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Usage of cobalt oxide particles as precursor for FEBID: Ab initio study

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Abstract The investigation of the fragmentation of $Co_{18}O_n$ ($n = 0$–17) particles is presented with the aim to demonstrate that the mentioned particles could be used as precursors for focused electron beam induced deposition (FEBID). The shape of Co_{18} and $Co_{18}O_n$ particles is confirmed. The study validates that oxygen atoms stabilize Co nanoparticles. The thermal and chemical stabilities, toxicity, hardness and softness of the particles under study are determined. It is found that the absorption of oxygen atoms could occur when the number of oxygen atoms is larger than the number of external Co atoms. A low volatility and high sticking on the surface probability of $Co_{18}O_{17}$ particles are proposed referring to the obtained results. The results of the calculated susceptibility exhibit $Co_{18}O_n$ particles as paramagnetics with some exceptions. The value of magnetic susceptibility of $Co_{18}O_{12}$ is the largest one among the particle under investigation. Referring to the obtained results several most effective reactions of fragmentation are proposed and their appearance energy is evaluated. The obtained results also evidenced that $Co_{18}O_{17}$ nanoparticle shows great potential to be used as a precursor for FEBID.

Introduction

Magnetic particles are in the focus of constantly growing interest from various points of view due to their unique properties. It is expected that magnetic properties of modified materials could open new technological possibilities in high-density data storage devices and magneto-optical sensors. However, to achieve technological goals, magnetic particles need to be supported by or embedded in other materials such as semiconductors or insulators.

Initial studies in this field were mainly performed on free and supported magnetic clusters; later they were focused on the magnetic properties of nanoclusters embedded into matrices, and now the time comes to find the most appropriate technology for the deposition of particles.

Focused electron beam induced deposition (FEBID) is a very promising technique for nanofabrication that enables the deposition of structures on the nanometer scale. FEBID is an emerging chemical vapor deposition method with the possibility of the resist-free 'direct-write' additive nanomanufacturing using a variety of the materials with a high degree of spatial and time-domain control. The possibility to deposit very small amounts of material for tuning purposes on a fully processed micro/nanodevice at the

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right place, at will, and without damage to surrounding sensitive areas can be very cost-effective even if the speed of the deposition is very low as compared to standard photolithography (Utke et al. 2008). However, this new technology relies on precursors that are not optimized for the electron-driven process.

Currently, cobalt nanoparticles are widely applied in various fields such as: coatings, plastics, nanofibers, nanowires, textiles and high-performance magnetic recording materials. They are also implemented as medical sensors in biomedicine as a contrast enhancement agent for magnetic resonance imaging (MRI) as well as site-specific drug delivery agents for cancer therapies. Cobalt oxide particles can be also used in several military applications such as: high-performance invisible materials for the absorbing extremely high frequency millimeter, visible and infrared light waves (AzoNano 2013). Researchers are looking for the ways of the exploring electrical, magnetic, optical, imaging, dielectric, catalytic, biomedical and bioscientific properties for wider applications.

However, the study of a Co nanoparticle deposited on AIN and embedded into the AIN matrix indicated that the growth conditions of Co on AIN impact the resulting system; apart from the growth mode, that is known to be the deposition temperature-depended, the size of Co particles and their magnetic and magneto-optical properties were found to strongly depend on the growth conditions (Huttel et al. 2004).

Co nanoparticles were grown by femtosecond pulsed laser depositions, too. The study indicated Co nanoparticles as nanodisks the maximum size of which and the particle number increase together with the increase in the laser power density (Cebollada et al. 2009). The studies also proved the partial oxidation of Co particles, while the magnetic properties of the structures were consistent with the presence of this partial oxidation. However, our study proved that magnetic properties of Co nanoparticles are oxygen atom dependent because of the disappearance of Co–Co bonds where uncompensated spins were present, i.e., some of the oxidized Co particles possess magnetic properties (Tamuliene et al. 2010a).

Hence, the reasons to apply Co nanoparticles more effectively are the following:

- Deposition of Co or Co oxide nanoparticles in such a way that their magnetic properties unchanged due to conditions of growth or oxidation process;

- Deposition of non-magnetic Co oxide particles in such a way that only paramagnetic or ferromagnetic Co or Co oxide particle is embed into other materials.

In FEBID, a tightly focused high-energy electron beam impinges on the substrate and, due to the collision interaction, produces backscattered primary and secondary electrons with low energy. Interactions of adsorbed molecules with these electrons of the appropriate energy result in a precursor dissociation forming a deposit. If the precursor of FEBID is non-magnetic Co oxide particle, the interaction of it with the previously mentioned electrons could lead to the removal of oxygen atoms and, as a consequence, to the forming of a magnetic Co nanoparticle. It is also possible to predict that a certain number of oxygen atoms could be removed due to the dissociation when the appropriate energy of the above high-energy electron beam is used. Hence, aiming to show that FEBID could be used to deposit nanostructured magnetic materials, we performed a theoretical study focusing our attention to the properties of $Co_{18}O_n$ ($n = 1–17$) and aiming to demonstrate that these particles could be used as precursors of FEBID.

Method of investigation

The structure of the nanoparticles and their fragments was studied by the Becke's three-parameter hybrid functional (Becke 1993) applying the non-local correlation provided by Lee, Yang and Parr (Miehlich et al. 1989)—a representative standard DFT method. The Gaussian and GAMESS program packages were applied here (Frisch et al. 2004; Gordon and Schmid 2005). The significant advantage of the DFT method is a noteworthy increase in time-saving computational accuracy. The present DFT method is derived for obtaining total energies as the function of the nuclei position and is often the method of choice for reaction calculations because the electron correlation energy is accounted, while the ignoration of the electron correlation is one of the most significant deficiencies of the Hartree–Fock method. However, the correlation energy, as well as the total energy of the investigated system, is highly dependent on the basis set used. Thus, our investigation was performed with the 6-311G basis set. This basis set is a triply split basis,

with an inner orbital represented by three Gaussians, while the middle and outer orbitals are represented as single Gaussians. This basis set is usually supplemented with polarization functions. The triply split and polarization functions improve the description of the outer valence region; thus, the requirements for both the accuracy of the investigations and appropriateness of the computing time and recourses are satisfied (Curtiss et al. 1995; McGrath and Radom 1991; Binning and Curtiss 1990).

The structures of the Co_{18} nanoparticles were modeled taking into account the presence of the key structures previously obtained by us (Tamuliene et al. 2007). It implies that each investigated nanoparticle is a collection of the key structures, and nanoparticles with structural defects are not modeled, although the total number of the Co18 particles investigated is ~ 30 and the number of $Co_{18}O_n$ is ~ 200. Approximately 30 symmetrically different structures were investigated. These structures together with the others, described below, were optimized with no symmetry constraint. The vibration frequencies were investigated to check the accuracy of the optimization results, i.e., the frequencies of the first six vibration modes were required to be approximately zero. The vibrational zero-point energy was included into the evaluation of the total energy. The total energies were compared aiming to obtain the most probable structure of the Co_{18} particle.

The most probable structure with the lowest energy was used to model $Co_{18}O_n$ ($n = 1$–18) particles. The largest number of oxygen atoms to be adsorbed was obtained taking into account both the aim of our study (to check the possibility to use Co oxidized particles as a precursor) and the results of the investigation on the stability of the particles (oxygen atoms stabilize Co particles). It implies that only 12 possible isomers with the same number of oxygen atoms were modeled and investigated. The unoptimized structures of these isomers were modeled so that no oxygen atom is to form a bond with the inner Co atom of the investigated particles. The particles are electrically neutral, hence only the closed-shell systems are investigated. The most stable isomers of $Co_{18}O_{(n-1)}$ were used to model $Co_{18}O_n$ particles. To study the influence of an oxygen atom on the stability of a pure cobalt particle, the binding energy per atom was calculated and compared. Additionally, the threshold of the binding

energy per atom was calculated to foresee when the adsorption of an additional oxygen atom has no significant impact on the stability of the particles investigated. In this case, the threshold of the binding energy per atom is the energy change when the number of oxygen atoms is increased by one. Additional structures of the $Co_{18}O_{(n-1)}$, $Co_{18}O_n$ and $Co_{18}O_{(n+1)}$ were investigated to obtain more precise results, when the value of the threshold of the binding energy per atom was remarkably higher. We also calculated the susceptibility for both the evaluation of magnetic properties of the investigated particles and the prediction of final products of the fragmentation reactions. The gauge-independent atomic orbital (GIAO) method (Ruud et al. 1993; Stephens et al. 2003) was implemented for the computing of the magnetic susceptibility.

The obtained results allow us to choose the most promising particles to be used as precursors and to foresee the most significant reactions of the fragmentation:

- The particle is capable of adsorbing only a certain number of oxygen atoms not exceeding the amount of Co on its surface;
- The reactant (the above particle) and product (the particle with the highest calculated susceptibility) were obtained.

The number of fragmentation reactions could be extremely large due to different oxidation and spin states of the particles under investigation. Hence, we limited ourselves and considered only those reactions where the predicted products could occur directly without any intermediary processes, i.e., cascade reactions were not investigated while the formed particle was neutral. However, we studied the cases where other products of the possible reactions were differently (negatively or neutrally) charged, and, as a consequence, various spin state systems were studied, too. It implies that the particle predicted to deposit is a closed-shell system, while the rest products in some cases are open-shell systems.

The appearance energy was calculated as the difference between the total energy of the particle and the sum of the total energies of the predicted fragments. The calculations for the final states of the compounds are presented for the case of the fragmentation without taking into account the activation energy of the reverse reaction (E_r).

To evaluate which of the investigated particles were thermally more stable, the binding energies per atom were calculated followingly:

$$\Delta E = \left| \frac{E_{tot} - \sum_i n_i E_i}{N} \right|$$

where E_{tot} is total energy of the particle; E_i is total energy of a certain atom; n_i is the number of certain atoms; and N is the total number of atoms in the particle.

Electronegativity, chemical hardness and chemical softness were calculated as follows:

$$\chi = -\frac{I - A}{2} \ \text{(Electronegativity)};$$

$$\eta = -\frac{I - A}{2} \ \text{(Chemical hardness)};$$

$$S = -\frac{1}{2\eta} \ \text{(Chemical softness)},$$

where I is ionization potential; A is electron affinity. The ionization potential and affinity were calculated as the energy of the highest occupied and lowest unoccupied orbital energies. We applied the time-saving way for the calculation of A and I because the sequence of the most reactive compounds is independent of I and A evaluation method.

Using this method, we took into account the processes where the molecular ions were formed with the energies in excess of the ionization potential, but later they may have no sufficient energy to be decomposed according to the lowest energy pathway. On the other hand, the above parameters allow us to foresee whether the particle could be a precursor for FEBID.

Results and discussions

Thermal and chemical stability

Let us remember that the investigation of the fragmentation of $Co_{18}O_n$ ($n = 0–18$) is performed to demonstrate that the above particle could be a precursor for FEBID to produce pure Co or cobalt oxide particles. Here, the formation of magnetic particles is the most important result of the fragmentation. Hence, as a potential precursor for FEBID, the

particle must be volatile and have high sticking on a surface probability (Utke et al. 2008).

First, it is necessary to mention that the most stable Co_{18} particle is ellipsoidally shaped (Fig. 1). (The coordinates of the most stable structure of Co_{18} and other data not presented in the paper could be presented as supplementary materials under request). A similar shape of the particle is obtained in the study of A. Cebollada et al. (2009), although the sizes of the particles differ substantially between those studies. The $Co_{18}O_n$ ($n = 1–17$) particles are also an ellipsoidally shaped. Hence, the shape of the pure Co particle could not be changed significantly due to the adsorption process.

The binding energy per atom was calculated to compare the thermal stability of particles. It is known that the binding energy is the energy required to disassemble a whole system into separate parts. This energy is divided by the number of atoms to compare the stability of the compounds made up of the different number of atoms. In Fig. 2, we plot the binding energy per atom of the particle when the oxygen number is increased from 0 to 18. The binding energy per atom increases monotonically in the range [0–17] and becomes significantly large when the number of oxygen atoms is equal to 18. The values of the binding energy per atom of the $Co_{18}O_{16}$, $Co_{18}O_{17}$ and $Co_{18}O_{18}$ particles are equal to 3.471, 3.528 and 3.688 eV, respectively; the last value of the binding energy per atom is out of logarithmic trends (Fig. 2). Hence, referring to the results of our investigation presented in Fig. 2, the dependence of the stability of the particle on the number of oxygen atoms is obvious. This result coincides with the results presented by Tamuliene et al. (2008). The value of the binding energy per atom is out of logarithmic trends (Fig. 2). The threshold of the binding energy per atom also exhibits the
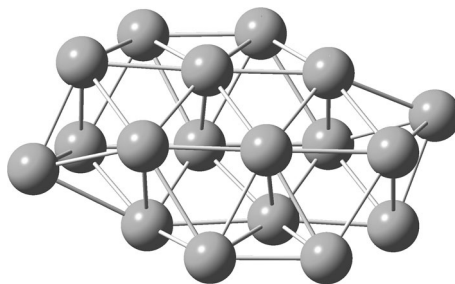
Fig. 1 View of the most stable structure of the Co_{18} nanoparticle

Fig. 2 Binding energy per atom of the investigated particles
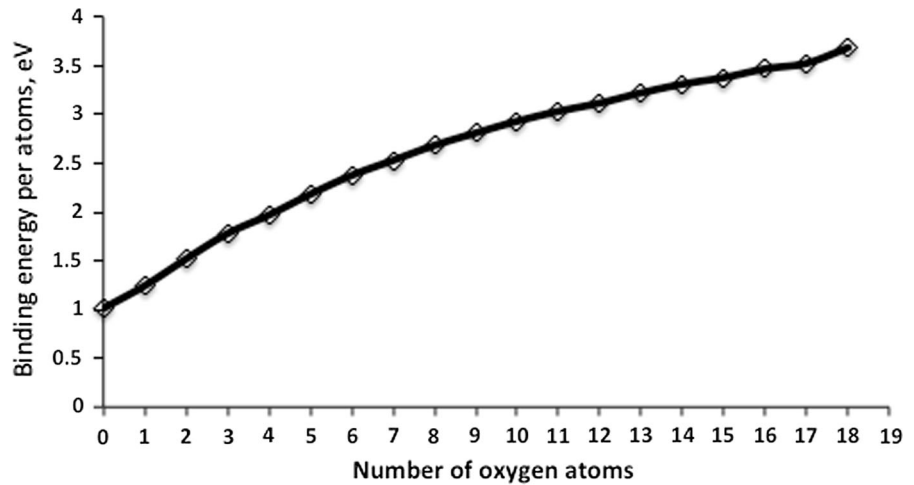
significantly increased stability of this particle (Fig. 3), i.e., the value of the threshold is the largest. This value, when the number of oxygen atoms increases from 17 to 18, is out of the exponential trend, while in other investigated cases the addition of oxygen atoms leads to the decrease in the threshold. Chemical hardness of the $Co_{18}O_{18}$ particle is 0.857, and this value is larger than that of (as example) $Co_{18}O_{17}$ and $Co_{18}O_{12}$ (Table 1). In our study of the electronic structure of the $Co_{18}O_{18}$, one O atom is attached to the inner Co atom at the equilibrium energy point of the structure. It implies that the absorption processes could occur, which is out of the scope of our study. On the other hand, it could be the reason why the properties and structure of the particle are strongly dependent on the conditions of growth (Huttel et al. 2004).

Referring to I. Utke et al., pure materials can be obtained in cases when a chemical reaction is initiated by electrons (Utke et al. 2008), i.e., the precursor is to be chemically stable. The calculated values of hardness and softness of the most promising particles, the equilibrium structure of which has been obtained, are presented in Table 2. The explanation why Co_{18}, $Co_{18}O_{12}$ and $Co_{18}O_{17}$ are most promising is presented below. Chemical softness is calculated to compare the reactivity, ability to resist the changes or degradation caused by interaction with air, light and pressure, etc., while hardness indicates the possibility to react with other derivatives. It should be taken into account that a small value of softness indicates high ability of degradation. Hence, in this respect, Co_{18} is more stable than $Co_{18}O_{12}$ and $Co_{18}O_{17}$. However, the values obtained are approximately six times larger than those of the precursors of FEBID (Dryden et al. 1993; Zialenina and Tamuliene 2015), which indicates high chemical stability of these particles and confirms our prediction that the Co oxide particles could be

Fig. 3 Threshold of the binding energy per atom (solid line), exponential trends (dashed line) and threshold of the binding energy per atom when the number of oxygen atoms in the particle increases from 17 to 18 (quadrangle)
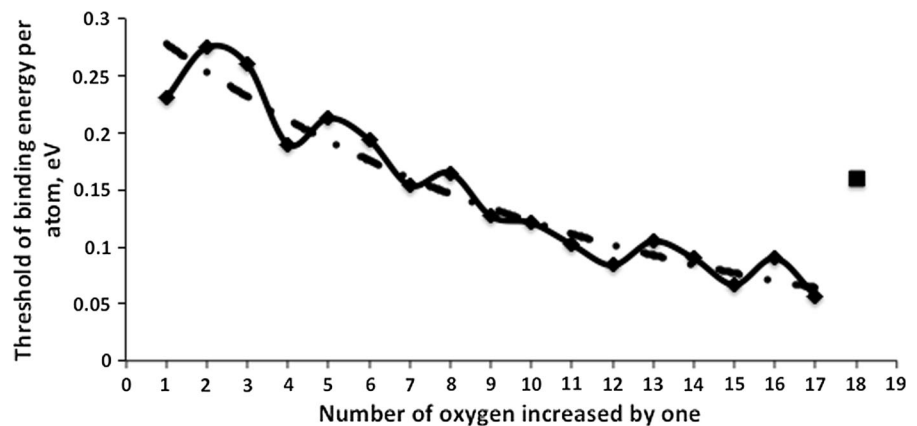
Table 1 Calculated values of the electronegativity, chemical hardness and softness

Number of O atoms	Electronegativity (eV)	Chemical hardness (eV)	Chemical softness (eV)
0	3.644	0.675	0.741
12	4.497	0.816	0.613
17	4.885	0.764	0.654

precursors for FEBID. The values of hardness indicate very promising features, too. Referring to the results obtained, we could rank the particles in the following way: $Co_{18} < Co_{18}O_{17} < Co_{18}O_{12}$. In this respect, chemical stability of Co_{18} is lowest, while that of $Co_{18}O_{17}$ is highest, i.e., the $Co_{18}O_{12}$ particle does not tend to react with other derivatives, which implies that the particle could be a final product of FEBID.Electronegativity that characterizes the capacity of a compound to attract electrons from the compounds bonded with it is used to compare toxicity of the compounds. It is well known that higher electronegativity indicates higher toxicity (Burello and Worth 2011). We have no possibility to compare the obtained electronegativity to that of other possible precursors of the Co particles for FEBID to make conclusions which of them is less toxic and more valuable to be used. However, the comparison of the electronegativity obtained with Pauling's electronegativity of silver atoms (6.12 eV) allows us to conclude that the particles under investigation are less toxic than a silver atom, i.e., their toxicity is low (Komorowski 1987). It is one of the reasons why the $Co_{18}O_{17}$ particle could be the preferred choice of the precursor for FEBID.

It is necessary to mention that metal carbonyls are often used as precursors despite their toxicity (Utke et al. 2008). The compounds are complexes with an electronic structure where the central atom is generally uncharged because electron densities from the transition metal d electrons are located on the C atoms of carbonyls. Therefore, carbonyls are complexes, which do not need any redox reaction in order to liberate uncharged metals (Utke et al. 2008). In the $Co_{18}O_{17}$ particle, d electrons of the Co atoms are located on the O atoms which are indicated by the molecular orbital analysis (Fig. 4). In this respect, the electronic structure of the $Co_{18}O_n$ particles is similar to that of metal carbonyls. Moreover, the Mulliken atomic charge of the Co atom varies in the range of [0.48–1.25] which is smaller than the respective range of 0.69 or 1.30 of the Ni or Fe atoms that form the most prominent carbonyls

used as precursors for FEBID (Fig. 5) (Farrugia and Evans 2005).

In the case investigated by us, electron densities from Co d electrons are located on the p orbitals of the O atoms which, at the first sight, could lead to the strengthening of the Co–O bonds and, as a result, complicate the dissociation of the particle by breaking these bonds. However, referring to the results of the molecular orbital analysis, the above bonds could not be stronger than those of the carbonyls used as the precursors for FEBID. The main reason for some Co–O bond weakening is the presence of antibonding orbitals in the structure of these bonds (Fig. 4). The weak bond between the Co and O atoms is another positive feature to use the suggested by us particles as a precursor for FEBID. It is necessary to mention that the obtained dipole moment of $Co_{18}O_{17}$ is 4.90 Debye and is approximately twice larger than that of carbonyls, or four times larger than that of hydrides used as precursors for FEBID. This implies that the volatility of $Co_{18}O_{17}$ is lower, while the sticking on the surface probability is higher as compared to the mentioned features of hydrides and carbonyls.
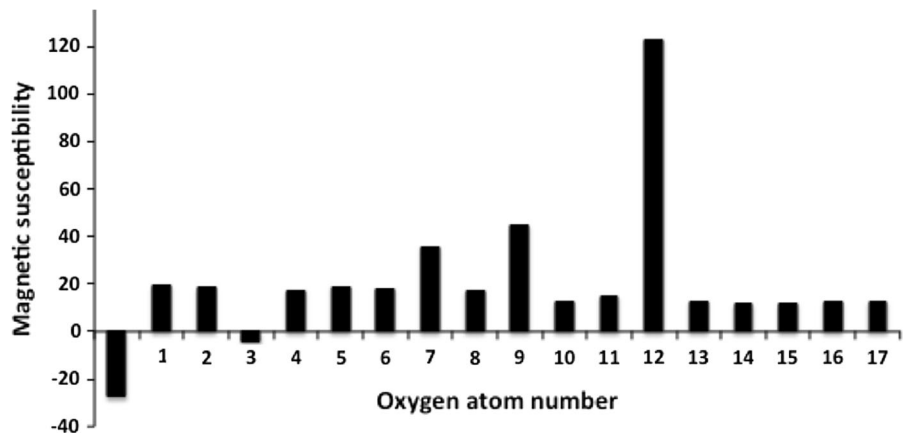
Magnetic susceptibility

Magnetic properties of the particles are investigated to study the most promising fragmentation reactions. Magnetizability (commonly known as susceptibility) is investigated as well (Handley et al. 2000). To avoid the dependence of magnetic properties on the number of atoms, the susceptibility per atom is presented in Fig. 5. As it is clear from Fig. 5, only Co_{18} and $Co_{18}O_3$ particles are diamagnetic, while the remaining one is paramagnetic although all the particles investigated are closed-shell systems. The $Co_{18}O_{12}$ particle possesses the largest susceptibility, while $Co_{18}O_{17}$ is the most stable among the rest particles. Hence, the reactant of the proposed reaction is $Co_{18}O_{17}$, while one of the reaction products is $Co_{18}O_{12}$, i.e., the final product of FEBID is the particle possessing the highest

Fig. 4 View of the $Co_{18}O_{17}$ particle (on the left) and charge redistribution in it (on the right)
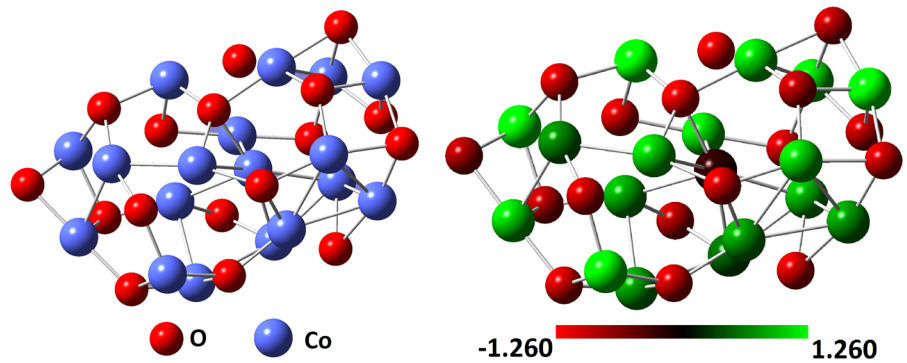
Fig. 5 Magnetic susceptibility per atom of the $Co_{18}O_n$ ($n = 0$–17)

degree of magnetization of the particle in response to the applied magnetic field. However, we must mention that it is possible to find other structures of $Co_{18}O_n$ (e.g., particles with structural defects) the magnetic susceptibility of which is larger than that of $Co_{18}O_{12}$, too, because geometrical structures of the uninvestigated particles could be such as:

- An uncompensated spin is present due to the weakly interacting electrons on the antibonding orbital; the particles are paramagnetic;
- This uncompensated spin is not quenched by additional spins occurring because some atoms of a nanoparticle lose an odd number of electrons (Tamuliene et al. 2010b).

Additionally, the magnetic properties of Co oxide structures are consistent with the presence of the partial oxidation state of Co atoms.

Energy of appearance

The requirement for the energy of the appearance of Co derivatives not to exceed the energy of FEBID is very important. For FEBID, the relevant energy range is from 1 meV (slowed-down secondary electrons) and up to the keV regime (typical primary electron regime, forwarded and backscattered electrons) (Utke et al. 2008). We investigated only some processes of the possible fragmentations under low electron impact as presented in Table 2. The comparison of the

Table 2 Fragmentation reactions and their energy of the appearance

Fragmentation reactions	Energy of appearance (eV)
$Co_{18}O_{17} + e \rightarrow Co_{18}O_{12}^0 + 5O^0 + e$	23.36
$Co_{18}O_{17} + 5e \rightarrow Co_{18}O_{12}^0 + 5O^{-1}$	18.61
$Co_{18}O_{17} + 10e \rightarrow Co_{18}O_{12}^0 + 5O^{-2}$	23.23

energies of the appearance proves that the dissociation of the $Co_{18}O_{17}$ particle into $Co_{18}O_{12}$ and O derivatives is most probable. The fragmentation processes where the energies of the appearance are smallest are presented in Table 2. Referring to these results, it is obvious that the energy of the appearance of $Co_{18}O_{12}$ lies in the relevant energy range for FEBID.

We also tried to obtain the energy of the appearance of the Co_{18} particle due to dissociation of the $Co_{18}O_{17}$ particle under electron impact. In this case, the products of the predicted reactions were neutral Co_{18} and variously charging (from 0 to -17) oxygen compounds. The results of our investigations exhibited that the dissociation of $Co_{18}O_{17}$ into pure Co_{18} is impossible. It allows us to predict that firstly $Co_{18}O_{17}$ dissociate into $Co_{18}O_n$ (where n is any number smaller than 17) and only then $Co_{18}O_n$ dissociates into pure Co_{18}. From the above, we may conclude that $Co_{18}O_{17}$ could be used as a precursor for FEBID.

Conclusion

The ab initio studies are performed to exhibit that $Co_{18}O_n$ ($n = 1$–18) could be a precursor for FEBID. Referring to the results obtained, the most stable investigated Co_{18} and $Co_{18}O_n$ particles are ellipsoidally shaped. These observations allow us to conclude that the shape of the pure Co particle could not change significantly due to oxygen adsorption. The study also confirms that oxygen atoms stabilize Co nanoparticles: The chemical and thermal stability of Co_{18} is lowest, while that of $Co_{18}O_{17}$ is highest in comparison to other particles under investigation.

It is evident that the absorption of oxygen atoms could occur when the number of oxygen atoms is larger than to the number of external Co atoms. It could be the reason why the particle properties and structure of the particles are strongly dependent on the conditions of growth.

The electronic structure, dipole moment and charge distribution indicate a low volatility and high sticking on the surface probability of $Co_{18}O_{17}$ particles. Moreover, the energy of the appearance of the particle fragmentation could not exceed the energy of FEBID, although the production of a pure Co particle could be a process of several steps. Hence, we conclude that $Co_{18}O_{17}$ could be used as a precursor for FEBID.

The particles could be synthesized by methods described by Zhu et al. (2012) and Yi et al. (2001).

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