e_g^0$ low-spin configuration, which is in agreement with the non-magnetic property of CoQ_3. From atom projected DOS is shown in Fig. 1(c), we can see that the projected DOSs have no exchange splitting between the majority and the minority spin channels and the DOS is identical for both projections of spin for the C, N and Co atoms. Thus, the isolated CoQ_3 molecule is non-magnetic. The highest occupied molecular orbital (HOMO) level consists of mainly Co, C and O states, the lowest unoccupied molecular orbital (LUMO) consists of mainly Co *d* orbital with an admixture of C, N and O states. This is different from atom-projected density of states of AlQ_3 and GaQ_3 molecule [24,25], in which the LUMO sets reside mainly on N *p* states, the spin polarization arises from the nitrogen *p* orbitals. This means if the pure CoQ_3 molecule is charged, the add electron charge prefer injecting to the Co *d* orbital rather than distribute in the N atom.

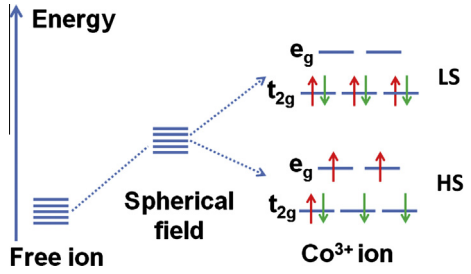

Fig. 2. Schematic description of the low- and high-spin states for Co^{3+} ion in octahedral field.

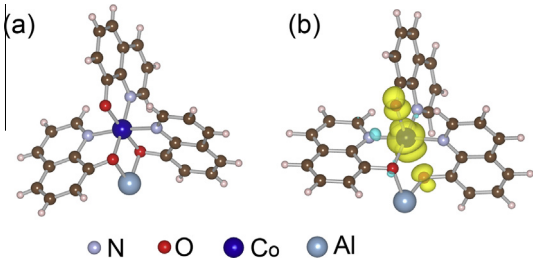

Fig. 3. (a) The configuration of Al-doped CoQ_3 molecule with Al atom at the center of two O atoms. (b) The spin density plot of Al-doped CoQ_3 molecule.

For the Al-doped CoQ_3, we added an Al atom on the CoQ_3 molecule. The doped Al atom was initially placed at different positions: (1) the hollow site at the center of the phenoxide ring; (2) at the center of the pyridyl ring; (3) near N and O; (4) near N and N; (5) near O and O. All the structures were full relaxed. Our structure stability analysis suggests that structure 5 is the most stable one, the structures 3 and 4 are less stable, the structures 1 and 2 give highest total energy. This is consistent with that of AlQ_3, in which the oxygens constitute the attraction center for the metal atom [26]. For all structures, the total magnetic moments are about 1 μ_B. We take the structure 5 (as shown in Fig. 3(a)) as a typical structure for a detailed discussion.

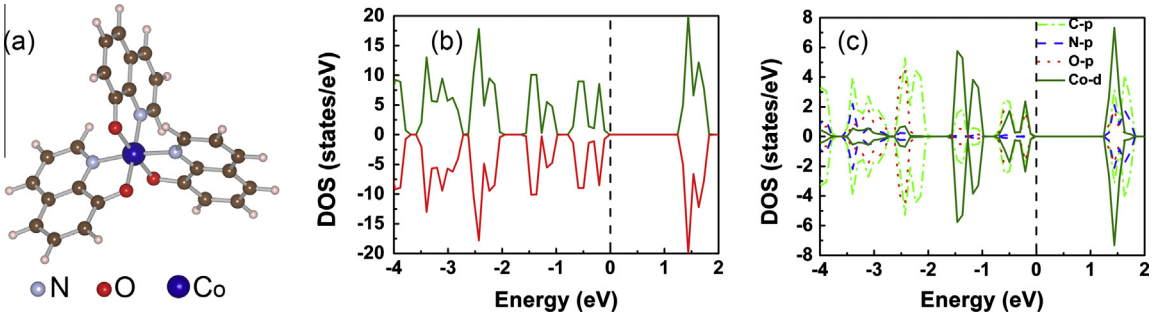

Fig. 1. (a) The configuration of CoQ_3 molecule; (b) the total DOS of pure CoQ_3 molecule; (c) the partial DOS of pure CoQ_3 molecule. The vertical dotted line represents the Fermi energy which is set to zero.