

Structure and magnetism of cobalt clusters

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The lowest-energy geometric structures and isomers of freestanding Co_N clusters ($4 \leq N \leq 60$) and their corresponding magnetic moments are calculated using an evolutive algorithm based on a many-body Gupta potential and a self-consistent *spd* tight-binding method, respectively. We found an icosahedral growth pattern for the global minimum with some hcp and fcc structures for some particular sizes, whereas for the second isomer, distorted icosahedral structures are obtained in general. With the aim to study the possible coexistence of isomers within the experimental cluster beam we assumed an equilibrium distribution and calculated for each cluster size the different coexistent structures and the relative populations at room temperature. Our results show that the coexistence is present only at some particular sizes, in agreement with chemical-adsorption and photoionization experiments. Our self-consistent tight-binding calculations considering $3d$, $4s$, and $4p$ valence electrons for the magnetic properties show that the magnetic moments for the global minima and the second isomers are in general very similar except in a small region of $20 < N < 40$ atoms where the magnetic moment of the global minimum is smaller than that of the second isomer. We compare our results for the magnetic behavior of the global minimum with theoretical calculations available in the literature as well as with experimental results.

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I. INTRODUCTION

Experiments on free ferromagnetic clusters in molecular beams¹⁻⁴ allow the study of the evolution of certain electronic properties in going from the atom to the bulk. New specific size-dependent cluster properties have even been revealed.⁵ The magnetic properties of clusters in a molecular beam are measured in an experimental setup where the free magnetic particles are deflected with a Stern-Gerlach magnet, and as a result of the inhomogeneous magnetic field, single-sided deflections are observed. Billas *et al.*¹ have measured the magnetic moments ($\bar{\mu}_N$) for Fe, Co, and Ni clusters as a function of the cluster size. For the three elements the global decrease of $\bar{\mu}_N$ with cluster size is superimposed by weak oscillations whose extrema occur at different sizes depending on the element. In order to explain this oscillatory behavior, they have applied a magnetic shell model that gives partial agreement over the experimental curve, but the most puzzling assumption they made is that the clusters are structureless and formed by several spherical atomic shells with no variation of the magnetic moment per atom of each shell when the cluster size changes. Bloomfield and co-workers²⁻⁵ have reported experimental giant magnetic moments for $3d$ and $4d$ transition metal (TM) clusters using a similar technique. Their results agree quantitatively with the predictions of the superparamagnetic model,⁶ although this model applies only under certain experimental beam conditions:^{1,7} namely, those corresponding to rotationally warm or hot clusters. The internal cluster temperature is one of the most controversial aspects of this kind of experi-

ment. In particular, for cobalt clusters, the deflection profiles show the possible coexistence in the cluster beam of two isomers in the region of $N=55-66$ atoms and they have pointed out that the differences between the isomeric sequences are substantial enough to require complete structural rearrangements in order to explain them.²

There are such factors like the symmetry of the cluster, the local coordination, and the interatomic distances that influence the magnetism in low-dimensional systems. From the theoretical point of view, small cobalt clusters have been extensively studied by several groups,⁸⁻¹⁶ mainly through *ab initio* schemes. Most of those calculations refer to clusters of a given geometric structure where interatomic distances are either those of the bulk or those obtained after an uniform local relaxation process starting from the bulk lattice constant.

In the context of the magnetic shell model,¹ theoretical calculations have been done assuming predetermined bcc, fcc, or hcp structures. The oscillatory behavior of the magnetic moment in the $3d$ TM clusters has been explained either from the purely electronic¹⁶ or geometric¹⁷ point of view. Since the magnetic moment mainly originates from the electron-hole pairs at the top of the $3d$ electron levels and the number of holes depends on the number of exchanged $4s$ electrons, it is expected that some shell structure may appear in the evolution of the magnetic moment versus cluster size. Following these ideas, Fujima and Sakurai¹⁶ have shown that the oscillatory structure in the size dependence of the magnetic moment is caused by the discreteness of the $4s$ electronic states by means of an electronic shell model assuming a spherical harmonic oscillator potential and a given integer

and invariant number of d and s electrons per atom. Their agreement with the experiment is good in the large-size region ($N > 80$).

Assuming a completely different point of view than Fujima and Sakurai by disregarding the electronic effects, Jensen and Bennemann¹⁷ have developed a simple geometrical theory for the atomic shell structure of $\bar{\mu}$. They have assumed that the magnetic moment of a specific atomic site is a monotonic function of the coordination number (\bar{z}), the former being lower for closed atomic shells. Thus, maxima of \bar{z} should correspond to minima in the magnetic moment, and an oscillatory behavior of $\bar{\mu}(N)$ as a function of the cluster size is expected by adding additional atomic shells to the cluster. However, there are still discrepancies between the predictions of these phenomenological models and the experimental data. Moreover, *ab initio* calculations do not give support to certain hypotheses like the integer and invariant number of d and s electrons per atom used in the model of Fujima and Sakurai¹⁶ or the monotonic behavior of $\bar{\mu}$ versus \bar{z} used in the model of Jensen and Bennemann.¹⁷ Recently, semiempirical electronic structure calculations of freestanding TM clusters have been performed by different groups using a bulk parametrized *spd* tight-binding Hamiltonian.^{14,15,18,19} These semiempirical models lead to good qualitative agreement with the experiments when the parametrization is good and when they are solved self-consistently.

Since the magnetism is very sensitive to the atomic environment, the average magnetic moment per atom of the clusters is expected to reflect the cluster geometry. However, the geometrical structures of clusters with sizes from a few tens to a few hundreds atoms have not been precisely determined, neither theoretically nor experimentally. Reactions of ammonia and water molecules on hydrogen saturated and bare clusters were used to probe the geometrical structures of Ni and Co clusters by Klots *et al.*²⁰ The technique they used determines, by adsorbate binding patterns, the number and nature of particular binding sites on cluster surfaces. These molecules prefer binding to single metal atoms that have minimum metal-metal coordination. The number of such sites is determined by counting the number of NH₃ molecules that saturates a given cluster. Following this work, Parks and co-workers^{21,22} have demonstrated that small clusters ($19 \leq N \leq 34$) of nickel, cobalt, and iron tend to adopt primarily polyicosahedral structures when saturated with ammonia, and photoionization experiments suggest that Ni_{*N*} and Co_{*N*} clusters are icosahedral up to about $N = 800$ atoms.²³ Recent theoretical calculations by Aguilera-Granja *et al.*¹⁸ for Ni_{*N*} clusters using an *spd* tight-binding Hamiltonian with geometries obtained from molecular dynamics calculations using a semiempirical Gupta potential have shown rather good qualitative agreement with the experimental data of the magnetic moment.⁴ In the case of Co_{*N*} clusters, such systematic studies have not been performed so far, and this is the aim of the present work.

In both magnetic^{2,3} and chemical reactivity^{22,24} experimental works, there is evidence for the coexistence of more than one isomer. In the present theoretical work we em-

ployed an efficient algorithm to obtain the global minima cluster geometries and higher-energy isomers, obtaining the relative populations of the clusters assuming equilibrium conditions in the cluster beam. We then calculated the magnetic moments through a self-consistent *spd* tight-binding method and compared the results obtained both for the global minimum and the second isomer with the experiment.

In the following section we present the theoretical models and approximations used for the geometric and electronic part of the problem. Next we discuss the results and compare them with the experiments and available theoretical data. The main conclusions are summarized at the end.

II. GEOMETRIC AND ELECTRONIC STRUCTURE CALCULATIONS

The optimizations for the determination of the geometrical structures were performed with an evolutive symbiotic algorithm by making 80 000 individual global optimizations starting from random initial configurations of the atoms within a sphere large enough to include all conceivable low energy geometries. The symbiotic algorithm used here is a very efficient variant of the genetic algorithm, the details having been published elsewhere.²⁵ 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 density of states within the tight-binding scheme and a Born-Mayer term which describes the repulsive pair interactions. The functional form of this potential is

$$V = \sum_{i=1}^n \left(A \sum_{j(\neq i)=1}^n \exp \left[-p \left(\frac{r_{ij}}{r_{0n}} - 1 \right) \right] - \left\{ \xi^2 \sum_{j(\neq i)=1}^n \exp \left[-2q \left(\frac{r_{ij}}{r_{0n}} - 1 \right) \right] \right\}^{1/2} \right). \quad (1)$$

The parameters $p = 11.604$, $q = 2.286$, $\xi = 1.488$ eV, and $A = 0.095$ eV for cobalt are obtained by fitting to the bulk cohesive energy, lattice parameters, and elastic constants.²⁶ The interatomic distances can be expressed in angstroms by taking r_{0n} equal to the bulk interatomic distance. To our knowledge, there are no systematic experimental data available in the literature which could be used for fitting the potential parameters. Available *ab initio* data are scarce and not performed at the required generalized gradient approximation (GGA) level. Furthermore, the small size of the systems which could be studied at the GGA level limits the application of the derived potential parameters to the larger clusters studied in this work. In any case, we have determined that slight variations of the potential parameters around those obtained from bulk Co affects the size of the cluster rather than the symmetry. The effect of cluster size on the cluster magnetic moment has been studied elsewhere.^{27,28}

The spin-polarized electronic structure of Co clusters is determined by solving self-consistently a tight-binding Hamiltonian for the $3d$, $4s$, and $4p$ valence electrons in a mean-field approximation (TB-HFA). The hopping integrals used between two orbitals α and β at different sites i and j

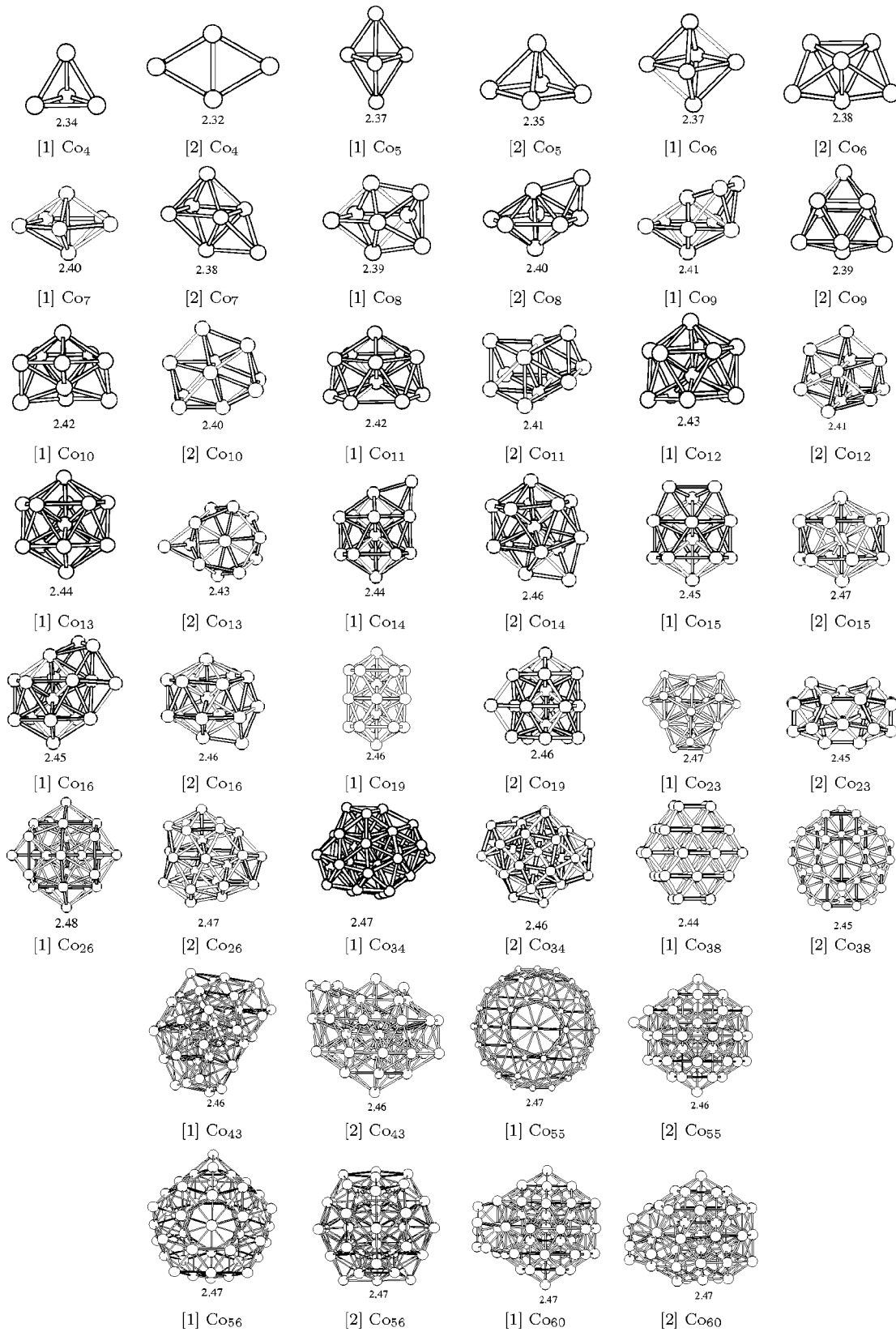


FIG. 1. Global minima structures for cobalt clusters and the second isomer for $N=4-60$ atoms. The global minima (first isomer) are denoted as [1] and the second isomer as [2]. The number below the structure is the average bond distance expressed in angstrom units.

are assumed to be spin-independent and have been fitted to reproduce the band structure of bulk fcc Co.²⁹ This parametrization is similar to that used in the study of Co nanoparticles supported on the (111) Cu substrate.³⁰ The variation of the hopping integrals with the interatomic distance is assumed to follow the typical power law depending on the orbital angular momenta of the states involved in the hopping process.²⁷ In this work, we are considering hopping integrals up to third nearest-neighbor distances. 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, $\bar{\mu} = 1.59\mu_B$.³¹ The spin-dependent local electronic occupations are self-consistently determined from the local densities of states which are calculated at each iteration by using the recursion method.³² In this way, the distribution of the local magnetic moments and the average magnetic moment per atom of Co_N clusters are obtained at the end of the self-consistent cycle.

Since details for the methods and approximations used in the present work both for structural²⁵ and magnetic^{18,27} parts have been published elsewhere, we refer the reader to these references.

III. RESULTS AND DISCUSSION

Figure 1 shows the geometries for cobalt clusters resulting from our optimization at some of the most representative sizes in the range studied in the present work. In the figure, [1] refers to the global minimum whereas [2] corresponds to the second isomer. 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 *et al.* suggest the icosahedral growth pattern.²³ In Co clusters there is experimental evidence that particle sizes and structures are strongly dependent on the growth conditions such as pressure and temperature.³³ The reactions of ammonia and water molecules on hydrogen-saturated clusters and photoionization experiments have been used to obtain clues to the geometrical structures of Fe, Co, and Ni clusters.²¹ These works give strong evidence of the polyicosahedral structure in ammoniated and bare Ni and Co clusters. Our theoretical results indicate that the icosahedral growth pattern is also obtained here for the global minima structures of Co_N (see structures denoted as [1] in Fig. 1). In general, this pattern is followed by incorporating atoms (one by one) to a stable closed-shell structure, reaching in this way the main and intermediate icosahedral sizes at 7, 13, 19, 23, 26, 34, 43, and 55 atoms. In the case of the second isomer there is not a well-defined family of structures although distorted icosahedra are generally present and occasionally some fcc and hcp fragments are present. Our results are consistent with experimental observations for larger clusters, suggesting an icosahedral pattern.

Figure 2 shows the average atomic coordination and the average nearest-neighbor distance for the freestanding clusters shown in Fig. 1. Notice that the average coordination in the two different series of isomers is similar regardless of the

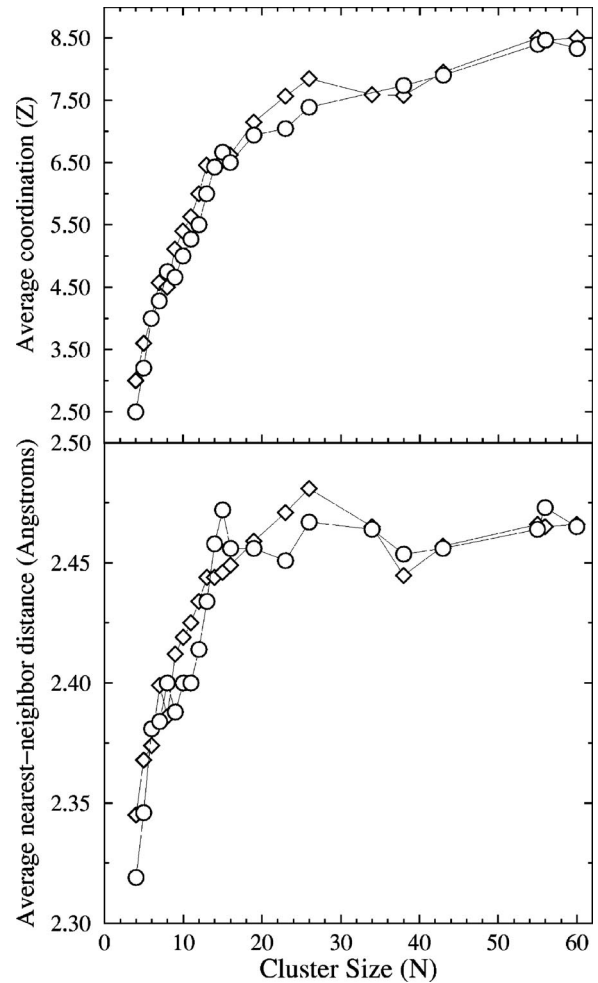


FIG. 2. In the upper panel we show the averaged atomic coordination and in the lower panel the averaged interatomic distance for cobalt clusters from $N=4$ to 60 atoms. The global minima are denoted using (\diamond) and the second isomer with (\circ). Only those structures for which we have calculated the magnetic moments are shown.

different geometries, except in a region between $N \approx 20$ and about $N \approx 40$ atoms. For the nearest-neighbor distances, small variations are obtained which are also more noticeable in the same region. Whether such variations are reflected in the evolution of $\bar{\mu}$ versus N will be analyzed later. The nearest-neighbor distance converges relatively fast toward the bulk value, reaching it in the range of $N=20$ – 40 atoms.

In Table I we summarize the results available in the literature that can be directly compared with our results. In this table only the global minimum structures are included for those works in which structural optimizations have been performed. Together with the structural properties we also present the average magnetic moment per atom. Note that there is not a very wide dispersion in the results.

In Fig. 3 we have plotted the relative stability of the global minimum ($\Delta E_2 = [E(N+1) + E(N-1) - 2E(N)]$) of each cluster of N atoms with respect to its adjacent clusters with $N-1$ and $N+1$ atoms. Notice the high stability of the main ($N=13, 19, 23, 26, 28, 43$, and 55 atoms) and intermediate ($N=10, 15, 28, 32, 36, 46, 49$, and 60 atoms) icosahedral sizes. Other maxima in the stability curve, not related

TABLE I. Cluster size, symmetry, average bond distance, and magnetic moments per atom for the global minima structures $\bar{\mu}_0$, from $N=4$ to 60 atoms, compared with available results in the literature. The method of calculation by Guevara *et al.* (Ref. 14), Andriotis and Menon (Ref. 15), and in the present work is TB-HFA ^a; all the others have used LSDA-DFT ^b. Experimental values have been reexpressed using $g_{\text{Co}}=2.0$ (Ref. 1).

N	Symmetry	r_n (Å)	$\bar{\mu}_0$ (μ_B)	Reference	N	Symmetry	r_n (Å)	$\bar{\mu}_0$ (μ_B)	Reference		
4	T_d	c	2.20	8	17	fcc	c	2.06	14		
	D_{2d}	2.09–2.65	2.00	12		fcc	c	2.11	14		
	D_{2h}	2.09–2.68	2.50	12		O_h	c	2.15	8		
		c	2.50	14			2.33	1.95	10		
	T_d	2.61–2.80	2.50	15			2.33	1.97	13		
	T_d	2.34	2.99	Present work	O_h	c	2.05	14			
5	D_{4h}	c	2.20	14	D_{5h}	2.54–2.94	2.16	15			
	C_{4v}	2.69–2.79	2.20	15		O_h	c	1.95	16		
	D_{3h}	2.37	2.94	Present work		hcp	c	2.05	16		
6	O_h	c	2.33	8	21	D_{5h}	2.46	2.21	Present work		
	O_h	c	2.33	14		fcc	c	2.06	14		
	T_d	2.76	2.33	15		hcp	c	2.05	16		
	O_h	2.37	2.73	Present work		fcc	c	2.00	14		
7	D_{5h}	2.40	2.81	Present work	23	fcc	c	2.00	14		
8	fcc	c	2.25	14	24	hcp	c	1.92	16		
	D_{2d}	2.39	2.69	Present work		26	D_{6d}	2.48	1.95	Present work	
9	fcc	c	1.89	14	27	fcc	c	1.96	14		
	C_{2v}	2.41	2.63	Present work		29	hcp	2.69–2.72	1.90	15	
10	fcc	c	2.00	14	30			2.08	Experiment		
	C_{3v}	2.42	2.45	Present work		34		2.46	2.02	Present work	
11	C_{2v}	2.42	2.39	Present work	35	fcc	c	1.97	14		
12	fcc	c	2.17	14	38	O_h	2.44	2.00	Present work		
	C_{5v}	2.43	2.37	Present work		39	hcp	c	1.87	15	
13	D_{3d}	c	2.10	8	43	fcc	c	2.12	13		
	O_h	c	2.11	8		fcc	c	1.93	14		
	I_h	c	2.33	8		fcc	c	1.79	15		
	I_h	2.33	2.38	9		fcc	c	1.93	16		
	O_h	2.30	2.08	10			2.46	2.07	Present work		
	I_h	2.26	1.77/2.23	10				2.01	Experiment		
	O_h	c	1.62/2.08	11		55	fcc	c	1.84	14	
	O_h	2.30	2.08	13			fcc	c	1.91	16	
	O_h	c	2.08	14				2.47	2.08	Present work	
	D_{3d}	2.71–2.75	2.08	15			fcc	2.47	2.20	Present work	
	O_h	c	2.08	16					1.92	Experiment	
		D_{3d}	c	2.38		16	56		2.46	2.07	Present work
		I_h	2.44	2.36		Present work		57	hcp	c	2.02
14	fcc	c	2.14	14	60		2.46	2.04	Present work		
	C_{3v}	2.44	2.38	Present work		63	fcc	c	1.89	14	
15	fcc	c	2.07	14		fcc	c	2.08	16		
	C_{3v}	2.45	2.35	Present work					1.89	Experiment	
16	C_s	2.45	2.34	Present work							

^aTight-binding Hartree-Fock analysis.

^bLocal spin density approximation in the density functional scheme.

^cNonoptimized bond, bulk distance used ($r_0=2.5$ Å).

to the icosahedral family, are located at $N=6$ (octahedral) and 38 (fcc fragment). For the second isomer (figure not shown) the relative stability has maxima stability at $N=5$ (square pyramid), 7 (capped octahedral), 9 (trigonal capped

prism), 11 (hcp fragment) 14 (distorted icosahedral), and 18, 20, 24, 29, and 32 atoms. In general, for the small cluster sizes, the cluster geometry is highly symmetric for the second isomers—i.e., tetrahedral packing, capped octahedral

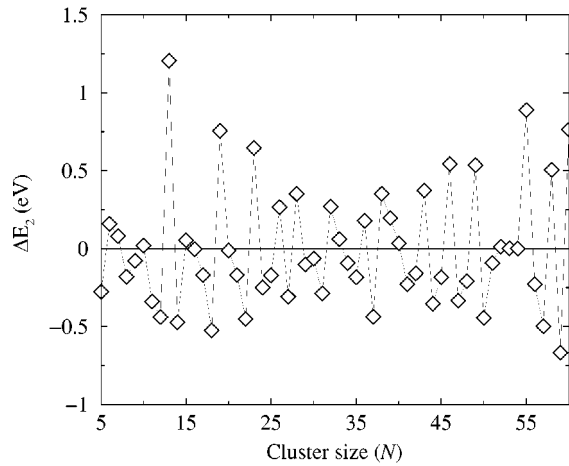


FIG. 3. Relative energy stability for the global minimum structures. Peaks of high stability at main ($N=13$ and 55 atoms) and intermediate icosahedral sizes ($N=19, 23, 26, 28, 43,$ and 46 atoms).

clusters, and hcp fragments—whereas in the case of larger clusters, they are slightly distorted structures generated from the icosahedral growth and the hexagonal capped antiprism.

The possible coexistence of different isomers in the cluster beam had been suggested experimentally.² To investigate this possibility, we have calculated theoretically the relative populations of the lowest-energy isomers of each cluster. We assumed an equilibrium distribution at 300 K. The result of this calculation is given in the Fig. 4. Room temperature seems to be a reasonable value for the internal cluster temperature as has been discussed by several authors.^{5,6} The free energy F was calculated according to³⁴

$$F = V + \sum_i \left(\frac{\hbar \omega_i}{2} \right) + k_B T \sum_i \ln \left[1 - \exp \left(- \frac{\hbar \omega_i}{k_B T} \right) \right], \quad (2)$$

where the first term represents the potential energy, the second the zero-point energy, and the third the vibrational contribution to the entropy. The frequencies of the normal modes

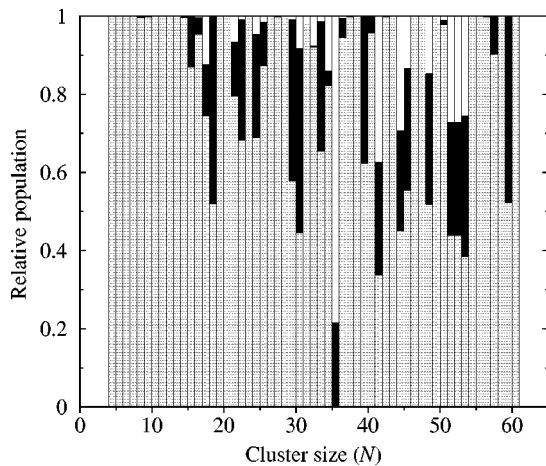


FIG. 4. The relative normalized populations for the global minimum structure (grey bars), the second isomer (darker bars), and the third isomer (white bars) as a function of the cluster size.

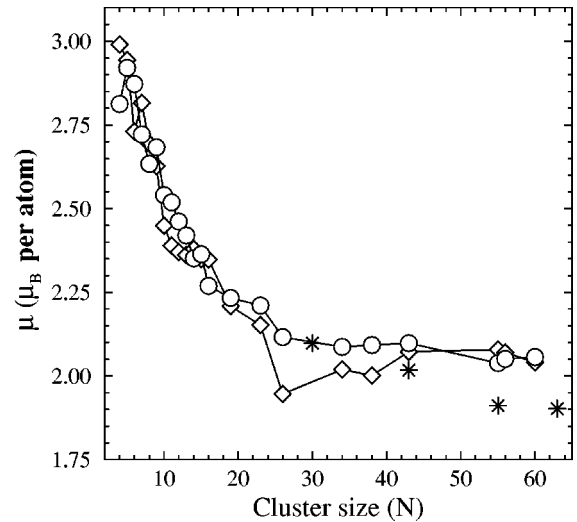


FIG. 5. Magnetic moments as a function of the cluster size ($4 \leq N \leq 60$), for the global minima (\diamond) and the second isomer (\circ) of cobalt clusters. Experimental points ($*$) have been reexpressed using $g_{Co}=2.0$ (Ref. 1).

ω_i were obtained in the harmonic approximation from the eigenvalues of the Hessian evaluated at the minima in the potential energy surface. Notice that there is coexistence of isomers of higher potential energy particularly between the closed-shell magic sizes of the icosahedral family, e.g., at sizes $N=15, 17, 18, 21, 22, 24, 25, 29, 30, 33, 34, 35, 41, 44, 51, 52,$ and 53 atoms. This is due to the influence of the entropic contribution of the low-frequency normal modes of the isomers to the free energy at these sizes where the potential energy of the global minimum and next isomer is almost degenerate. Our results show that the coexistence of different isomers is present particularly in between two adjacent closed-shell structures. However, on average, the global minimum contributes 81% to the relative populations, the second isomer 12%, and the third 7%. There is not a significant contribution from the other higher-energy isomers.

In Fig. 5 we have plotted the results for the average magnetic moment per atom as a function of the cluster size for optimized global minima and for the second isomer. 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. For both the global minimum and the second isomer we obtain a similar nonmonotonic decreasing behavior of the magnetic moment as a function of the cluster size. The main difference between the global minima and the second isomer arises for clusters between $N \approx 20$ and $N \approx 40$, the difference in the magnetic moment being smaller than the 10%, and this is the same region where the average coordination and nearest-neighbor distance display differences between both sets of geometries (see Fig. 2). However, inspection of Fig. 2 reveals that the magnetic behavior in this size range is driven by two competing effects. On the one hand, the average coordination is lower for the second isomers than for the global minima, so that higher magnetic moments are expected for the second

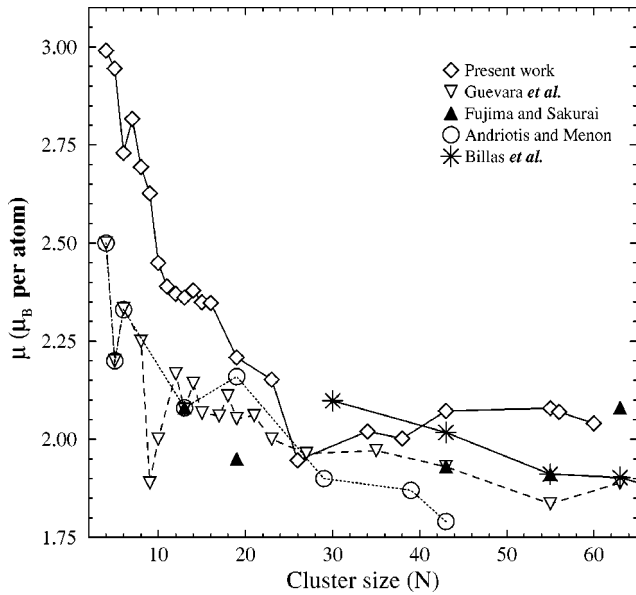


FIG. 6. The magnetic moment of the global minimum (\diamond) compared with the results by Guevara *et al.* (∇) (TB-HFA) (Ref. 14) and by Fujima and Sakurai (\blacktriangle) (LSDA-DFT) (Ref. 16), both using bulk interatomic distance and fcc structures, while Andriotis and Menon (\circ) used a combined MD-TB scheme (Ref. 15). Experimental values by Billas *et al.* ($*$) (Ref. 1).

isomers compared with the global minima. On the other hand, the average nearest-neighbor distance is lower for the second isomers than for the global minima (except for $N > 35$), so that lower magnetic moments are expected for the second isomers. Figure 5 shows that the average coordination effect dominates, and this argument holds in general for all sizes.

Regarding the magnetic moments of the higher-energy isomers, their magnitudes are expected to be similar to the global minima and the second isomer due to the fact that the coordination and nearest-neighbor distances are very similar, these two properties being the main factors that influence magnetism in $3d$ TM clusters.

Finally, considering that the coexistence of the second isomer in the size range studied here is relatively low, together with the fact that the average magnetic moment of the global minimum and the second isomer are very similar, we conclude that the isomerization effects (the coexistence of energetically different isomers at a given temperature) do not affect the general magnetic behavior present in cobalt clusters and comparison with experiments can be made using the global minimum structures. In a recent work on Rh clusters,²⁷ we also have found that isomerization does not play a significant role in the general magnetic behavior.

It is pertinent now to compare our results with those available in the literature. The most systematic calculations done in the same size range as our study are those by Guevara *et al.*,¹⁴ Andriotis and Menon,¹⁵ and Fujima and Sakurai¹⁶ (see Fig. 6). 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 molecular dynam-

ics scheme. Their calculated structures are mainly a combination of fcc and hcp relaxed geometries and some icosahedral for particular clusters sizes. Finally, the calculations of Fujima and Sakurai were done using an *ab initio* LSDF scheme for fixed fcc and hcp clusters without structural optimization. In general all the results present a smooth oscillatory behavior superimposed onto 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 values for larger clusters.

There are various possibilities for the discrepancy between our and previous calculations. First, the electronic structure and the resulting magnetic moments in our work were calculated using a spd tight-binding model parametrized to the Co bulk. In particular, the exchange parameter was chosen so as to reproduce the bulk magnetic moment. It would be possible, however, to choose this parameter in different ways. For instance, one can perform an *ab initio* calculation of a given cluster and fit the exchange parameter in order to reproduce its average magnetic moments. Slight variations in the absolute values of the magnetic moments are expected among the different parametrizations of the exchange parameter. Also, the overall size of the cluster (average interatomic distance) has an effect on the absolute value of the magnetic moment, as noted above.

Let us now focus on some selected cluster sizes. For $N = 4$ our calculation predicts a tetrahedral cluster, in agreement with Andriotis and Menon. Our value of the magnetic moment is larger than theirs, which is also larger than that calculated by Li and Gu⁸ for the nonoptimized tetrahedral geometry with bulk interatomic distances. For $N = 6$ we have an octahedral cluster, generally accepted as the most stable structure for this size, although Andriotis and Menon's calculation predicted a different geometry with T_d symmetry. Calculations performed by Guevara *et al.*¹⁴ and Li and Gu⁸ for the nonoptimized octahedral geometry with the bulk interatomic distance report the same magnetic moment ($\bar{\mu} = 2.33\mu_B$), larger than the bulk value but slightly lower than our result ($\bar{\mu} = 2.73\mu_B$).

For $N = 13$ we have an icosahedral cluster. Although the icosahedral structure is generally accepted to be the global minimum at this size, there are some theoretical calculations that consider the fcc or the hcp as the most stable structure.^{13,15} Our magnetic moment for this cluster size is in agreement with first principles calculations performed by Li and Gu⁸ and Jinlong *et al.*⁹ although the cluster size is slightly different. For $N = 13$, different values for the magnetic moment are reported in the literature, ranging from $\bar{\mu} = 2.08\mu_B$ for the cube-octahedral (fcc) cluster to $\bar{\mu} = 2.36\mu_B$ in the case of our icosahedral cluster. For $N = 19$ atoms we have the typical double icosahedron that is also generally accepted as the global minimum structure, although fcc and hcp fragments have also been proposed.^{10,8,14} For this cluster size our magnetic moment is in good agreement with that calculated by Andriotis and Menon although the cluster size is slightly different.

For $N=23$ and 26 atoms we have polyicosahedral structures, consistent with the icosahedral growth pattern; the respective magnetic moments are $\bar{\mu}_{23}=2.15\mu_B$ and $\bar{\mu}_{26}=1.95\mu_B$, the calculation of Guevara *et al.* for $N=23$ is an fcc fragment, and the corresponding magnetic moment is $\bar{\mu}_{23}=2.0\mu_B$. For $N=38$ atoms, the fcc structure is more stable than the icosahedra, and similar behavior is also observed for Ni and Rh clusters.^{18,27} In the case of $N=43$ the most common structure used in the calculations is the 55-atom cube-octahedral (CO) minus the 12 atoms at the vertices (fcc) (CO55-12); the reported values for the magnetic moments vary between $\bar{\mu}_{43}=1.79\mu_B$ reported by Andriotis and Menon to $\bar{\mu}_{43}=2.12\mu_B$ reported by Chuanyum *et al.* In our case, the calculated structure is the partially capped icosahedral (following the umbrella growth process) and the magnetic moment is $\bar{\mu}_{43}=2.07\mu_B$. For $N=55$ most of the reported calculations are done using the cluster with cube-octahedral (fcc) symmetry, although there is experimental evidence by Parks *et al.*²² that the most stable structure is the icosahedral cluster. In this size, our global minimum is in agreement with the experimental evidence, and the calculated magnetic moment ($\bar{\mu}_{55}^{lh}=2.07\mu_B$) is slightly larger than the experimental one.

IV. CONCLUSIONS

We have reported a systematic study of the geometric structure and magnetic properties of small cobalt clusters as a function of cluster size. Our results indicate that the global minimum structure for the small clusters follow mainly an icosahedral pattern with the exception of fcc and hcp fragments for certain sizes. The icosahedral pattern is particularly clear from $N=7$ to $N=19$ whereby incorporating at-

oms, one by one, the icosahedral and the double-icosahedral structures are built. Other polyicosahedral clusters are observed at $N=23$, 26, 34, 43, and 55 atoms. For the second isomer, distorted icosahedral clusters are obtained in general, although some fcc and hcp distorted fragments are occasionally obtained. Our results are consistent with experimental observations for relative large clusters that suggest an icosahedral growth.

At room temperature, the coexistence of isomers is present, although it is relatively low. The global minimum contributes on average approximately 81% to the total. The contribution of the second isomer is 12%, whereas for the third isomer, just 7%. We did not find significant coexistence of higher-energy isomers. The average magnetic moments of the global minimum and the second isomer are in general similar. Considering the above facts, we conclude that the influence of the isomerization on the magnetic behavior versus cluster size is not important for cobalt.

Our results 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.

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