Theoretical approach for determining the relation between the morphology and surface magnetism of Co$_3$O$_4$

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**Abstract**

Precisely controlling the different aspects of the morphology and magnetic properties of metal oxides are fundamental to materials design. A theoretical approach, based on the Wulff construction and magnetization density (M) index, is presented to clarify the relation between the morphology and surface magnetism. The M index allows us to evaluate the uncompensated spins at the (1 0 0), (1 1 0), (1 1 1) and (1 1 2) surfaces of Co$_3$O$_4$ with a spinel structure. The investigated morphologies show an excellent agreement with the experimental results, with the main contribution coming from the (1 0 0) and (1 1 1) magnetic planes. The present results are also helpful in clarifying the intriguing magnetic properties reported for Co$_3$O$_4$ nanoparticles, suggesting that the same technique may serve as a guide for the study of shape-oriented magnetic materials.

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**1. Introduction**

The functionality of nanomaterials is strongly related to their structure in terms of size and shape as well their corresponding electronic and spin densities, which are fundamental in controlling their nanoscopic, microscopic and macroscopic properties. Currently, remarkable advancements in a combination of theoretical and experimental techniques have allowed new functional materials to be designed as well as the main features behind nanostructures to be understood, enabling the enhancement of the performance of solid-state materials through morphological control. Indeed, kinds of applications such as catalysis, gas sensing, energy conversion and storage, and magnetoresistance depend on the atomic-level surface arrangement [1–4].

In recent years, many theoretical and experimental efforts have been dedicated to determining the morphologies of several metal oxides and explaining the existence of superior photocatalytic, photoluminescent and fungicidal activities. In general, such studies assume that morphological transformations are imposed by geometric constraints (dangling bonds, metals with low-coordination numbers, etc.), which control the surface energy. Then, the shape-oriented materials predicted in silico can be obtained in situ through the combination of different experimental techniques (synthetic methods, reaction times, surfactants and others) allowing the rational design of nanomaterials [2,5–17].

Recently, magnetic materials have attracted some interest because of the development of spintronic technologies and the revival of the discussion of multiferroic candidates. In this field, a large number of experimental studies have discussed the dependence of the surface morphology and unusual magnetic properties for different materials such as Co$_3$O$_4$, Mn$_x$O$_y$, Fe$_x$O$_y$, CoFe$_2$O$_4$ and MnS. Such shape-controlled nanoparticles exhibit different saturations, Neel temperatures and remanent magnetizations, showing a remarkable potential for technological applications involving high-density storage and processing devices [2,18–31]. However, from a theoretical point of view, it is well established that the atomic distributions control the spin coupling among unpaired electrons at the surface, and the relation between surface magnetism and morphology control remains unclear.

Co$_3$O$_4$ is a normal spinel (Fd-3m symmetry) that has been widely investigated because of its superior surface redox reactivity and electronic and magnetic properties, which have found several applications in energy conversion and storage, magnetic devices and catalysis. [32–34] The primary objective of this work was to demonstrate how the surface energies obtained from density functional theory calculations can be combined with the number of unpaired electrons per surface in order to determine the...
magnetization of different morphologies. This theoretical approach is capable of finding a relationship between the magnetism of Co$_3$O$_4$ and the obtained morphologies under the equilibrium conditions of electronic and spin densities.

2. Theoretical method and computational procedure

In order to study the morphology, the classical Wulff construction is employed, which is based on the thermodynamic theory that the energy of the crystal facets ($E_{surf}$) determines the equilibrium morphology. The Wulff proposal refers to a simple relation between ($E_{surf}$) and the distance in the normal direction from the center of the crystal lattice, which also allows this ideal morphology to be modified by tuning the surface energies of the different facets [4,9,35,36].

In this work, we use the surface energy ($E_{surf}$) values calculated by Su et al. [27], where Density Functional Theory (DFT) calculations were performed employing LDA exchange-correlation functional and ultra-soft pseudopotential (USPP) formalism. The geometry of the (1 0 0), (1 1 0), (1 1 1), and (1 1 2) surfaces were described using the slab construction with thickness large enough to ensure full relaxation of the surface ions and convergence of the surface energy. In all cases, the atomic positions were relaxed using 0.001 eV as convergence criteria and the finite surface energy ($E_{surf}$) was calculated from the stoichiometric difference between the slab energy ($E_{slab}$) and the bulk energy ($E_{bulk}$) per unit area ($A$) [27].

What is new about this study is that the definition of the magnetization density ($D_m$) index of a given surface is related with to the magnetic moment ($\mu_B$) per unit cell area ($A$):

$$D_m = \frac{\mu_B}{A}$$

($D_m$) resembles the broken bonding density index proposed by Gao et al. and is widely used to clarify the nature of surface stability [37]. In addition, Beltrán et al. investigated the magnetic properties of cubic and tetragonal HfO$_2$ surfaces through a similar approach, which was helpful in clarifying the surface magnetization associated with vacancies and showed an excellent agreement with the experimental results [38–40].

Here, considering the magnetic ordering of the surfaces which is composed of different morphologies, we assume the $D_m$ index can be used to classify the surfaces by following magnetic criteria. Therefore, from the combination of the polyhedral representation, $c_{i(hk)}$ derived from the Wulff construction and $D_m$, it is possible to predict the total magnetization density ($M$) index of a given morphology as follows:

$$M = \sum c_{i(hk)} \cdot D_m^{(hk)}$$

3. Results and discussion

The crystal structure of Co$_3$O$_4$ consists of a cubic close-packed array of oxygen anions where 1/8 of the tetrahedral interstices are occupied by high-spin Co$^{2+}$ cations, while half the of octahedral interstices are occupied by low-spin Co$^{3+}$ cations. Each Co$^{2+}$ cation (e$^{t_2g}$) is surrounded by four nearest neighbors of opposite spin, giving rise to an antiferromagnetic network. In contrast, the Co$^{3+}$ cations exhibit a closed-shell configuration ($t_2g^6$) and nil magnetic moment, as depicted in Fig. 1.

The experimental and theoretical results indicate that the low index (1 0 0), (1 1 0), (1 1 1), and (1 1 2) surfaces control their morphology and can describe the structural arrangements commonly found in such materials [9,27,32,34,41]. In this case, considering the experimental antiferromagnetic arrangement (AFM) (Fig. 1), each surface has a number of unpaired electrons per unit area, as depicted in Fig. 2 [42]. For instance, the (1 0 0) surface is composed of one Co$^{2+}$ cation coordinated with two oxygen anions (Co$_{2}^{2+}$) and five-coordinated Co$^{3+}$ cations (Co$_{5}^{3+}$) resulting in three unpaired electrons per unit surface area. Similarly, the (1 1 1) surface exhibits the same spin density as the (1 0 0) plane, being composed of one three-coordinated Co$^{2+}$ cation (Co$_{3}^{2+}$) and octahedral Co$^{3+}$ cations (Co$_{8}^{3+}$). In contrast, the (1 1 2) surface is formed by AFM planes containing two (Co$_{2}^{2+}$) and (Co$_{3}^{3+}$) cations, generating an antiparallel slab. In addition, some authors have reported that the (1 1 2) surface is more stable than the (1 1 1) surface, indicating that it can contribute to the morphology of the Co$_3$O$_4$ nanoparticles [9,27,43,44]. However, a deep analysis of the magnetic ordering along this plane reveals an antiparallel arrangement between two (Co$_{3}^{3+}$) cations, resulting in an exposed plane with $D_m = 0$ (Fig. 2). Especially for Co$_3$O$_4$, the understanding of the relation between the surface composition and its energy play a fundamental role in the clarification of the superior properties associated with the Co$^{3+}$/Co$^{2+}$ ratio and the electronic and magnetic structure of such nanoparticles [45,46].

In this work, the Wulff construction for the Co$_3$O$_4$ structure was obtained from the surface energy ($E_{surf}$) values calculated by Su et al. [27] It is important to ascertain that such results are reason-

Fig. 1. Crystalline unit cell of Co$_3$O$_4$, local structures, and corresponding crystal field diagram for high-spin (HS) tetrahedral and low-spin (LS) octahedral cobalt atoms. The black and gray arrows indicate the up and down spin orientations following the experimental antiferromagnetic ordering. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
able approximations to understand the physical and chemical properties of \( \text{Co}_3\text{O}_4 \) surfaces, though the stabilizing effects such as surface reconstructing and chemical adsorption could be helpful to clarify the superficial mechanisms. Table 1 summarizes the values of \( E_{\text{surf}} \), \( \nu_B \), and \( D_m \) of the surfaces used in the Wulff construction.

From Table 1, it is observed that the order of stability of the surfaces based on the energy criteria is \((1 \, 0 \, 0) > (1 \, 1 \, 0) > (1 \, 1 \, 2) > (1 \, 1 \, 1)\). Furthermore, it is noted that both \((1 \, 0 \, 0)\) and \((1 \, 1 \, 1)\) surfaces exhibit similar values of unpaired electron densities along the slabs, while the \((1 \, 1 \, 0)\) and \((1 \, 1 \, 2)\) surfaces exhibit a zero magnetic moment along the plane.

Therefore, the computed surface energies induce a significant change in the equilibrium morphologies of \( \text{Co}_3\text{O}_4 \). The morphological modulations of \( \text{Co}_3\text{O}_4 \) proposed in this work are summarized in Fig. 3, in which the transformations are obtained by tuning the surface energies of the different facets.

The ideal morphology for \( \text{Co}_3\text{O}_4 \) predominantly exposes the \((1 \, 0 \, 0)\) surface and, to a minor extent, the \((1 \, 1 \, 2)\) surface, following the thermodynamic criteria from the values of the surface energies. In addition, it is observed that different shapes are obtained by tuning the \( E_{\text{surf}} \) for \( \text{Co}_3\text{O}_4 \) (Fig. 3). In the past few years, different strategies have been used to obtain different kinds of shape-oriented \( \text{Co}_3\text{O}_4 \) nanoparticles. For instance, Su et al. reported the synthesis of cubes and pseudo-octahedral \( \text{Co}_3\text{O}_4 \) nanoparticles, demonstrating an excellent agreement with theoretical morphologies 1 and 2.1, respectively. Especially, they argue that pseudo-octahedral nanocrystals expose the \((1 \, 0 \, 0)\) and \((1 \, 1 \, 0)\) planes, in which it is necessary to modify one of the \((1 \, 1 \, 0)\)-surface groups as described by Ferrer et al. [9,27] In contrast, Chen et al. and Dutta et al. synthesized a different kind of corner-truncated octahedral nanoparticle, which exposes the \((1 \, 0 \, 0)\) and \((1 \, 1 \, 1)\) surfaces, according to the theoretical morphology 3.2 [47,48]. They also report the existence of corner-truncated cubic shapes, which predominantly expose the \((1 \, 0 \, 0)\) surface with different percentages of the \((1 \, 1 \, 1)\) surface. A comparison and analysis of the morphologies reported by these authors with those found in our tree of morphologies, 3 and 3.1, show a great similarity [47]. Gao et al. studied the electrocatalytic performance of shape-oriented \( \text{Co}_3\text{O}_4 \) and reported the existence of octahedral shapes with the exposed \((1 \, 1 \, 1)\) plane, according to morphology 3.3 presented in Fig. 3 [49]. Moreover, Kang et al. revealed the shape evolution of \( \text{Co}_3\text{O}_4 \) nanocrystals and proved the existence of polyhedra with the exposed \((1 \, 0 \, 0), (1 \, 1 \, 0),\) and \((1 \, 1 \, 1)\) surfaces, which are in excellent agreement with morphology 2.3 [50]. It is important to clarify that Scanning Electron Microscopy (SEM) technique was employed to obtain the different morphologies reported by these authors [27,47–50]. In addition, several other authors reported similar shapes for \( \text{Co}_3\text{O}_4 \), showing that these nanoparticles exhibit a weak ferromagnetic ordering commonly attributed to the uncompensated spins obtained from the cleavage planes [18,21,48,51–57].

In order to relate the surface magnetism and morphology modulation of \( \text{Co}_3\text{O}_4 \), Table 2 presents the calculated surface area contributions for each polyhedron presented in Fig. 3, as well as the total magnetization density \( M \) index calculated by Eq. (2).

Regarding the uncompensated spin density for the different morphologies predicted for \( \text{Co}_3\text{O}_4 \), it is observed that higher \( M \)
index values are obtained by tuning the contribution of the (1 0 0) and (1 1 1) surfaces, while the presence of (1 1 0) and (1 1 2) surfaces induces the smallest $M$ index values. In addition, the experimental reports for the Co$_3$O$_4$ nanoparticles indicate that the (1 0 0) and (1 1 1) surfaces play a key role in the morphology transformations, indicating that the unpaired electron density contributes to the stabilization of shape-oriented nanoparticles. In this case, we can assume that the unusual magnetic properties related to the Co$_3$O$_4$ nanoparticles are related to the uncompensated spin density originating from the exposition of magnetic planes found along the AFM ordering.

From the analysis of the results reported in Table 2, it is possible to propose a different kind of morphology map, based on the combination of $E_{\text{surf}}$ and $M$ values. In this case, we only consider the (1 0 0) and (1 1 1) planes, which exhibit non-zero values of the magnetic moment. The modulation process associated with the change of morphology is depicted in the schema in Fig. 4. Regular/truncated cubes and octahedral shapes with exposed (1 0 0) and (1 1 1) surfaces are observed, respectively. The increase in magnetization as the $E_{\text{surf}}$ values of the (1 1 1) surface decreases can be explained by the surface spin disorder of the Co$_3$O$_4$ particles being more easily aligned in the direction of the core spins via the applied magnetic field. Indeed, experimental results for Co$_3$O$_4$ nanoparticles suggest the relation between crystal size/shape and its magnetism arguing that the increased ferromagnetic component is associated with the magnetic moments on the magnetic sublattices, which do not cancel out completely. In such studies, the authors report the presence of cubic, regular and...
truncated-octahedral morphologies showing an excellent agreement with theoretical polyhedrons depicted in Fig. 4, indicating that ferromagnetic (1 0 0) and (1 1 1) planes play a fundamental role on the unusual magnetism of Co₃O₄ nanoparticles [48,55].

It is important to note that the incorporation of the total magnetization density, M index, along the Wulff construction produces a particular variety of morphologies that coincide with the experimental modulations found for the Co₃O₄ nanoparticles [27,47,49,50]. The geometric constraints imposed by the morphology map, obtained by the Wulff construction, are modified when the magnetic surfaces are considered through a reorientation of the crystalline structure which induces a different spin distribution along the material surfaces. Thus, we can argue that such procedures can be used as a guide for the theoretical/experimental study of shape-oriented magnetic nanoparticles.

### 4. Conclusions

A novel approach was proposed to analyze the magnetic properties of shape-controlled materials. This procedure combines the Wulff construction and the values of spin density to predict the morphology while considering the uncompensated spins for magnetic materials. By controlling the ratio of the surface energy values, a complete set of morphologies for Co₃O₄ were predicted, showing an excellent agreement with the experimental results. In addition, the reported results confirm that such morphologies have a singular spin density along the exposed area, which is helpful for understanding the unusual magnetic deviations commonly found for Co₃O₄ nanoparticles. From the viewpoint of applications, the ability to produce Co₃O₄ nanoparticles with high magnetization is highly desirable. Therefore, the present work on Co₃O₄ magnetic materials in silico can be directly related to the experimental findings, and can lead to innovation of the materials design through multifunctional shape-oriented nanoparticles. Based on these results and the facts reported in the literature, we can conclude that controlling the crystallinity and the exposed surface of the nanoparticles, it is possible to influence the magnetization properties of Co₃O₄ nanoparticles.

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