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View on the Magnetic Properties of Nanoparticles Co_m ($m=6,8,10,12,14$) and Co_6O_n ($n=1-9$)

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1. Introduction

Currently there are several potential applications for magnetic nanomaterials in medicine including magnetic resonance imaging contrast agents, magnetic-field-directed drug delivery systems, bio-toxin removal, gene therapy, and magnetic fluid hyperthermia. Cobalt nanoparticles are one of the most promising materials for both technological applications and academic studies as a model system to study how effects of the nanoparticle size, shape, structure, and surface anisotropy on macroscopic magnetic response. The magnetic behaviour of Co nanoparticles reveals how the magnetic metal nanoparticles can be used to enhance the signal due to their magnetic resonance imaging.

Today it is very well known that in a paramagnetic material there are unpaired electrons, that are free to align their magnetic moment in any direction, while paired electrons by the Pauli Exclusion Principle are to have their intrinsic ('spin') magnetic moments in opposite directions, causing their magnetic fields to cancel out. It implies, that in many cases, the magnetic properties of the Co nanoparticles are explained by the presence of unpaired electrons because the particles consist of an odd number of cobalt atoms. However, in experimental studies the number of atoms in the particle has never been mentioned only the description of their size and main structure along with their magnetic properties have been provided. It is not a surprise, because a magnetic behaviour of materials depends on their electron configuration that is strongly related with a geometrical structure, and on temperature.

The dependence of magnetic anisotropy energy on crystal symmetry and atomic composition is observed in both ferromagnetic bulk materials and thin films. Even the structural parameters such as the shape of particles or the inter-atomic distances, in some cases, are affected by the above dependence. The importance of the electronic structure of

particles exhibits the dependence of magnetic anisotropy energy on a single-atom coordination. Current, experiments exhibited that the coercivity of some particles at 10 K increased from 640 to 1250 Oe while the particle size increased from 1.8 to 4.4 nm. The saturation magnetization increases with decreasing of particle size. Pure CoO nanoparticles in the 4.5-18 nm exhibit a super-paramagnetic behaviour at room temperature, and a large orbital contribution to the magnetic moment at low temperatures was also observed.

It was mentioned, that an electronic structure of both the materials and particles is strongly related with the geometrical structure. However, there are some difficulties to identify the structure of a cobalt nanoparticle. The crystallinity was evidenced by the transmission electron microscope (TEM) indicating that Co particles sized around 4.7 nm are a well-crystallized FCC. While the particles with the average diameter smaller than 4,7 nm are almost perfectly spherical. The lattice of Co nanoparticles with inter-planar distance of around 0.23 nm was obtained and explained that such crystalline structure could originate either from BCC cobalt particles observed along the [001] direction or due to Co-FCC particles since the lattice would be formed by two [002] perpendicular planes. Both a high-resolution TEM and powder x-ray diffraction profiles reveal the presence of 8-15 nm diameter crystallites that are identified as hcp-Co, FCC-Co nanocrystals. S. Ram reports two crystalline phases of cobalt FCC and BCC structures, while S. P. Gubin and et al. report that hcp and FCC structures or their combination can be realized in Co nanoparticles. C. G. Zimmermann and et al. investigate Co nanoparticles the diameter of which is 13 nm and the variance of 4 nm; the first four FCC rings were visible in the diffraction pattern. Hence, there is no evidence what a crystalline phase of cobalt is more preferable and it is difficult to define which structure type of Co is realized in nanoparticles. Theoretical investigations of the Co clusters are not complete. J. Guevara and et al. calculated those Co clusters that are part of FCC or BCC block without distortion of the initial geometry structure. In other works, the structural distortion of the above clusters was performed by moving one or several atoms along the main axis of the clusters, i.e. this operation does not change the symmetry if the configuration of the cluster belongs to a point group with a single main axis. Hence, we begin at the results of the investigation of the structure of the Co nanoparticles aiming to recognize the most important structure features influencing the magnetic properties of the Co nanoparticles.

Other very important results obtained are that the nanoparticle behaviour is influenced by the proximity of neighbouring particles, i.e. dipolar inter-particle interactions lead to the appearance of collective behaviour. Such a collective behaviour due to dipolar interactions has been observed in the low susceptibility measurements corresponding to a highly ordered fine particles system. Puentes and et al. observe that when the density of particles per unit area is higher than a determined threshold, the two-dimensional self-assemblies behave as a continuous ferromagnetic thin film. A weak interaction among the assemblies of the Co nanoparticle is obtained by Park and et al. and this assembly leads to hysteresis disappearance. We shortly explain why the assembly of Co nanoparticles leads to loosing of the particle magnetic properties and make predictions how to avoid the loosing.

One of the reasons of the above assembly of the particles is their stability that is an important factor for the particle application in technology. Small cobalt nanoparticles not only self-assemble, but also easily oxidize in the air and, as a consequence, loose their magnetic properties. Thus, Co nanoparticles need to be coated with organic surfactants

aiming to prevent them from both irreversible aggregation and loosing of magnetic properties.

For coating of Co nanoparticle different materials such as graphite, nanoroads, nanocapsules and oxygen are used. The core-shell nanoparticles (Co-CoO) are examined and, it is established, that the magnetic properties of these particle strongly depend on the plane coverage. The results reported demonstrate the essential role played by shells in stabilizing the magnetism of Co-CoO nanoparticles. Few reports on the preparation and properties of pure CoO in bulk are due to difficulties to obtain the materials in pure form by simple methods. The particles are often contaminated with Co_3O_4 or Co metal. The greater stability of Co_3O_4 than CoO is also established.

Herein, we report on the several very important issues related to magnetic properties of Co nanoparticles such as:

1. What are electronic and geometric structure properties of pure and oxidized Co nanoparticles and how these properties change with the increase of the size of particle ;
2. Could Co nanoparticles consisting of the even number of atoms exhibit magnetic properties because their electronic structure is such that an uncompensated electron-magnetic-moment appears? What are the main reasons of the above appearance?
3. Some Co oxide particles exhibited magnetic properties and have large perspective to be used in electronics.

2. Description of method

The structural origin of clusters has been studied by using the generalized gradient approximation for the exchange-correlation potential in the density functional theory (DFT) as it is described by Becke's three-parameter hybrid functional, using the non-local correlation provided by Lee, Yang, and Parr. The DFT method is commonly referred to as B3LYP, - a representative standard DFT method. The 6-31G basis set has been used as well. The basis set was chosen keeping in mind relatively minimum computational costs. The structures of the investigated nanoparticles have been optimized globally without any symmetry constraint and by starting from various initial geometries which have been constructed according to a certain symmetry in order to determine the lowest energy structures of each cluster. The GAMESS and Gaussian program suites were used for all simulations here.

It is necessary to mention that there are different ways to theoretically investigate the magnetic properties of the materials. Aiming to exhibit why closed shell particles could be paramagnetic, we have chosen the most simple method to investigate magnetic properties of the Co nanoparticles. Hence, magnetizability (commonly known as susceptibility) was investigated. The magnetizability is the second-order response to an external magnetic field:

$$\xi = \left. \frac{-\delta^2 E(B)}{\delta B^2} \right|_{B=0}$$

Where E is energy, B is an external magnetic field.

When $\xi < 0$, the induced magnetic moment is opposite to the applied field, i.e. the investigated materials are diamagnetic; while for paramagnetic materials the magnetizability is larger than zero ($\xi > 0$) in this case the induced magnetic moment enforces the magnetic field. Experimentally, magnetizability is often poorly determined or it is only known in the liquid or solid state, thus it is difficult comparisons between calculated and experimental results, while rotational g-tensors are known as precisely determined. However, a rotational g-tensor behaves in the same manner as magnetizability, with a near cancellation of large nuclear and electronic contributions in a large system.

A calculation of rotational g tensors is closely related to that of magnetizabilities via:

$$g = -4m_p \left(\xi^{LAO} - \xi_{cm}^{dia} \right) I_{nuc}^{-1} + \frac{1}{2\mu_N} \sum Z_k \left(R_K^T R_K I_3 - R_K R_K^T \right) I_{nuc}^{-1}$$

where m_p is the proton mass, ξ^{LAO} is the magnetizability tensor calculated with London orbitals, ξ_{cm}^{dia} is the diamagnetic contribution to the magnetizability tensor calculated with conventional orbitals and the gauge origin at the centre of mass, and the sum of all nuclei with charges Z_K and positions R_K , while I_{nuc} is the moment-of-inertia tensor. Although not explored in a large number of studies, obtained theoretical results fit experimental. Hence, the above close relationship allows us to expect that our methods chosen that are well suited to the calculation of rotational g tensors should also be well suited to the calculations of magnetizabilities. Moreover, this simple enough method is suitable to describe general magnetic properties of the investigated particles and to explain the results obtained.

The isotropic magnetizability of the most stable clusters was calculated by adopting quantum mechanical response theory and London atomic orbital to ensure both gauge-origin independent results and fast basis set convergence by using Dalton program. The approach used allows us to calculate accurate magnetizability even for quite large molecules at a moderate cost of computing time. In this case, the B3LYP method with Ahlrichs-pVDZ basis set was used. These basis sets were obtained by optimizing the exponents and contraction coefficients in the ground state ROHF calculations. There are total 241 contracted functions in the basis mentioned. It is showed, that the isotropic magnetizability and its anisotropy are remarkably constant with respect to the basis set and close to the experiment. So, the performances obtained allow us to foresee how magnetic properties of the particles depend on their structures.

3. Structure, stability and magnetic properties of Co_m (m=6, 8, 10,12, 14) nanoparticles

3.1 Structure and stability

Let us remember that magnetic properties of the materials are related with an electronic structure. The electronic structure is mostly geometrical-structure-depended. On the other, hand when the geometrical structure of a compound is know, it is possible to predict some properties of the compound. Thus, the first step to understand the nature of the magnetizability of the Co nanoparticles and why this property is shape- and size-depended is to investigate the geometrical structure.

Let us remember that, there is an infinite number of possible surfaces which can be exposed for every crystal system. In practice, only a limited number of planes are found to exist in any significant amount. Thus, the attention was concentrated on the above surfaces, because it is possible to predict the ideal atomic arrangement for a given surface of a particular metal by considering how the bulk structure is intersected by the surface. It is necessary to remember that investigated nanoparticles consist of a small number of atoms, thus, it is not possible to obtain a very strict crystalline structure; the crystalline structure that is expected to be in the investigated Co nanoparticles was obtained on the basis of the symmetry of a bond and atom location in the planes.

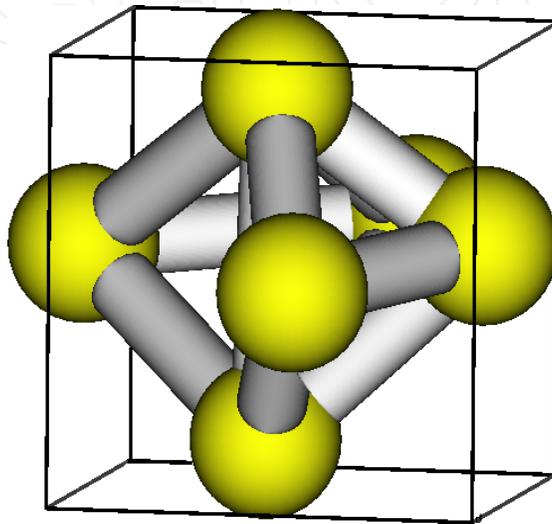


Fig. 1. Co_6 nanoparticle located in the cubic cell.

It is necessary to mention that the structure of the Co_4 particle was found, too. The results obtained indicate that Co_4 is planar and a nice equilateral is formed. In the case of Co_6 nanoparticle, we have the three-dimensional structure with a slightly disordered cubic symmetry. The structure was obtained after global optimization of the D_{4h} isomer of a Co_6 particle. It is important that each atom of the Co_6 nanoparticle is possible to approximately be located in the centre of the plane of the cubic cell (Fig. 1). The three surfaces are obtained. So, this nanoparticle is the element of a FCC structure.

It is possible to see two planes of the Co_8 nanoparticle (Fig. 2). The location of atoms on these planes as well as the symmetry of bonds allows us to predict that the element of FCC structure has been formed, too. This assumption is supported by following: i) each Co atom is four-fold coordinated; ii) the structural element of the Co_6 particle is obtained (see the structure that form atoms 5, 6, 7, 8 or 1, 2, 3, 4 in Fig. 2). So, the element of FCC structure has also been obtained in the Co_8 nanoparticle. The conformation of Co_8 nanoparticle has proved to be the most stable.

One of more interesting situations arises in case of Co_{10} nanoparticle. In this case, we have the two-dimensional disordered symmetry structure consisting of two planes and two atoms in the middle of each plane (Fig.3). The atoms mentioned join these planes. Roughly speaking, the structure of the Co_{10} nanoparticle is formed when the planes of the Co_8 nanoparticle are rotated in respect of each other when two Co atoms are added and a nice cubic structure is formed. This has also been confirmed by bond order investigations. On the

other hand, each Co atom is four-fold-coordinated and a structural element of the Co_6 particle could also be foreseen. In case of Co_{12} and Co_{14} particles there are three planes where the location of atoms is as in the FCC structure: the atoms lie on the corners of the cube with additional atoms in the center of each of four cube of faces. The structure of Co_6 particle is also obtained. The element of BCC structure is also present because some atoms are out of the cube face. The most important for us is that the structure of a Co_6 particle was also obtained.

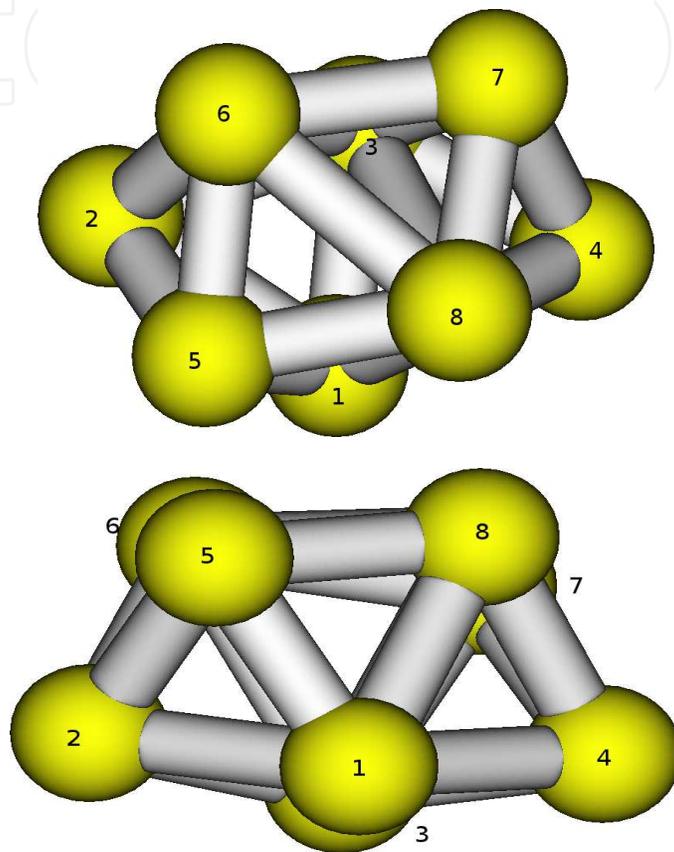


Fig. 2. The view of two planes of Co_8 particle from two different sides take places. T

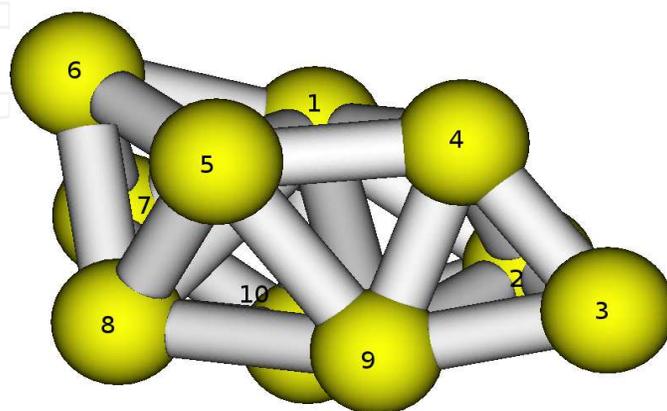


Fig. 3. The views of two formed by atoms 4,5,8,9 and 1,2, 7, 10 planes where atoms 3 and 6 is between the planes in Co_{10} particle.

Let us describe the structure of this Co_{16} particle on the basis of the Co_{14} particle. Firstly, it is necessary to mention that the additional atoms are joined with three-fold coordinated atoms placed above the centre of the cube face. The joining leads to the deformation of the cube because the above atoms of the Co_{14} particle are pushed to the centre of the cube face. On the other hand, several structures of the Co_6 particle are possible to be seen. Hence, in this case, the deformed FCC structure also takes place, but the BCC structure element tends to disappear in the inner part of the particles although the exterior part the element remains unchanged. So, the tendency to form FCC is possible to predict. It allows us to speculate, that in large particles (particles with the diameter more than 10 Å) the main structure could be FCC, while in the external part the BCC structure could be present.

When considering the electronic properties of the above Co_n particles, a singlet state is a ground one. The triplet state of these particles lies higher in total energy. These results disagree with the results presented by H.J. Fan and et al. It is necessary to mention that in the paper of H.J. Fan and et al. only high spin multiplicity particles were investigated applying Amsterdam density functional method with STO basis set with no report on how the geometry of the most stable compound was obtained. The calculated binding energies (per atom) of the Co nanoparticles, as a function of the number of these atoms in the particle, indicate that the Co_{14} particle with the primitive cell of FCC structure is one of the most stable species among those presented in this section (Table 1). We also received, that Co_6 and Co_{12} particles are more stable among the investigated by us particles that consist of less than 12 atoms and this result coincides with that presented by Q. M. Ma and et al. very well.

Number of atom	Binding energy per atom, eV	HOMO-LUMO gap, eV
6	0.45	1.47
8	0.20	1.32
10	0.36	1.18
12	0.48	1.53
14	0.69	1.64
16	0.78	1.24

Table 1. The dependence of calculated binding energy per atom and HOMO-LUMO gap on the atom number in the particle.

The above results confirm the investigation of HOMO-LUMO gap.

Hence, the main important observations on the geometrical structure of the pure Co nanoparticle are the following:

- The Co_8 , Co_{10} , Co_{12} , Co_{14} , Co_{16} particles consist of Co_6 , thus this particle can be regarded to as the key element of the large Co nanoparticles.
- The face centered cubic structure which is slightly less close packed occurred in the Co_{14} nanoparticle, while the other particles described are the elements of the FCC structure. When increasing the number of Co atoms in the particle, the atoms that are above the centre of the cube face are pushed both to the cube face centre and the inner part of the particle. Hence, in the inner part of the particle there is a FCC structure while the BCC structure element is obtained in the exterior part the particle. Thus, the obtained results allow us to speculate that in a large cobalt nanoparticle the FCC structure should be

clearly seen, while in a smaller one the FCC structure with the element of BCC structure should be obtained.

It is necessary to mention that the bond length and the bond order were also investigated. The obtained results are summarized in Table 2.

Atom number in a particle	Single bond length, Å	Double bond length, Å	Coordinated bond length
6	2.2	2.0	2.3
8	2.1 - 2.2	2.0	2.3
10	2.1 - 2.2		2.4
12	2.27		2.3
14	2.15- 2.27		2.3
16	2.15- 2.27		2.3

Table 2. The bond lengths obtained in the investigated particles

It is emphasized, that EXAFS MFT provides a Co-Co inter-atomic distance in the nanoparticle as equal to 2.561 ± 0.015 Å. The comparison of the theoretical investigation of the Co particles with the corresponding experimental data is rather complicated quantitatively. The use of a restricted basis set of Co which can limit the quantitative analysis in the theoretical calculations should be taken into account. Hence, the obtained bond length fits well enough into the above-mentioned results. That obtained structures of the Co nanoparticle are to be mentioned as not fully spherical. The results obtained fit the results of the high magnification TEM image perfectly. In any case it is possible to see that double bonds are ruptured when the number of Co atoms is increased while coordinate bonds remain. The Co-Co bond elongation within the increasing atom number in the particles is not possible to explicitly be exhibited, while the presence of the coordinated bond allow us to foresee that the total electron density in this Co-Co bond is smaller than that in the other bonds what leads to non-compensation of the electron spins. On the other hand, the results exhibit that investigated Co nanoparticles are not homogeneous systems, i.e. the systems consist of different-fold-coordinated atoms. The obtained results indicate that a Co atom is three-to-seven-fold coordinated in the most stable nanoparticles. The presence of a coordinated bond, that is a kind of 2-centre, 2-electron covalent bond in which the two electrons derive from the same atom, prove the above results, too. Additionally performed analysis of the molecular orbital nature indicates that in the Co derivatives the number of bonding molecular orbitals, that may be occupied, is insufficient to locate all electrons of the system. It implies that some electrons are displaced on the anti-bonding orbitals, the energy of which is higher than that of the bonding orbitals. This electronic non-uniformity (a different oxidation state of an atom in the particle) of Co atoms, as we will prove below, and the electron displacement on the anti-bonding orbitals are important for the magnetic properties of the Co nanoparticles consisting of the even number of atoms.

3.1.1 Magnetic properties of the pure Co nanoparticles

Aiming to explain the results on magnetic properties of the particles investigated as well as particle dependence on the size, we paid our attention to the nature of molecular orbitals and their placements, because the studies on the Co_2O_m ($m=0-7$) compound indicate that

both the increase of the number of oxygen atoms in the compound and the changeability of the oxidation state of the Co atoms led to the increase of the Co-Co bond length and weakening of the Co-Co bonds. The weakening of these bonds is important for the magnetic properties of these compounds. The results obtained indicate that the displacement of the two electrons on d_{z^2} orbitals of Co atoms creates Co-Co bonds. The energy of these orbitals is similar to that of other ones. Thus, the repulsion between the electrons on the d_{z^2} orbitals is larger than in other cases investigated, therefore these electrons tend to be as far as possible from each other and the correlation between them is weakened, resulting in the elongation of Co-Co bonds and, as a consequence, presence of an unpaired spin.

Let us remember that in the Co derivatives the number of bonding molecular orbitals that may be occupied is insufficient to locate all electrons of the system. As example, in Co_6 compounds all bonding orbitals are occupied and, as it has already been mentioned, some electrons are displaced on the anti-bonding orbitals, the energy of which is higher than that of the bonding orbitals.

It should be mentioned that the increased number of Co atoms in the compound leads to weakening of Co-Co bonds what, as we think, is important for the magnetic properties of these compounds, because magnetic properties depend on the bonds' nature and the number of bonds as well as on the charge distribution. Thus, aiming to explain the magnetic properties of the investigated particles, the attention is paid to the bonds' nature (what orbitals consist of bonds), the dipole moment and its components as well as on the isotropic g-tensor which depends on a spin angular moment.

In Table 3 the data on magnetizability, dipole moment, isotropic g tensor and the number of bonds consisting of anti-bonding orbitals are presented. The analysis of the most important orbitals (HOMO) of the described particles has been performed (Figs. 4-9). Fig.6 represents a full view of the HOMO of the Co_6 particle and the additional schematic presentation of the bond places in the particle is given to better illustrate the results presented.

Compound	Magnetizability, a.u.	Isotropic g-tensor	Dipole moment, a.u.	Number of bonds consist of anti-bonding character
Co_6	58.77	-0.513	0.097	5
Co_8	25.79	-0.289	0.468	3
Co_{10}	-26.13	-0.071	0.084	5
Co_{12}	-35.11	-0.038	0.213	20
Co_{14}	-39.27	-0.046	0.157	8
Co_{16}	69.84	-0.163	0.331	3

Table 3. The data on magnetizability, dipole moment, g tensor and the number of bonds consisting of anti-bonding orbitals.

Firstly, it is necessary to mention, that in the g-tensor of a molecule, there is a nuclear contribution and an electronic sum-over-states contribution. The electronic contribution represents an isotropic g-tensor. Here, it should be mentioned, that an isotropic g-tensor along with magnetizability is calculated to recognize what contributions (nuclear or electronic) are more important for the magnetic properties of the particle investigated.

It is possible to see that only Co_6 , Co_8 and Co_{16} particles exhibit paramagnetic properties although the bonds that are of anti-bonding character are present in all the particles investigated. The different number of bonds formed of anti-bonding orbitals is present in the Co_6 , Co_8 and Co_{16} particles. The view of the particles and location of the above bonds are presented in Figs. 4-9. The conclusion on the character of bonds was made on the basis of the analysis of the most important atomic orbitals on atoms, bond lengths, bond order and views of the orbitals.

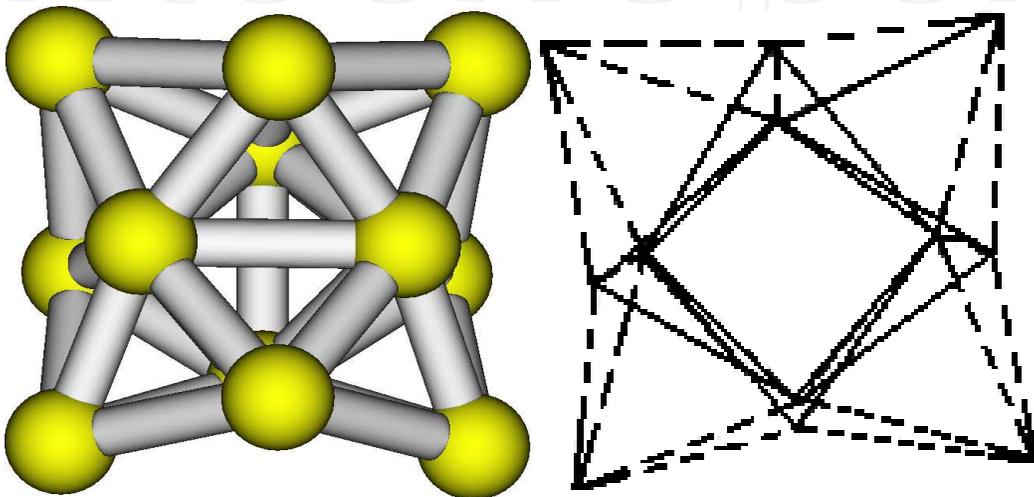


Fig. 4. The views of Co_{12} particle on the left and the view (on the right) when the bonds form of anti-bonding orbitals are marked by dash lines.

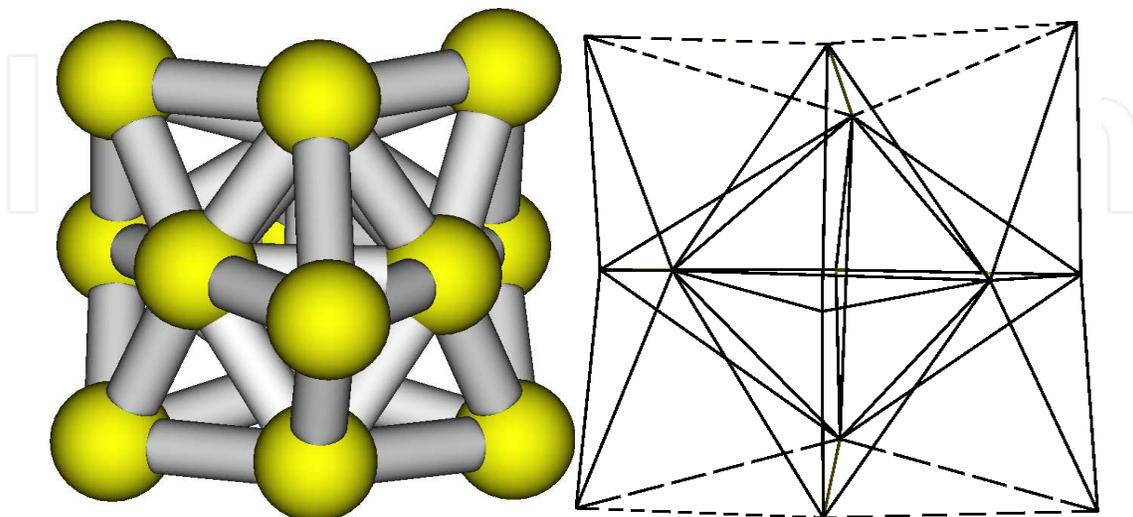


Fig. 5. The view of Co_{14} particle on the left and the view (on the right) when the bonds form of anti-bonding orbitals are marked by dash lines.

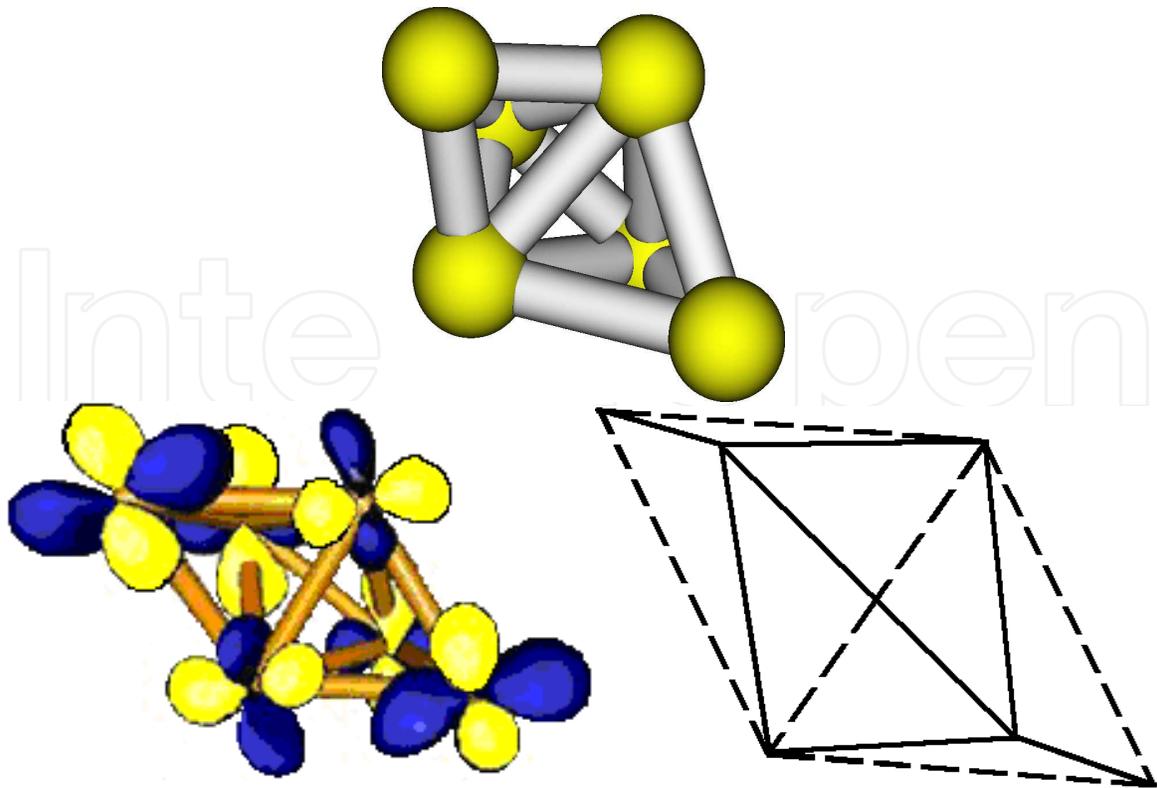


Fig. 6. The views of Co_6 particle (on the left) and their most important orbital (HOMO) (in the centre). The same view (on the right) is given when the bonds form of anti-bonding orbitals are marked by dash lines for simple guidance.

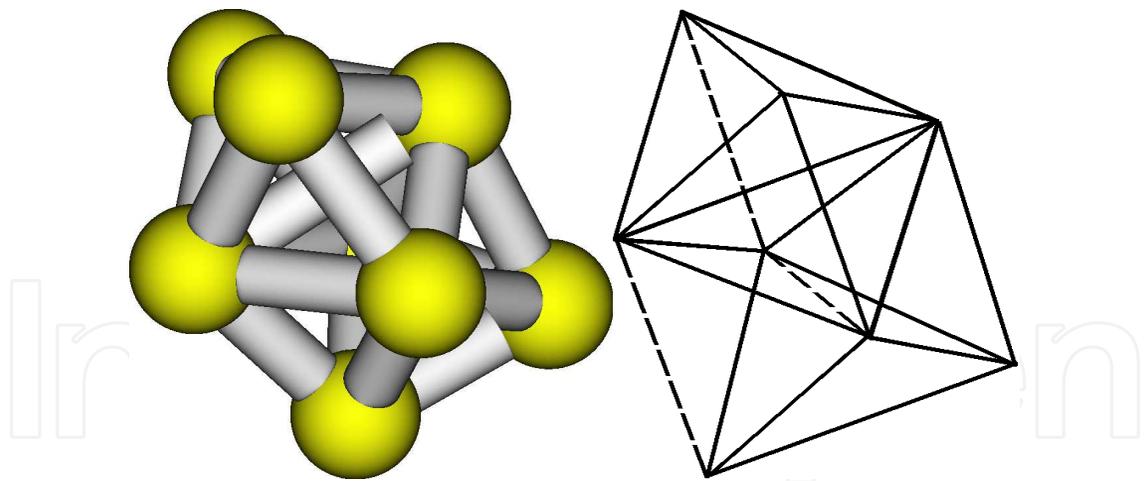


Fig. 7. the views of Co_8 particle (on the left) and the same view are given when the bonds consisting of anti-bonding orbitals are marked by dash lines.

Hence, it is possible to see that Co_{12} and Co_{14} are diamagnetic because in these particles there are 18 and 4 respectively symmetrically placed bonds with weakly interacting electrons what leads to the disappearance of non-compensate spins. These non-compensated spins quench each other what indicates the isotropic g -tensor value being equal to 0.038 and 0.046 in comparison to the value 2.00 for a free electron and indicates the absence of free electrons or a non-compensate spin.

In case of Co_{12} , the oxidation state of Co atoms is even. So, a non-compensate spin can not appear because the atoms of this particle loose the even number of electrons (below, it is exhibited that the oxidation state of atoms is also important to the explanation of Co particle magnetic properties).

The electronic properties of the Co_{14} particle fit described properties of the bond nature and oxidation state of the atoms very well. In the case the even number of bonds that are of anti-bonding character is found. Hence, electron spins are compensated and this particle exhibits diamagnetic properties. Additionally, even number (four) of atoms with oxidation state +3 are present

In case of Co_6 , Co_8 , Co_{10} , Co_{16} there are non - symmetrically placed bonds with weakly interacting electrons. Thus, we may suspect that these particles could be paramagnetic.

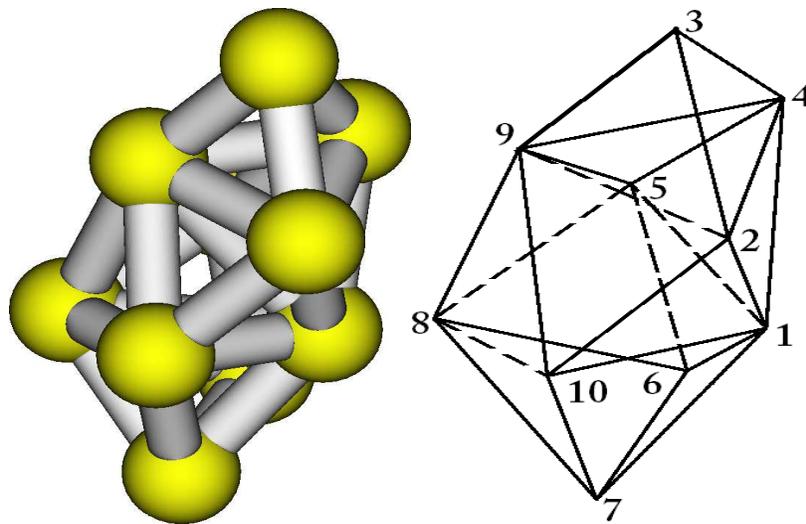


Fig. 8. The views of Co_{10} particle (on the left) and the view (on the right) when the bonds form of anti-bonding orbitals are marked by dash lines.

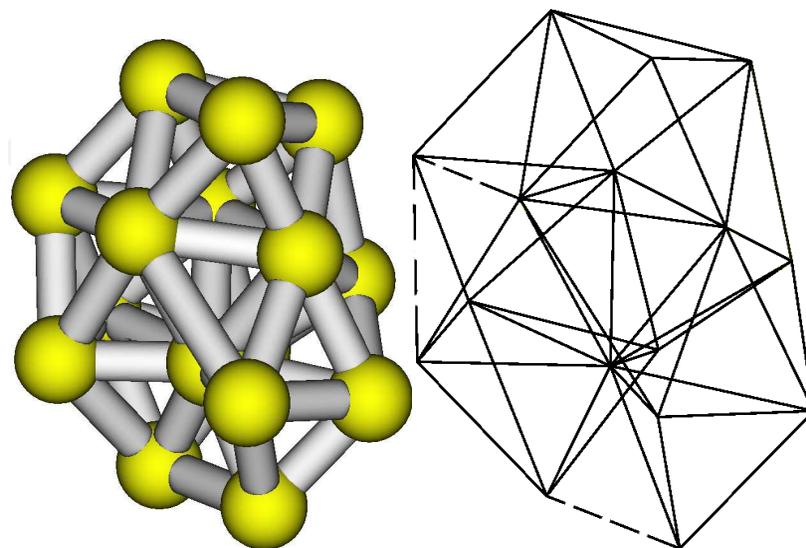


Fig. 9. The views of Co_{16} particle (on the left) and the view (on the right) when the bonds form of anti-bonding orbitals are marked by dash lines.

The magnetizability and g -tensor of the Co_6 particle are approximately twice larger than those of the Co_8 particle. In the Co_6 particle the number of bonds of anti-bonding character is five and these bonds are non-parallel. The dipole moment of the particle is approximately zero. It allows us to conclude that this particle is paramagnetic due to the electronic contribution, i.e. the repulsion between the electrons located on the anti-bonding orbital is large, therefore, they tend to be as far as possible from each other and become non-strongly correlated. Thus the spins of the electrons are not compensated, while the unparalleled displacement of the bonds leads to that that spins of all non-strongly-correlated-electrons are not compensated. It implies, that magnetic properties of the Co_6 particle are related with an electronic contribution.

A similar situation is obtained in case of Co_8 particle. Approximately twice smaller magnetizability of this particle than that of Co_6 is present because in the particle the number of non-strongly- correlated electrons is smaller than that in Co_6 .

The largest magnetizability is the Co_{16} particle, although, its isotropic g -tensor is approximately twice smaller than that of Co_6 particle. To explain the above mentioned contradictions, we investigated a dipole moment of these particles. The dipole moment indicates electron concentration places in a particle. On the other hand, the components of these dipole moments allow us to foresee the distribution of the above places. Both the concentration of electrons and their distribution helps us to find the appearance of the additional spins due to the different oxidation states of the Co atoms, i.e. if the even number of atoms loose the odd number of electrons and the particle possesses a dipole moment, we may suspect the presence of the localization of electrons and non-compensation of their spins. We named the above spin an ion one to simplify the discussion.

The dipole moment components of the particles are presented in Table 4 and indicate the electron charge delocalization in the Co_8 and Co_{16} particles, while in case of the Co_{10} and Co_{12} particles, the charge localization occurs (see the component of dipole moment). It is necessary to add, that in Co_8 and Co_{12} cases, the oxidation states of Co atoms are even. It allows us to predict, that electron spins occurring when the atoms loose an electron are compensated.

In case of Co_{16} particle, the dipole moment components indicate charge delocalization, while the isotropic g - tensor value is smaller than that of Co_6 and Co_8 . It allows us to conclude that the magnetic properties of this particle are mostly related with nuclear contribution. However, it is not explicitly possible to recognize the folding of atoms such as 3.49 or 3.51 on the results of these calculations. Thus, it is only speculation based on the comparison of the magnetizability of the investigated results that, in case of Co_{16} particle, the ion spins and electron spins are not compensated.

The Co_6 , Co_8 and Co_{16} particles are paramagnetic, while Co_{10} , that possesses the odd number of anti-bonding character bonds as the particles mentioned, indicates diamagnetic properties. In case of Co_{10} particle, the oxidation state of the Co1 atom is +5 (Fig. 8). The four bonds with anti-bonding character are displaced like in case of Co_6 , however, one bond is in the same direction of the largest component of the dipole moment. Thus, it is possible to suspect, that in this case a weakly interacting electron spin is quenched by the ion spin. It may be concluded that paramagnetic behaviour is dominating when the uncompensated

spin is present due to the presence of a weakly interacting electron on the anti-bonding orbital and this spin is not quenched by the ion spins.

Compounds	Dipole moment, a.u.	Dipole moment components, a.u.		
		x	y	z
Co ₆	0.097	-0.09	-0.01	-0.01
Co ₈	0.468	0.147	0.298	0.329
Co ₁₀	0.084	0.076	0.031	0.021
Co ₁₂	0.213	0.198	-0.051	-0.061
Co ₁₄	0.157	-0.077	0.094	-0.098
Co ₁₆	0.331	-0.107	0.167	-0.264

Table 4. Dipole moments and their components of the investigated particles that are paramagnetic or weakly diamagnetic.

It is possible to see that the investigated systems are very flexible and it is possible to predict that any dipole interaction or Co particle agglomeration could change their magnetic properties. To confirm the above prediction, the magnetic properties of the Co₆ and Co₆ as well as those of Co₆ and Co₁₂ derivatives have also been investigated.

The structure of Co₆ and Co₆ particles was found after global optimization. The results obtained indicate possible agglomeration of these particles, i.e. the Co₁₂ particle should formed. The magnetizability of this compound is -12.55 a.u., what indicates diamagnetic properties.

In case of the Co₆ and Co₁₂ compound, we did not perform any geometry optimization to avoid agglomeration of particles because the changes of geometrical structure lead to dramatical changes of the electronic structure and consequential changes of magnetic properties. The investigated particles were placed randomly. Indeed, a compound consisting of Co₁₂ and Co₆ particles is paramagnetic and its magnetizability is equal to 24.65 a.u. The results clearly indicate that dipole interaction and particle agglomeration change magnetic properties of the Co nanoparticle.

4. Structure, stability and magnetic properties of Co₆ O_m nanoparticles

4.1 Structure and stability of Co₆O_m particles

As exhibited above, the stability of small Co nanoparticles is not very high. On the basis of our previous investigations it was speculated that those nanoparticles were non-rigid structures. It implies that the geometrical structure of these particles could change very quickly due to the tunnelling effect. Let us remember that Co₆ particle is found as the most stable one and it is the key element of other particles investigated. So, Co₆O_n (n=0-9) derivatives were also investigated to establish how the magnetic properties of the Co particles may change due to oxidation. On the other hand, these investigations allow us to foresee the conditions under which the metal Co-Co bond is broken. It is also proved our prediction that the particles consisting of the even number of atoms possess magnetic properties due to the weakly interacting electrons on the anti-bonding orbital and this spin is not quenched by additional spins that occurred because some atoms of the nanoparticle loose the odd number of electrons.

The most stable structures of the Co_6O_n derivatives are presented in Fig.10.

Firstly, it is necessary to mention that oxygen stabilizes the Co nanoparticle and the increasing number of oxygen atoms increases the binding energy per atom up to $n=7$ (Table 5). Furthermore, when a certain limit is reached, oxygen atoms do not influence the stability of the Co_6O_n particles.

The Co_6O_{12} particle was investigated too. The binding energy per atom of this particle is equal to 3.26 eV what is similar to that of Co_6O_n ($n=7, 8, 9$). The difference of the binding energy of the above particles is too small (0.2 eV or less) to make the conclusion on the most stable particle.

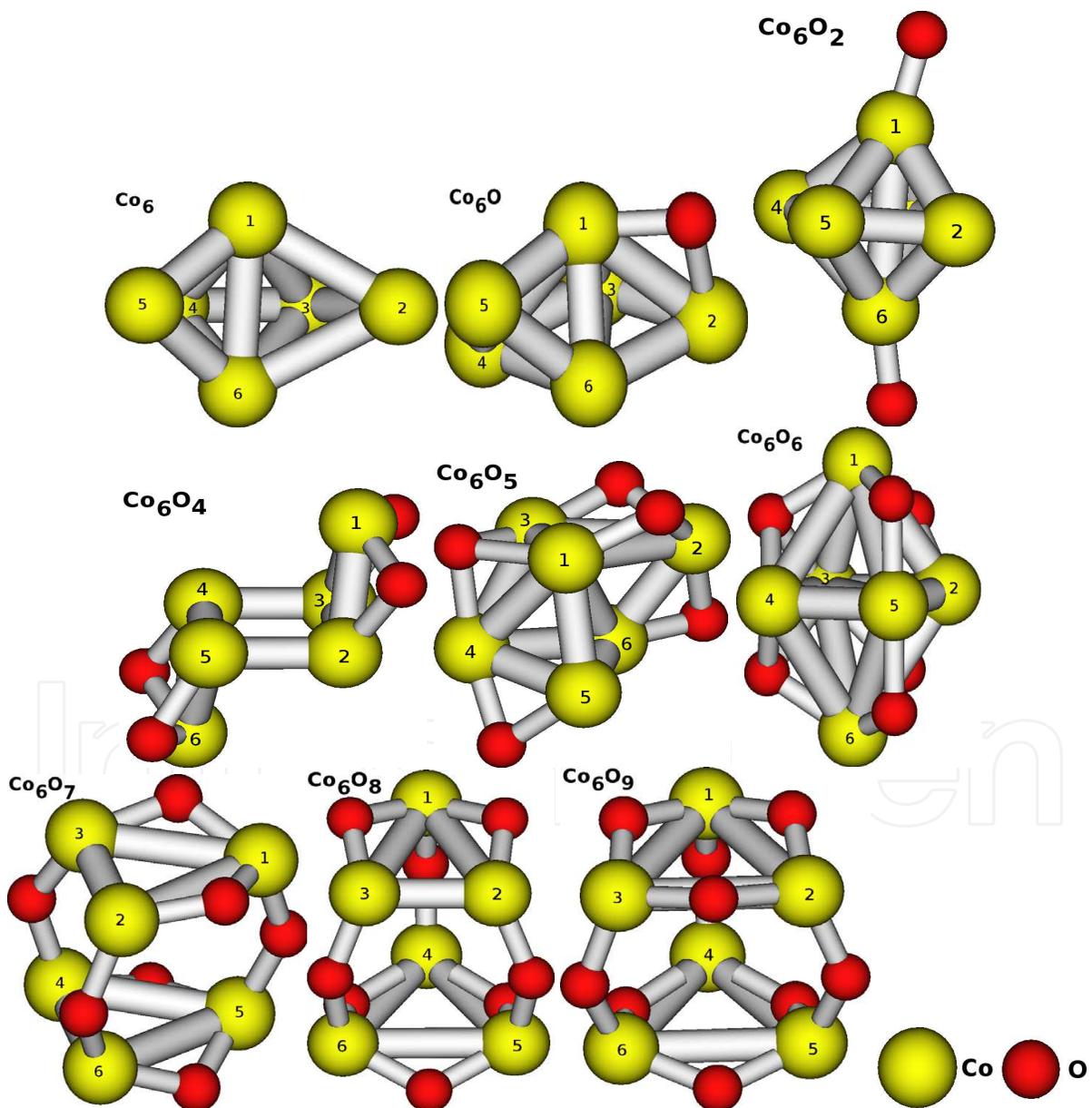


Fig. 10. Views of the particles investigated. Grey lines do not indicate real chemical bonds, but are implemented for the sake simple guidance.

Particle	Co ₆	Co ₆ O	Co ₆ O ₂	Co ₆ O ₃	Co ₆ O ₄	Co ₆ O ₅	Co ₆ O ₆	Co ₆ O ₇	Co ₆ O ₈	Co ₆ O ₉
Binding energy per atom, eV	0.45	0.93	1.21	2.22	2.49	2.85	3.22	3.43	3.33	3.48

Table 5. Binding energy per atoms for the Co₆O_n (n=0-9) particles

The difference of the binding energy per atom for Co₆ and Co₆O is equal to 0.48 eV, while that between Co₆O₆ and Co₆O₇ is only 0.21 eV, i.e. twice less. On the other hand, the changing of the number of oxygen atoms from 2 to 3 leads to the largest increase of the binding energy per atom (1.01eV), while the binding energy per atom increase only up to 0.27 eV when the oxygen atom number in a particle increases from 3 to 4. Thus, the results of our investigations allow us to foresee that starting with n=6 (n is the number of oxygen atoms) the further increase of the number of oxygen atoms will not influence the stability of these particles very strongly and the main structure (the key-element) is not considerably changed (Fig. 10). The binding energy per atom of the Co₆O₆, Co₆O₇, Co₆O₈ and Co₆O₉ is approximately equal and proves these particles to be the most stable. These results coincide with the experimental measurements that indicate the presence of CoO and Co₃O₄; CoO₂, Co₂O₃ and Co₆O₇ particles should also be found among them what was proved by the results we obtained.

Such a changeability of the binding energy per atom in some cases could be explained by changes in geometrical structure of Co particle. In case when the additional oxygen atom does not significantly increase the binding energy per atom, the main part of the energy of this atom is used to deform the structure of the key element (Co₆). Thus, the binding energies per atom of Co₆O₃ and Co₆O₄ or Co₆O₆, and Co₆O₇ are approximately equal.

The key element of the Co₆ is also present in the Co₆O_n (n=0-9) derivatives. However, this key element is slightly deformed. The changeability of the initial form is oxygen atom depended. The largest deformation is obtained in Co₆O₇, when the distance between the planes (formed of atoms 1, 2, 3 and of 4, 5, 6) is increased and one plane is rotated in respect of the other one by angle of $\pi/4$. Actually, one more structure of the Co₆O₇ which looks like Co₆O₆ was also obtained, but the energy of this formation of the particle is 1.23 eV higher than that of the particle, the structure of which was described above.

In the Co₆O₄ particle the key element (Co₆) is deformed twice: 1. firstly, when the distances between the atoms Co2-Co5 decrease; 2. Secondly, when Co1 and Co6 positions in respect of the plane that is formed of atoms 2,3,4,5 is changed. Here, it should be emphasized, that this structure of the particle has been obtained after global geometry optimization starting with several completely different initial geometries. Thus, the geometrical structure of the Co₆O₄ particle is confirmed.

Hence, the largest deformations of the Co₆ particle are obtained when the number of oxygen atoms is changed from 3 to 4 and from 6 to 7. In these cases the stabilization energy per atom is smaller than in other cases investigated. Thus, the main part of Oxygen energy is used to deform the key structure of Co₆.

It is necessary to mention, when the number of oxygen atom is 2 and 6, the structure of the Co₆O_m particle looks like the octahedron, while in case of odd numbers of oxygen the octahedron form is strongly deformed (except the results for Co₆O₄). It is interesting to note

that the most stable structure of Co_6O_8 (prototype of Co_3O_4) has a deformed spinel structure. Thus, it is not surprising that a large effective magnetic moment estimated from the inverse susceptibility has not been explained properly.

Compound	Co-Co bond length, Å								
	1-2	1-3	1-4	1-6	2-3	2-6	4-5	4-6	3-4
Co_6	2.15	2.33	2.15	2.24	2.04	2.23	2.04	2.31	2.33
Co_6O	2.54								
Co_6O_2				3.01					
Co_6O_3				2.18	2.37	2.33	2.14		
Co_6O_4	2.27	2.27	2.27	4.72				2.27	
Co_6O_5	2.25				2.61	2.25			2.39
Co_6O_6	2.83	2.67	2.89		2.32	2.87			2.44
Co_6O_7	2.93			3.11	2.93		2.93	2.93	
	1-2	1-3	1-4	2-3	2-5	3-6	4-5	4-6	5-6
Co_6O_7	2.92	2.93	3.21	2.21*	3.07	3.11	2.92	2.91	2.22*
Co_6O_8	2.88	2.90	3.21	2.24*	3.18	3.16	3.03	3.03	2.93
Co_6O_9	3.04	3.04	3.15	3.04	3.14	3.15	3.04	3.05	3.05

* the Co-Co bond is present.

Table 6. The distance between the Co atoms which are connected with the O atom.

According to the results of our investigations, the Co-Co bond length of the single bond is longer (2.2 Å) than the bond length of a double bond (2.0 Å) in a Co_6 particle. On the other hand, three bonds were obtained where the length is equal to 2.3 Å. The bond order of the largest bond is twice smaller than that of a single bond. Here, we the commonly observed that the Co-Co bond lengths are marginally changed only between the atoms that are connected with the oxygen atom (Table 6) and, as a consequence, the bond enlargement leads to Co-Co bond dissolving. For example: in the Co_6 particle the bond order between Co1-Co5 is equal to 1.018, while that in Co_6O_4 is approximately twice smaller and equals to 0.55. Additionally, the two, one and zero Co-Co bonds are respectively found in the Co_6O_7 , Co_6O_8 and Co_6O_9 nanoparticles. To shed some light on the present observation, the analyzes of the most important orbitals of the Co_6 particles have been investigated. HOMO (the highest occupied orbital)- LUMO (the lowest unoccupied orbital) gap dependence on the number of oxygen atoms is represented in Fig. 11. The HOMO-LUMO gap indicates that chemical stability of Co_6 , Co_6O_4 and Co_6O_6 is very low, i.e. they tend to form new chemical bonds. These results coincide well with the results of binding energy per atoms.

However, the electronic structure of the investigated particles is quite different because the oxidation state of Co atoms exchanges when the number of oxygen atoms in the particle is increased. For example, in Co_6O particle oxidation state of Co atoms is +3 and +4; in the Co_6O_2 particle the oxidation state of these atoms is +4 and +5 and in Co_6O_4 it is +1 and +3. We have not observed any relationship between number of oxygen atom in the particle and the oxidation state of Co atoms.

Let us remember that in the Co derivatives the number of bonding molecular orbitals, that may be occupied, is insufficient to locate all the electrons of the system. This leads to the

presence of electrons on the anti-bonding orbital and, as a consequence to, the dissolution of Co-Co bonds.

On the other hand, the electronic configuration of cobalt for the ground state neutral gaseous atom is $[\text{Ar}].3d^7.4s^2$, while that of oxygen is $[\text{He}].2s^2.2p^4$. The configuration, associated with Cobalt in its compounds, is not necessarily the same, but it could be used to explain formally obtained results.

As it was mentioned above in Co_6 compounds some electrons are displaced on the anti-bonding orbitals, the energy of which is higher than that of the bonding orbitals. Therefore, the stability of the pure cobalt nanoparticle is low. When the Co_6 nanoparticle is joined to one or two oxygen atoms, the number of electrons that occupy anti-bonding orbitals, decreases because these electrons occupy the oxygen orbitals (Fig.12)

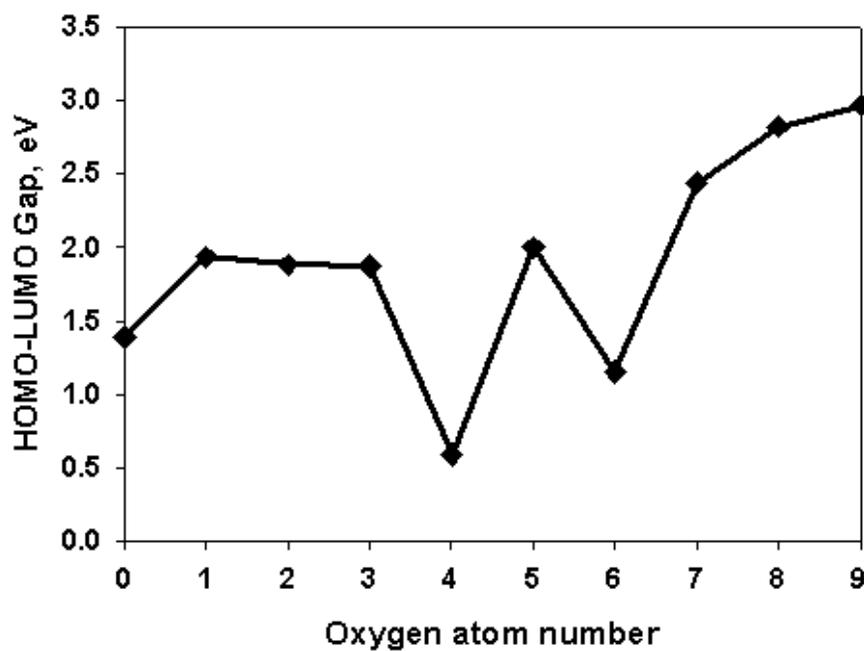


Fig. 11. The HOMO-LUMO gap of the Co_6O_m ($m = 1 - 9$)

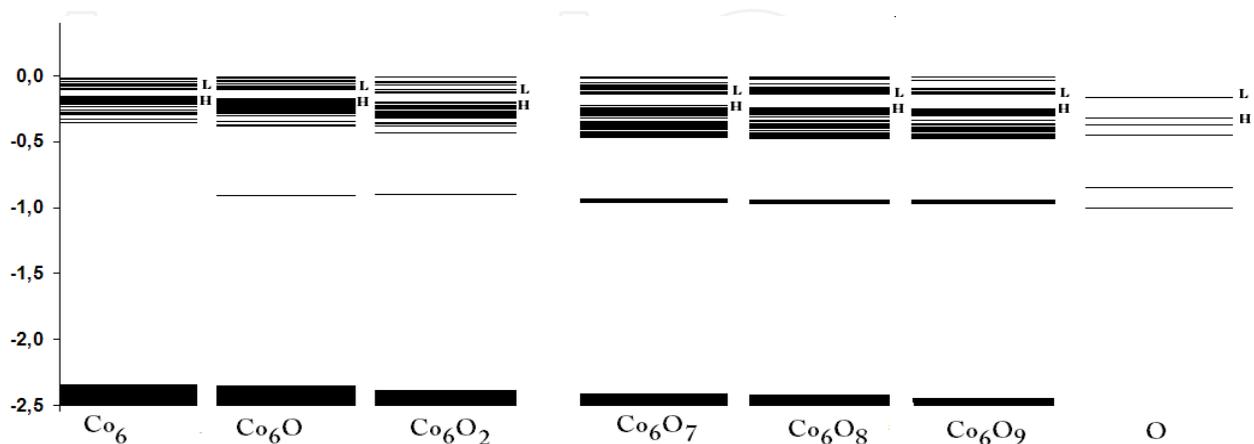


Fig. 12. Displacement of orbitals of several Co_6O_m ($m=0, 1, 2, 7, 8, 9$) and oxygen atoms in respect of each other. Here, H and L indicate HOMO and LUMO respectively. Additionally, the ground state (triplet) of oxygen atoms are calculated. It is possible to see that with the

increasing number of the oxygen atoms in the particle, the number of occupied orbital also increases. i.e. the number of bonds of anti-bonding nature decrease.

Oxygen atoms in the Co_6O_4 , Co_6O_3 , Co_6O_2 , and Co_6O particles are joined to atoms between which the anti-bonding orbitals occur. Having in mind that the joining of oxygen atoms leads to the increase of the bond length and dissolution of Co-Co bonds, what confirms the above mentioned prediction. In case of the Co_6O_3 particle, one O atom is joined to Co4-Co5 atoms (Fig.10). The anti-bonding nature of the bonds has not been observed between those atoms. In this case, a steric effect is more preferable because other positions of the oxygen atom should complicate Co1-Co2 and Co2-Co6 elongation or leads to the destruction of this particle. Hence, oxygen atoms stabilize Co_6 particles due to dissolving of Co-Co bonds that possess anti-bonding character.

It is very well known, that a semiconductor must have at least two characteristics: 1. the bonding and anti-bonding orbitals must form a delocalized band; 2. the HOMO-LUMO gap in molecular species should be generally of the order of 0.5eV to 3.5 eV. HOMO-LUMO gaps of the investigated derivatives belong to the above range. However, the number of anti-bonding orbitals decreases with increasing of the number of oxygen atoms. The results allow us to predict that Co_6O_m are semiconductors but the particles should lose their semiconductor properties if the number of oxygen increases.

4.1.1 Magnetic properties of Co_6O_m particles

In the above chapter we proved that oxygen atoms stabilize cobalt nanoparticles, although, in some cases, the structure of particles changes insufficiently while the electronic structure is dramatically changed because the increasing number of oxygen atoms decreases the difference between the number of electrons and the number of atomic orbitals that they may occupy. Hence, the bonds of anti-bonding nature as well as uncorrelated spins disappear. So, we may suspect, that all Co oxide particles could be diamagnetics. Let us analyze the results presented in Table 7.

Compound	Magnetizability, a.u.	Isotropic g tensor a.u	Co-Co bond number
Co_6	58,77	-0,51	5
Co_6O	-11,24	-0,14	6
Co_6O_2	-15,47	-0,11	6
Co_6O_3	-3,26	-0,16	5
Co_6O_4	-9,62	-0,12	4
Co_6O_5	-15,97	-0,11	2
Co_6O_6	-2,11	-0,16	1
Co_6O_7	-25,94	-0,07	2
Co_6O_8	25,42	-0,18	1
Co_6O_9	-24,28	-0,05	0
Co_6O_{12}	-24,25	-0,07	0

Table 7. Data on magnetizability, isotropic g tensor, and Co-Co bonds number and the number of Co-Co bonds that was found based on the electron density investigation results. Only those bonds with unpaired spin electrons are mentioned.

It is obvious to see, that the particles with odd number of Co-Co bonds are paramagnetic or lightly diamagnetic. On the other hand, the isotropic g-tensor value of the cobalt oxide particles is not large, thus we may suspect that a ion spin in these cases is very important.

It is necessary to mention that based on the results described above, we may divide the described particles into the following groups:

1. The particles that posses shape of Co_6 : Co_6 , Co_6O , Co_6O_2 , Co_6O_3 , Co_6O_5 , Co_6O_6 (A group)
2. The particles Co_6O_7 , C_6O_8 , Co_6O_9 in which the distance between the planes (formed of atoms 1, 2, 3 and of 4, 5, 6) is increased and one plane is rotated in respect the other one by the $\pi/4$ angle (B group).
3. The rest (Co_6O_4)

It has to be pointed out, that a lot of reports concluded that magnetic properties of the nanoparticles depend on their shape. So, we suspected that magnetizability of the particles belonging to one group should be the same. However, the results of our investigations do not prove the above prediction (Table 7).

According to our investigations, the Co_6 nanoparticle is a strong paramagnetic, while other particles, belonging to group A, are diamagnetics. The same phenomenon is obtained in case of B group. In this case, the Co_6O_8 particle is paramagnetic, while other particles are diamagnetics. Moreover, the diamagnetic properties of the similarly shaped particles are quite the same only in the following cases: Co_6O_7 , Co_6O_{12} , Co_6O_9 ; Co_6O_3 , Co_6O_6 ; Co_6O_2 , Co_6O_5 . It implies that the shape of the particle has no influence on the magnetic properties of the nanoparticles. To confirm this conclusion, we have calculated magnetizability of several isomers of Co_6O_8 particles (Fig. 13). It is possible to see, that the shapes of isomers II and III are similar, but the shape of isomer I differs. However, the magnetizability of isomers II and I with different shapes is approximately alike, while the magnetizability of isomer III is smaller than that of isomer II with the same shape (Table 8).

Isomers	I	II	III
Magnetizability, a.u.	25.42	24.76	14.24

Table 8. The Magnetizability of different isomers of Co_6O_8 particle.

Hence, the magnetic properties of these particles does not depend on their shape.

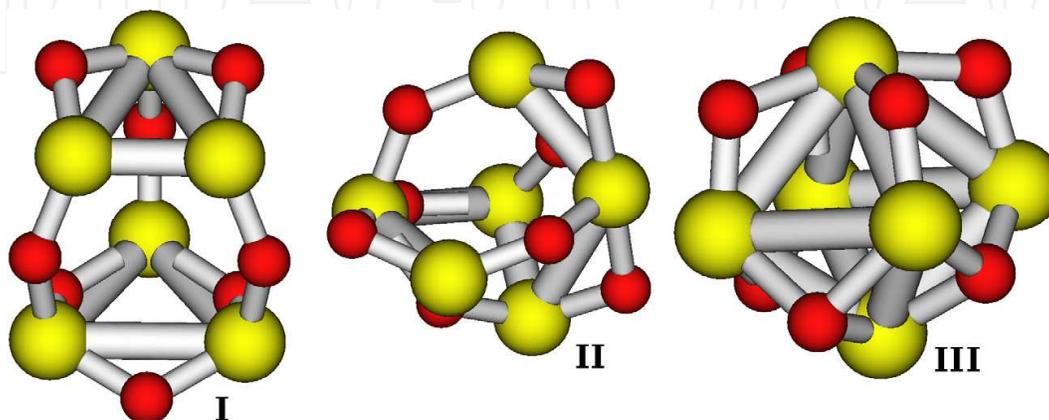


Fig. 13. The view of several isomers of Co_6O_8 .

Let us remember, that the nanoparticles could be paramagnetic due to several reasons: 1) the unpaired electron location on the Co-Co bonds; 2) the small total electron charge density between Co atoms which appears due to overlapping of p orbitals of oxygen atoms; 3) the significant contribution of atoms that loose odd number of electrons. The second reason mentioned could not be realized in case of the Co_6O_n particles due to their relatively large size and small number of oxygen atoms. The first and third reasons could be realized thus supporting the previously found results. It is necessary to mention, that non-compensation of spin for CoO/SiO₂ multilayers was also observed.

Now, we shall describe the particles of group B in detail. Firstly, it is necessary to mention, that the particles of this group have the different number of Co-Co bonds: Co_6O_7 , has two, Co_6O_8 has one, and Co_6O_9 has zero. Only Co_6O_8 particle exhibits paramagnetic properties.

Let us remember that in the Co derivatives the number of bonding molecular orbitals, that may be occupied, is insufficient to locate all the electrons of the system. This causes the presence of electrons on the anti-bonding orbital and, as a consequence, a weaker correlation of these electrons. Similar states are obtained in biradicals where the number of atomic orbitals, that may be occupied, is smaller than that of electrons. That leads to the appearance of electrons on the anti-bonding orbitals and serves predicts a large orbital contribution to the magnetic moment of a small Co_mO_n particle (Fig.14).

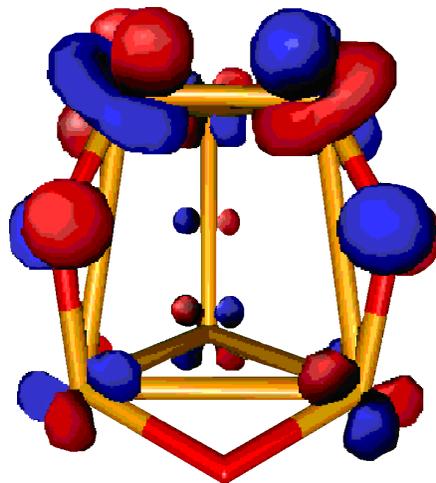


Fig. 14. HOMO orbital antibonding character of the Co_6O_8 particle.

It implies, that a non-compensate electron spin should be obtained. This situation is realized in the Co_6O_7 and Co_6O_8 particles. However, in the Co_6O_7 particle two pairs of weakly correlated electrons are present what leads to the disappearance of non-compensate spins. This is indicated by the isotropic g-tensor value which equals to 0.007. However, in case of the Co_6O_8 particle, only one Co-Co bond is present and only one pair of weakly correlated electrons should be found. This weak correlation indicates the nature of HOMO orbital that consists of anti-bonding d_{z^2} type orbitals (Fig.14). Hence, the total spin of electrons is not compensated and, as a consequence, the particle exhibits paramagnetic features. This presumption is also confirmed by the isotropic g-tensor value, that is one of the largest between the particles described (Table 7). The small value of the isotropic g-tensor indicates that the electronic contribution to the magnetic properties of the particle is not very large, but it is essential.

Additionally, we may supplement the proposition, that Co_6O_n particles should be paramagnetics when the number of Co-Co bonds on which the unpaired electrons are located might be odd (Table 7). It should be emphasized, that the number of Co-Co bonds was found on the basis of the electron density investigation results and only the bonds, where unpaired spin electrons could be presented, are mentioned. Indeed, the investigated particles with the odd number of Co-Co bonds exhibit paramagnetic or weak diamagnetic properties. However, it is not clear why the magnetic properties are different, i.e., formally, some, different features should appear.

Aiming to explain the above mentioned discrepancy, we investigated a dipole moment of these particles. The dipole moment indicates electron concentration places in the particle. On the other hand, the components of these dipole moments allow us to foresee the distribution of the above places. Both the concentration of electrons and their distribution helps us find additional spins that appeared due to the different oxidation state of the Co atoms (formally, we call the above spin as an ion one). The exception concerns Co_6 .

The components of the dipole moment of the particles that are paramagnetics or weak diamagnetics are shown in Table 9.

Compounds	Dipole moment, a.u.	Dipole moment components, a.u.		
		x	y	z
Co_6	0.096	-0.09	-0.01	-0.01
Co_6O_3	1.689	0.55	0.23	-1.58
Co_6O_6	1.639	-1.06	-1.16	0.44
Co_6O_8 (I isomer)	2.652	2.60	0.45	0.23
Co_6O_8 (II isomer)	2.059	-1.08	-0.01	-1.75
Co_6O_8 (III isomer)	1.372	1.37	-0.06	-0.03

Table 9. Dipole moments and their components of the investigated paramagnetic or weak diamagnetical particles.

The Co_6O_8 particle is a paramagnetic due to the presence of non-compensate spin what indicates the value of the isotropic g -tensor of 0, 51 (a free electron g -value is 2.00) because of the appearance of electrons on the anti-bonding orbitals.

So, as it was mentioned, the following different types of magnetic interactions could be obtained in the Co_6O_m nanoparticles: 1. an uncompensated spin of weakly interacting electrons on the anti-bonding orbital; 2) the presence of Co ions that loses the odd number of electrons (Co^{+3} and the like) leads to the emergence of the additional non-compensated spin.

The results obtained exhibit that the magnetic properties of nanoparticles could depend on the above interactions. The paramagnetic behaviour dominates when the non-compensated spin is present due to weakly interacting electrons on the anti-bonding orbital and this spin is not quenched by the ion spins. Let us remember, that Co_6O_3 and Co_6O_6 particles are weak diamagnetics, though the isotropic g -tensor is not smaller than that of the Co_6O_8 particle. In

these particles the ion spin is also presented what indicates a high dipole moment. The number of the Co^{+3} ions is 2 and 4 respectively in the Co_6O_3 and Co_6O_6 particles. However, the components of the dipole moment indicate that the ion spins are delocalized. The interaction between these spins leads to the quench of an electron spin, i.e. both spins (ion and non-compensated spin of electrons located on the anti-bonding orbital of Co-Co bond) are oriented so that the total spin equals to zero.

The opposite situation is realized in the Co_6O_8 particle: an ion spin is localized and one Co-Co bond is present. In this case, the spins are oriented so that they are relatively parallel to each other. This prediction is supported by additional investigations of the isomers of the Co_6O_8 particle. It is necessary to mention, that one Co-Co bond is present in isomer II and a detailed investigation of the dipole moment indicates that it lies approximately in parallel to the Co-Co bonds. Therefore, the unpaired spins of a different nature support each other. Thus, the magnetizability of the I and II isomers of the Co_6O_8 particle is the same. In case of isomer III, all Co-Co bonds are dissolved, but an ion non-compensated spin is present. It implies that magnetic properties of the particle are determined by the localized ion spin only. Thus, the magnetizability of isomer III is lower than that of the other isomers investigated.

Hence, the paramagnetic behaviour of the cobalt oxide particle is dominating when the non-compensated spin is present due to weakly interacting electrons on the anti-bonding orbital and this spin is not quenched by the ion spins.

It is necessary to pay attention to other important observations. As it was earlier mentioned, the cobalt oxide particles are semiconductors and Co_6O_8 exhibits magnetic properties. It implies that this Co_6O_8 particle could be magnetic superconductor and could be implemented in electronic devices to provide a new type of the control of conduction, i.e. of the charge carrier and quantum spin state. Hence, this particle could be used in quantum computing.

5. Absorption spectra of the C_6O_m ($m=1-9$) nanoparticles

It is known that the growing metallic particles are stabilized by the absorption of the polymer chains on the surface of the growing metal fragments, lowering their surface energy and creating a barrier to further aggregation. On the other hand, the organic coating of a particle prevents the surface from oxidation, rendering the particle stable over a long period. So, it is necessary to have a tool to investigate and control the process of stabilization of nanoparticles because the stabilization could be related to the oxidation of a metal particle and, as a consequence, it loses its magnetic properties. We believe that the knowledge concerning the shape and the nature of the absorption spectra of the Co_6O_m particles in the Vis and UV region could be a good tool for the investigation of the oxidation processes of Co nanoparticles. The above assumption is based on the results obtained that indicate the Co_6 particle as a key element of larger particles.

As it was to mention in 3.1.1 we may divide the described particles into groups based on the changes of the Co_6 structures. The groups are the following:

1. The particles that possess a shape of Co_6 : Co_6 , Co_6O , Co_6O_2 , Co_6O_3 , Co_6O_5 , Co_6O_6 (group A).
2. The particles in which the distance between the planes (formed by atoms 1, 2, 3 and of 4, 5, and 6) is increased and one plane is rotated in respect of the other one by $\pi/4$ angle: Co_6O_7 , Co_6O_8 , Co_6O_9 (group B).

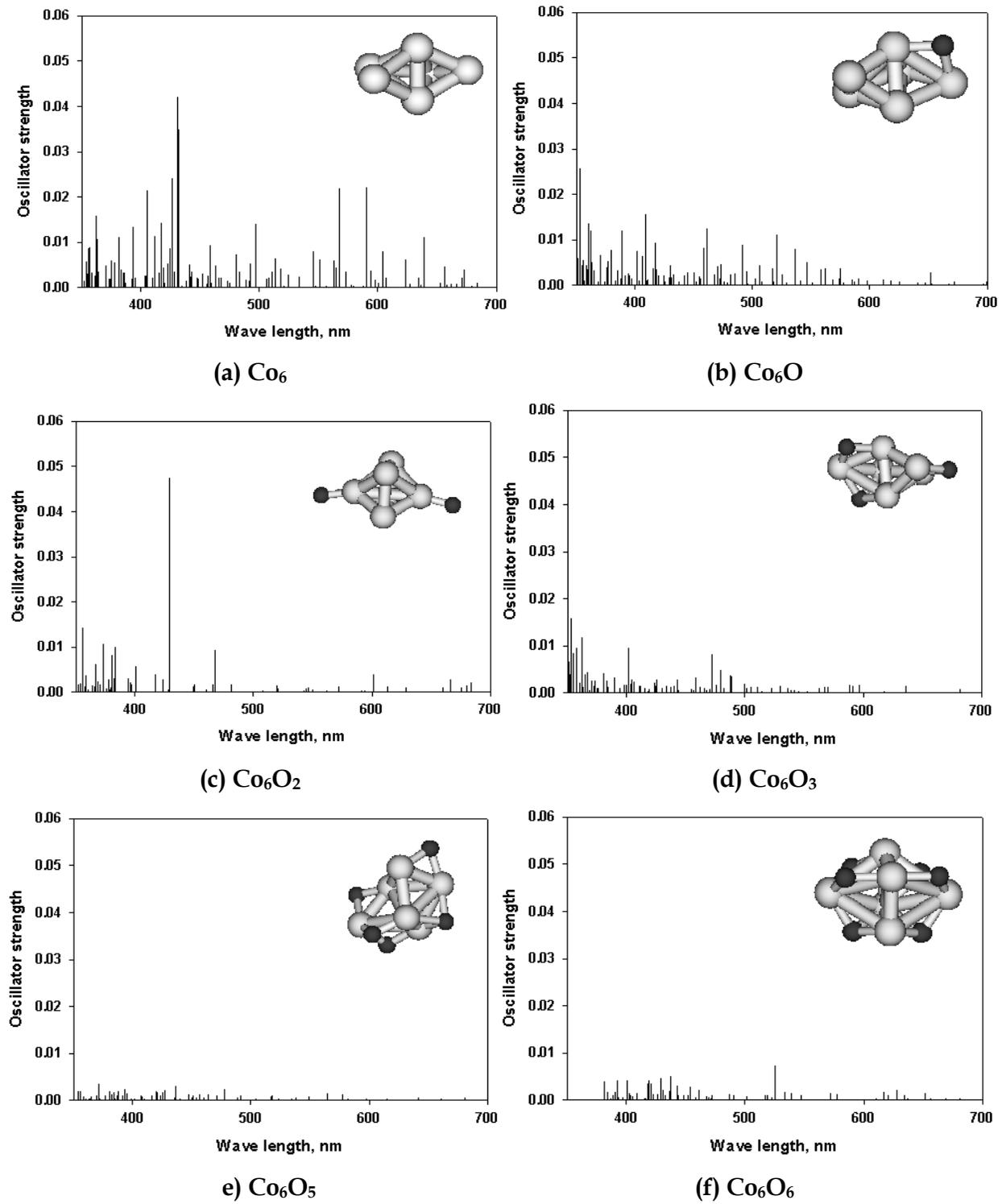
3. The rest (Co_6O_4).

Fig. 15. Absorption spectra of group A. At (a) there are spectra of a Co_6 particle, while (b) - those of Co_6O ; (c) in the middle, on the left, there is a spectrum of Co_6O_2 ; (d) on the right - Co_6O_3 ; (e) at the bottom, on the left, there are spectra of Co_6O_5 ; (f) on the right - those of Co_6O_6 . The black circle indicates oxygen atoms, while the grey one - cobalt atoms.

The obtained absorption spectra of the particles making up groups A and B and their structures are presented in Fig. 15 and Fig. 16. The case of Co_6O_4 particle is different and should be investigated deeper, although the general tendency of absorption spectra changes described below are possible to foresee in the spectra of this particle, too.

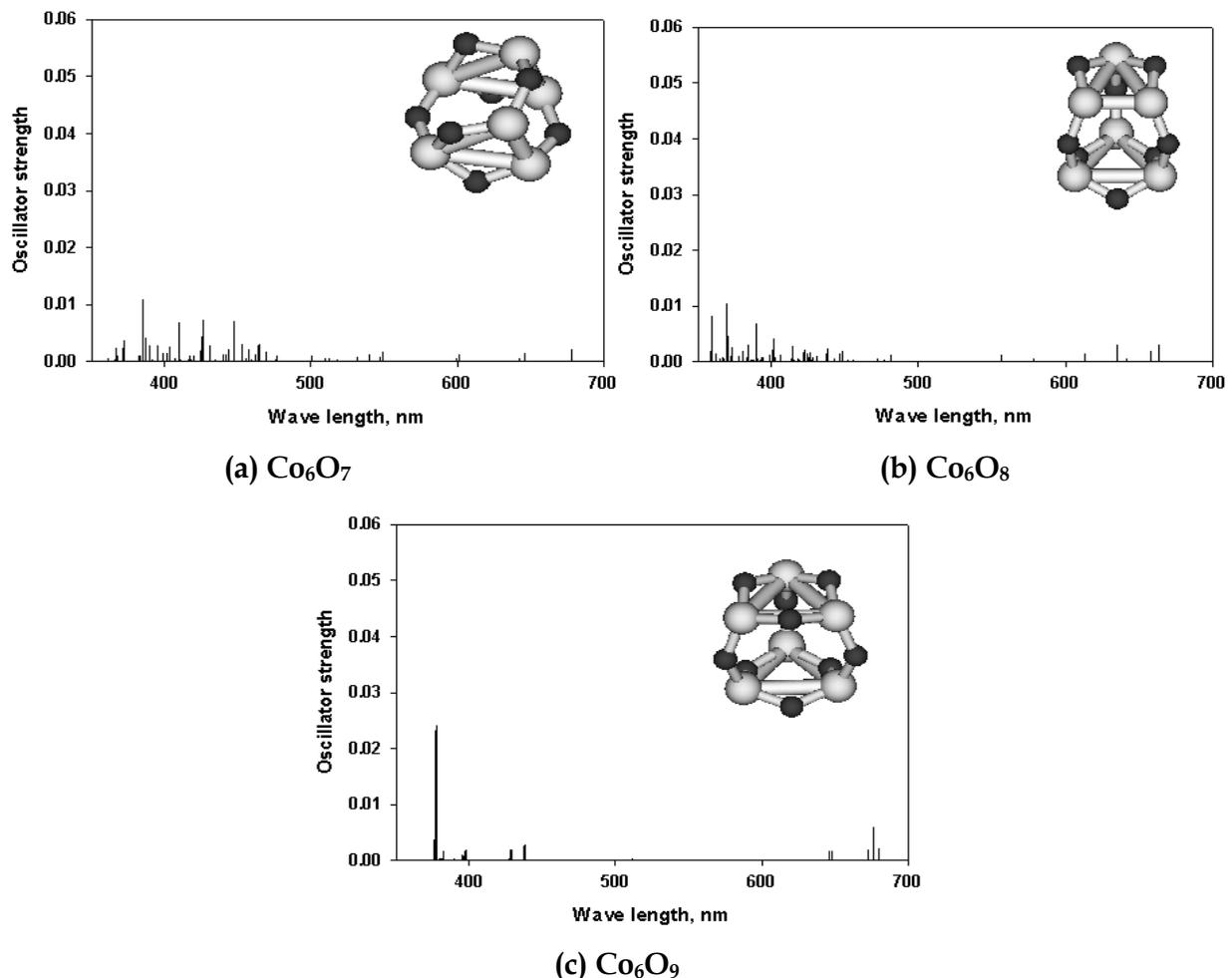


Fig. 16. Absorption spectra of group B: **(a)** at the top on left there is a spectrum of Co_6O_7 particle, **(b)** on the right -those of Co_6O_8 ; **(c)** at the bottom, there are spectra of Co_6O_9 . The black circle indicates oxygen atoms, while the grey one – those of cobalt.

Let us analyze the spectra of group A. It is obvious, that the intensity of absorption decreases especially in the [500;700] nm region with increasing of the oxygen number up till 5, and starts increasing again when the number of oxygen atoms is 6. The appearance of more intense absorption in the above region of the Co_6O_6 is related to the structure of this particle (Fig.15). The structure of the Co_6O_6 particle looks like the octahedron, while in the case of other particles investigated, the octahedron form is strongly deformed. The intensity of absorption in the region 300 to 400 nm increases when the number of oxygen atoms in the particle increases from 7 to 9 (Fig.16).

It is obvious, that with the increasing of the number of the oxygen atoms by one, the number of occupied orbitals in the [-1;0] a.u increase by three (Table 10). Moreover, the gap of the Co_6 particle between occupied orbitals in the]-2; -1[a.u. region is not filled what is explained

by the displacement of the orbitals of both Co_6O_m ($m=0-9$) and an oxygen atom in respect of each other (Fig. 12). In case of Co_6 particle, only three orbitals (HOMO, HOMO -1 and LUMO) of oxygen interact with the occupied orbitals of the particle, while in case of Co_6O_m particles, the number of interacting orbitals increases. Starting with Co_6O , the additional occupied level occurred in the gap of the Co_6 particle between the occupied orbitals in the region of $]-2; -1[$ a.u. However, the HOMO-LUMO gap increases. So, semiconductor properties of the Co_6O_m particles become stronger.

Naturally, that with the increasing number of oxygen atoms in the Co_6 particle, the mixing orbital (the molecular orbital consists of cobalt and oxygen atomic orbitals) increases due to the Co and O atomic orbital interaction. The analysis of the contribution of the atomic orbital to the molecular orbitals confirms the predicted interaction. Moreover, due to the above interaction, the orbital splits and several orbitals that are occupied in Co or Co oxide nanoparticles should become virtual and vice versa. Hence, the transitions in the spectra region of $[350;700]$ nm are of $\text{Co}3d \rightarrow \text{Co}3d$ type and they are allowed in a pure Co particle or particles with the oxygen number of 1-2 because the above mixing is not very strong.

When the number of oxygen atoms in the Co particle is 3-7, the transitions in the spectra region of $[350;700]$ nm are of $\text{Co}3d \rightarrow \text{Co}3d\text{O}2p$ or $\text{Co}3d\text{O}2p \rightarrow \text{Co}3d$ types. It is emphasized, that starting with the number of six of oxygen atoms, only occupied orbitals of nanoparticles interact with the occupied orbital of oxygen atom, i.e. the above mentioned interaction between LUMO of the oxygen atom and the occupied orbital of Co_6O_m nanoparticle does not occur. The analysis of the most important orbitals for excitation indicates, that in the spectra of Co_6O_m ($m=0-5$) the most intensive excitations correspond to $\text{Co}3d \rightarrow \text{Co}3d$ ones. Other partly allowed excitations correspond to $\text{Co}3d \rightarrow \text{Co}3d\text{O}2p$ ones. So, the number of $\text{Co}3d \rightarrow \text{Co}3d\text{O}2p$ excitations increases with the increased mixture of orbitals. Moreover, when the number of oxygen atoms is up to 7, the $\text{Co}3d\text{O}2p \rightarrow \text{Co}3d\text{O}2p$ excitations are more relevant. On the other hand, the symmetry of particles is different what leads to different number of the transitions allowed. It is very well known, that a part of the possible excitations is forbidden when the symmetry group of the particles is high, while all possible excitations are allowed when the symmetry group of the particle is the lowest (C_1).

Particles	Virtual orbitals		Occupied orbitals	
	$[-1;0]$ a.u.	$[-1;-0]$ a.u.	$[-2;-3]$ a. u.	$[-3;-4]$ a. u.
Co_6	11	27	18	6
Co_6O	13	30	18	6
Co_6O_2	13	33	15	5
Co_6O_3	12	36	17	6
Co_6O_4	15	39	14	6
Co_6O_5	13	42	18	4
Co_6O_6	13	45	18	6
Co_6O_7	15	48	18	6
Co_6O_8	15	51	18	6
Co_6O_9	16	54	18	6

Table 10. The number of states of the Co_6O_m ($m=0-9$) particles in the regions of different energy.

Particle	Co_6	Co_6O	Co_6O_2	Co_6O_3	Co_6O_5	Co_6O_6	Co_6O_7	Co_6O_8	Co_6O_9
Symmetry group	C_{2v}	C_1	C_{2v}	C_1	C_1	C_{2v}	C_{2v}	C_{1h}	C_{3v}

Table 11. Approximate symmetry of the particles investigated.

Hence, the particles with higher symmetry absorb certain wave lengths more intensively, while the absorbance of non-symmetrical particles is not intensive, but a very broad one (Table 11, Figs. 15, 16). It allows us to conclude, that the investigated spectra of the Co nanoparticles in the region of [300; 700] nm could explain the oxidation of the particles and, as a consequence, their structure changes what lead to changes of magnetic properties.

Basing on the results obtained, we speculate that the dependence on the place of excitation could be related with the particle oxidation when considering the excitation of large particles (approximately of 200 nm).

6. Conclusions

Herein, we report on the several important results related to magnetic properties of the Co nanoparticle.

The main important observations of the pure Co and oxidized nanoparticle are the following:

- The Co_8 , Co_{10} , Co_{12} , Co_{14} , Co_{16} particles consist of Co_6 , thus these particles could be regarded to as the key element of the large Co nanoparticles.
- The face centered cubic structure which is slightly less closely packed, occurred in the Co_{14} and Co_{16} nanoparticles, while the other particles described are the elements of the FCC structure in the sense of the above conclusions.
- The key element of the Co_6 is present in the Co_6O_n ($n=0-9, 12$) particles.
- The present investigations of the magnetic properties of Co and Co oxide particles resulted in the conclusion that a paramagnetic behaviour is dominating when the non-compensated spin is present due to the anti-bonding orbitals and such a spin is not quenched by the ion spins.
- The results of our investigations indicate that both a dipole interaction and particle agglomeration change magnetic properties of the Co nanoparticle.
- The intensity of absorption of Co_6O_m ($m=0-9$) particles should be decreased in the [500;700] nm region with increasing of the number of the oxygen atom up to 5, and should be increased again when number of oxygen atoms is 6.
- The spectra of investigated particles become linear when the number of oxygen atoms in the above particle is even, while the absorption lines in spectra should be difficult to observe with odd number of oxygen.
- It is obtained, that in the spectra of Co_6O_m ($m=0-3$) the most intensive excitations correspond to $\text{Co}3d \rightarrow \text{Co}3d$ excitations. The $\text{Co}3d\text{O}2p \rightarrow \text{Co}3d\text{O}2p$ excitations are more relevant in the spectra of the particles where the number of oxygen atoms is up to 7, while in the rest particles the $\text{Co}3d \rightarrow \text{Co}3d\text{O}2p$ or $\text{Co}3d\text{O}2p \rightarrow \text{Co}3d$ types of excitation are obtained.

7. References

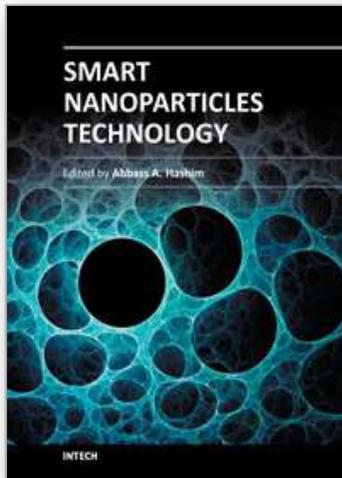
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