Stair Magnetism: Distinct Magnetic States of Co$_5$C$_5$ Carbide Isomers

Andrew Kuznetsov
ATG:biosynthetics, Merzhausen, Germany
Email: kuznet61@gmail.com

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ABSTRACT

Ruffle magnetic landscape of transition metals (TM) is a trouble of material science that makes it hard to predict properties of nanomagnets [1,2]. It is not quite clear, whether jumps in magnetic activity is the intrinsic property of TM complexes or a controversy of computational experiments. To solve this problem, isomers of Co$_5$C$_5$ carbide with various positions of carbon atoms on the vertices of Co$_5$ cluster were investigated in DFT (Density Functional Theory) computer simulations. It was found that magnetic moments of the carbide isomers increased with the decreasing number of Co–C bonds. However, C-2 isomers have three Co–C bonds demonstrated distinctive magnetic states. The Co$_5$C$_5$ carbide system showed a discrete magnetism. It was supposed that similar magnetic arrangements take place in endohedral metallofullerenes and filled nanotubes.

Keywords: The Metal Cluster; Carbon Shell; Magnetization; Emergence of Atypical Properties

1. Introduction

Interaction of transition metals (TM) with carbon atoms [3,4] is a significant interest for material science because the contact between Me- and C-atoms can affect electronic properties of metals, in particular their magnetic characteristics [5]. Even this kind of interaction could lead to a new property of a whole metal-carbon complex [6].

Several papers were recently published on the putative endohedral metallofullerenes Me$_n$@C$_m$ obtained by an encapsulation of transition-metal clusters (Fe, Co, Ni, Tc, $n = 2 - 7$) into carbon fullerenes ($m = 60, 70, 80, 82, 90$) in the frame of quantum mechanical simulations employing Density Functional Theory (DFT) [2,7-9]. The “encapsulation” means the merging of available or previously calculated atomic coordinates for the TM cluster and the fullerene with the following structural optimization and prediction of physical characteristics. Those reports presented rough magnetic plots for fullerenes with introduced metal clusters of increasing size. I called this phenomenon “Dragon’s Teeth (DT) problem”. This effect is not restricted only by metallofullerenes. For example, the DFT study on binding of Co clusters ($n = 2 - 19$) with chitosan molecules demonstrated an even more ruffle magnetic landscape [10], which caused me to think about the DT-problem.

Following those experiments, I investigated carbides in addition to metallofullerenes [11,12] to distinguish the effects of exchange-correlation functionals in DFT, as well as the efficiency of structural relaxation to ground state, and the role of carbon atoms covering a magnetic cluster. To be mentioned, it was demonstrated before that there is no difference in usage between Perdew and Wang (PW91) as well as Perdew, Burke, and Ernzerhof (PBE) functionals in case Tc$_n$@C$_{60}$ ($n = 2 - 7$) complexes [7]. In my own experiments, the local density (LDA) and generalized gradient (GGA) approximations yield similar results for carbides and endohedral metallofullerenes on the basis of Co$_5$ and Co$_{13}$ clusters. The gradient and subspace optimization methods did not always allow reaching a ground state, rather than that they finished sometimes at local minima in case of large Co$_{13}$ systems [11]. The data obtained from Co$_5$ systems allowed me to report on the reduction of magnetism for cobalt clusters encapsulated in fullerenes [12]. As was shown, the magnetic moment of a metallofullerene depended on the orientation of metal cluster in fullerene, particularly on the distances between C- and Me-atoms. That gave me a possibility to speculate upon the role of Me-C binding in the spin-orbit coupling between electrons, leading to a silencing of the total spin magnetic moment for the Me-C complex. Nevertheless, the “ruffle” magnetism of metallofullerenes as a result of possible emergent effect is still a puzzle.

To decompose the problem, I supposed that a small TM cluster covered by few C-atoms could mimic a behavior of the same cluster inserted in a fullerene. A simple model of the Co$_5$ metallic cluster covered by five carbon atoms in various positions was used to demon-
strate discrete magnetic properties of Co₅C₅ carbide isomers that may clear up the DT-problem.

2. Experimental Procedure

The Co₅ cluster was enclosed by carbons using Avogadro v.1.0 software [13]. Density Functional Theory [14] was implemented within the OpenMX v.3.5 code [15-18]. The calculation was made using the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [19] with parameters fitted to d-orbitals of Co-atoms. Structural relaxation was performed by direct inversion iterative sub-space optimization (DIIS) [20]. The atomic species were defined as C₄.₀-s₁p₁ and Co₅.₅-s₂p₂d₂f₁ [21] with energy cutoff 200.0 Ryd. The energy convergence criterion (SCF) was set to 1.₀e⁻⁶ Hartree, electronic temperature was 300.₀ K.

3. Results and Discussion

Table 1 shows twelve isomers of Co₅C₅ carbide divided into two groups depending on the arrangements of carbon atoms at the apexes (a) or at the equator (b) of the trigonal bipyramid Co₅ cluster.

From Figure 1, one finds a trend of the increasing magnetic moment with the reducing number of Co–C bonds in the investigated compounds. The fully carbon covered C-0 compound demonstrated 23.₀₈% of the magnetic activity of a reference, i.e. the pure Co₅ cluster. Reducing the number of the Co–C bonds led to 38.₄₈% for C-1 compounds on the one hand and in general to 8₄.₆₂% for C-₃ and C-₄ compounds on the other side of the progression.

That is interesting, the magnetism changed not monotonically nor smoothly, but particularly stepwise like a stair with about 1₅.₄% discrepancy between each of six separate magnetic states. I found that isomers of C-2 compound with two reduced Co–C bonds can occupy the three different magnetic levels, such as about 5₃.₇₉%, 6₉.₂₅% and 8₄.₆₂% of initial activity of the pure cobalt cluster.

The most interesting isomer b-C-2″, with two reduced apical Co–C bonds and carbon atoms disposed near the

Table 1. Examples of Co₅C₅ carbide isomers with magnetism related to pure Co₅ cluster (%).

|     | C-0 | C-1 | C-2 | C-2' | C-2″ | C-3 | C-4 |
|-----|-----|-----|-----|------|------|-----|-----|
| a   |     |     |     |      |      |     |     |
|     |     |     |     |      |      |     |     |
|     |     |     |     |      |      |     |     |
| b   |     |     |     |      |      |     |     |
|     |     |     |     |      |      |     |     |
|     |     |     |     |      |      |     |     |
| 23.08 | 38.48 | 53.74 | 84.62 | 84.62 | 84.62 | 84.62 | 84.62 |

Figure 1. Total spin magnetic moments of Co₅C₅ carbide isomers (µB).
equator, demonstrated “atypical” high magnetic activity similar to C-3 and C-4 compounds with reduced three and four Co–C bonds, respectively.

It should be pointed out that the rough “Dragon’s Teeth” appeared in calculations of spin magnetic moments of covered metal clusters via both VASP [2,7] and OpenMX [8,9] software, as well as LDA + U [10], GGA-PW91 [7], or GGA-PBE [2,7-9] functionals. Vienna ab initio Simulation Package (VASP) using the projector augmented wave (PAW) method is one of the most accurate packages, which is also considered as a state of the art in DFT codes [22-25]. OpenMX’s basis set is mainly designed to simulate large systems [15-17], but its basis set is less accurate than the plane-wave basis set in PAW method, which is implemented in VASP. A priori, VASP code would be more correct than OpenMX code for small systems like small magnetic clusters. However, this difference was not apparent in computational experiments on metallofullerenes. Both kind of code generated similar “Dragon’s Teeth” within various approximations.

To avoid the DT-problem in earlier experiments [11, 12], I carefully planned the experimental set of metal clusters and carbon fullerenes. Unambiguous results were obtained on alternative orientations of the same cluster in the same fullerene cage [12]. Functional dependence of magnetism on average Me–C distances and number of Me–C bonds was found [11]. I also observed “smooth” suppression of magnetism for carbides with an increasing number of covering C-atoms. Nevertheless, as we can see now, I lost evidences about quantum magnetism. It should be mentioned that Ni-atom clusters \( (n = 2 - 6) \) demonstrated the similar stair magnetic trend in a gas phase and in fullerene cages \( (m = 60, 70, 80, 90) \), however, authors did not emphasize this interesting fact [2].

4. Conclusion
The set of Co\(_{5}@C_{n}\) carbide isomers allowed me to shed light on the “Dragon’s Teeth” problem. From the experiment presented here it follows that the C-2 isomers with the same number of Co–C bonds showed distinctive magnetic moments depending on the arrangements between cobalt and carbon atoms. This control setup demonstrated the quantum feature of magnetism at atomic level and the absence of injective relations between isomer conformations and magnetic states. Thus, I suspect even more sophisticated behavior in magnetisation of complex systems like fullerenes and nanotubes by doping magnetic clusters. It will be interesting to see if the same features are found in real nanomagnets.

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