

Magnetic structure of cobalt clusters

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Abstract

The magnetic moments of free standing Co_N clusters ($4 \leq N \leq 55$) were calculated through a self-consistent spd-tight-binding method. The lowest energy geometrical structures of these clusters were obtained by exhaustive global searches on a many-body Gupta potential energy surface using an evolutive algorithm. The relevant structures mainly follow an icosahedral growth pattern with some fcc-type structures at some particular sizes. The calculated magnetic moments demonstrate a decreasing behavior with cluster size with small superimposed oscillations. The calculations are in good agreement with the available experimental data. Our results are briefly discussed and compared with other published theoretical results.

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1. Introduction

One of the main goals of materials science is the development of self-assembled transition metals (TM) nano-systems due to its potential application in the electronics and magnetic recording industries [1]. Supported, embedded, and free standing magnetic clusters are of crucial interest in this context [2]. Furthermore, these systems are relevant for understanding the magnetic properties in low-dimensional devices [3]. The study of free ferromagnetic clusters in molecular beams [4–7] has permitted the delineation of the electronic properties of these systems from the atom to the bulk and has even revealed new specific size dependent cluster properties [8]. Billas et al. [4] have measured the magnetic moments ($\bar{\mu}_N$) for Fe, Co, and Ni clusters as a function of the cluster size. For these three elements a global decrease of $\bar{\mu}_N$ with cluster size is found with superimposed weak oscillations whose extrema occur at different sizes depending on the element. Bloomfield and co-workers [5–8] have reported experimental giant magnetic moments for 3d and 4d TM clusters using a similar technique. Their results agree quantitatively with the predictions of the super-paramagnetic model [9], although this model applies

only under certain experimental beam conditions [4,10], namely those which correspond to rotationally warm or hot clusters. The internal cluster temperature is one of the most controversial aspects in this kind of experiment.

From the theoretical point of view, small cobalt clusters have been extensively studied by several groups [11–15], mainly through ab initio schemes. Most of these calculations were performed on clusters of a given geometric structure where inter-atomic distances are either those of the bulk or those obtained after a uniform relaxation process starting from the bulk lattice constant.

Recently, semi-empirical electronic structure calculations have been performed by different groups with a bulk parametrized spd-tight-binding Hamiltonian [13,14,16,17]. These models lead to a good qualitative agreement with the experiments when the transferability of the parameterization is good and when the Hamiltonian is solved self-consistently.

Theoretical calculations by Aguilera-Granja et al. [16] for Ni_N clusters using a spd-tight-binding Hamiltonian with geometries obtained from molecular dynamics calculations using a semi-empirical Gupta potential have shown a rather good qualitative agreement with the experimental data for the magnetic moments [7]. In the case of Co_N clusters, such systematic studies have not been performed so far, and this was the aim of the present work.

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In the present work we used an evolutive algorithm [18] to obtain the global minima cluster geometries. We then calculated the magnetic moments through a self-consistent spd-tight-binding method and compared the results obtained with experiment and some theoretical results present in the literature.

2. Geometric and electronic structure calculations

The optimizations were performed with an evolutive symbiotic algorithm, an efficient variant of the genetic algorithm [18]. The atomic interaction was modeled with the Gupta potential. This potential has an attractive many-body term formulated in the second moment approximation of the electron density of states within the tight-binding scheme, and a Born-Mayer term which describes the repulsive pair interactions. The potential parameters describing the attraction ($p = 11.604$) and the repulsion ($q = 2.286$) for cobalt were obtained by fitting to the bulk equilibrium distance and elastic constants. The values of the amplitudes $\xi = 1.488$ eV (an effective hopping integral) and $A = 0.095$ eV (scaling the repulsion) were obtained by minimizing the bulk fcc cohesive energy [19].

The spin-polarized electronic structure of Co clusters was determined by solving self-consistently a tight-binding Hamiltonian for the 3d, 4s and 4p valence electrons in a mean-field approximation.

The exchange integrals involving s and p electrons are neglected and $J_{dd} = 1.44$ eV is estimated in order to get the

bulk magnetic moment (without orbital contribution) of fcc cobalt $\bar{\mu} = 1.59 \mu_B$ [20].

Since details of the methods and approximations used in the present work, for both the structural [18] part, and the magnetic [16,21] part have been published elsewhere, we refer the reader to these references.

3. Results and discussion

Fig. 1 shows the geometries for cobalt clusters at the most representative sizes in the range studied in the present work. The bond distances and the coordination numbers of the clusters have a monotonic dependence with the cluster size. The average bond distance is given below each structure in the figure in Angstroms units.

There are no experimental works concerning the geometrical structures of Co_N clusters in the small size range considered in this study, although in the case of larger clusters, experimental results from Pellarin suggest an icosahedral growth pattern [22]. There is some experimental evidence that Co cluster size and structure are strongly dependent on the growth conditions such as pressure and temperature [23]. The reaction of ammonia and water molecules on hydrogen saturated clusters and photo-ionization experiments are used to obtain clues with respect the geometrical structures of Fe, Co and Ni clusters [24]. These works provide strong evidence for the poly-icosahedral structure in ammoniated and bare Ni and Co clusters. Our theoretical results presented in the Fig. 1 indicate that the icosahedral pattern is present also

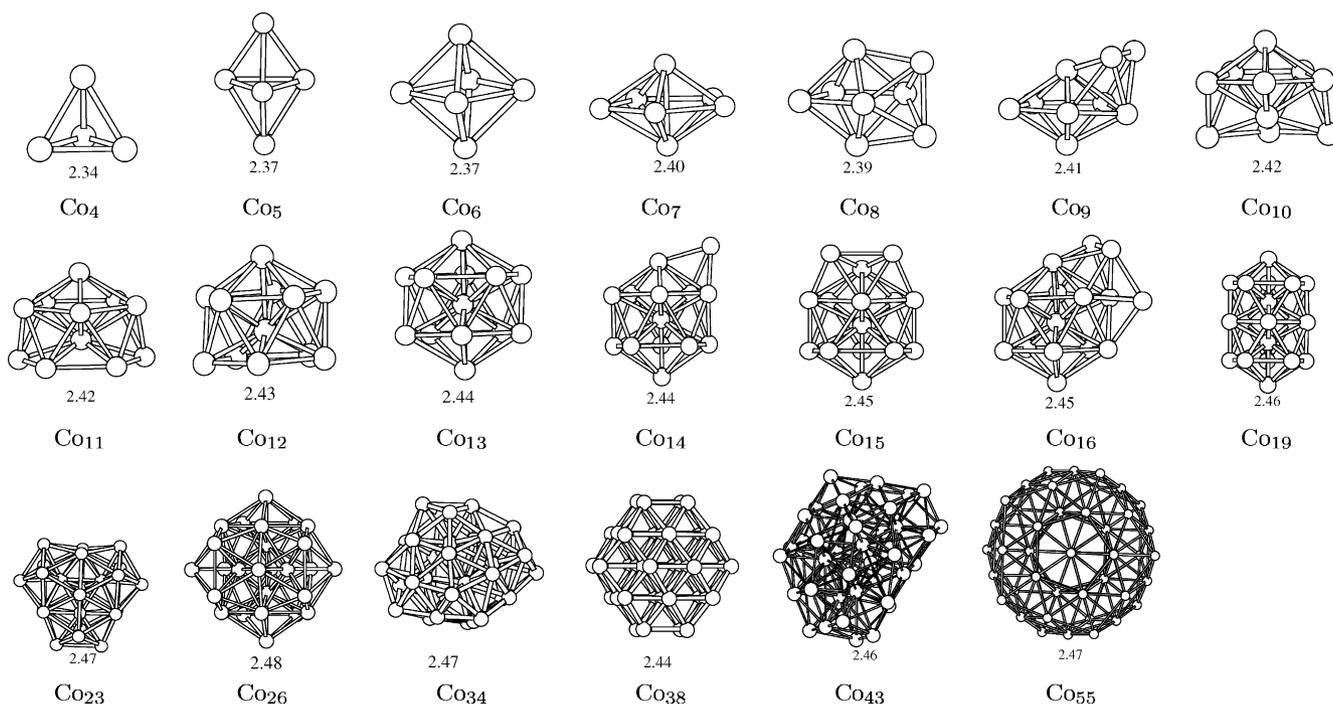


Fig. 1. Global minima structures for cobalt clusters from $N = 4$ to 55 atoms. The number below the structure is the average bond distance expressed in Angstroms.

at very small cluster size (as early as $N = 7$ where the five fold symmetry is observed). Closed shell icosahedral clusters can be clearly identified in Fig. 1 at $N = 13, 19, 23, 26, 43$ and 55 atoms.

We have plotted the results for the average magnetic moment per atom as a function of the cluster size for optimized global minima. The available experimental results in the size range considered in this work are also included. Our calculations agree with the experimental results for clusters smaller than 40 atoms whereas for larger cluster sizes we slightly overestimate (about 7%) the value of the magnetic moment. We obtained a decreasing behavior of the magnetic moment, with small superimposed oscillations, as a function of cluster size. This behavior is driven mainly by two competing effects, i.e., the average coordination and the interatomic distances. A decrease in the coordination and an increase of the inter-atomic distance enhances the magnetic moments because both factors tend to reduce electron de-localization. The competition between these two elements can give us an insight of the discrepancies present in the right part of the Fig. 2, and we refer the reader to the Ref. [25] for a detailed analysis.

The most systematic calculations in the same size range as our study are those of Guevara et al. [13], Andriotis and Menon [14] and Fujima and Sakurai [15]. We will briefly discuss their results and compare them with ours. Guevara et al. used a tight binding formalism although they only considered fixed fcc geometries without structural optimization. Andriotis and Menon also used a tight binding model but combined with a MD scheme. Their calculated structures are mainly a combination of fcc and hcp relaxed geometries and some icosahedra for particular cluster sizes. Finally, the calculations of Fujima and Sakurai were performed using an ab initio LSDF scheme for fixed fcc and hcp clusters with-

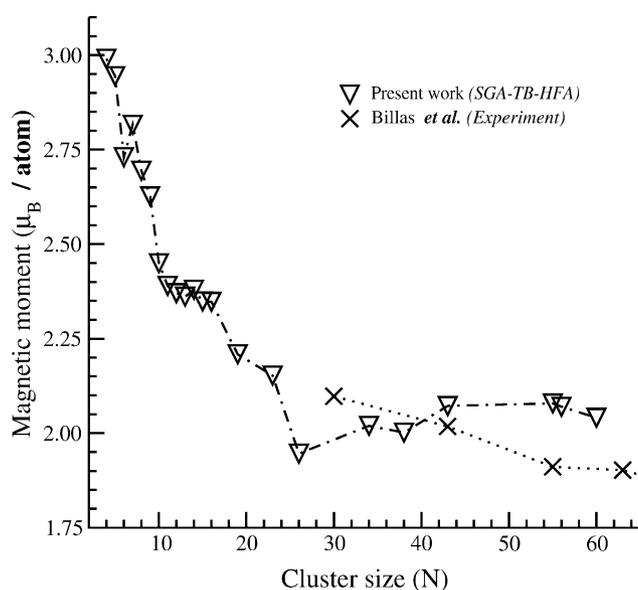


Fig. 2. The magnetic moment of the global minimum (∇) compared with the experimental results by Billas et al. (\times) [4].

out structural optimization. In general all the results present a smooth oscillatory behavior superimposed on a continuous decrease of the average magnetic moments versus cluster size. Our results predict larger magnetic moments than the former three calculations for the smaller clusters ($N < 23$) and similar moments for larger clusters.

More systematic results and discussions are highlighted and published elsewhere [25].

4. Conclusions

We have reported the geometric structures and magnetic moments of small cobalt clusters as a function of cluster size. Our results indicate that the global minimum structure for the small clusters follows mainly an icosahedral pattern with some exceptions of fcc fragments at certain sizes. The icosahedral pattern is particularly clear from $N = 7$ to 19, where by incorporating atoms one by one, the icosahedral and the double-icosahedral structure are built. Other poly-icosahedral clusters are observed at $N = 23, 26, 34, 43$ and 55 atoms. Our results are consistent with experimental observations for relative large clusters that suggest an icosahedral growth pattern.

Our results for the magnetic moment compare qualitatively well with the available experimental data. In general all the theoretical results for the magnetic moments present a smooth oscillatory behavior superimposed on a continuous decrease of the average magnetic moment. The absolute values are slightly different due to the different approximations employed and to the different geometrical structure assumed or calculated, but qualitative trends are similar. The magnetic moment of Co clusters is not very sensitive to the geometrical structure, in contrast to other transition metals that have more d-holes available to be polarized.

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