Chapter 17

STUDY OF THE PROPERTIES OF IRON OXIDE NANOSTRUCTURES

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1. INTRODUCTION

Iron oxides exist in a rich variety of structures and occur in a great variety of settings, from geological to nanoscale technological applications. Ferrous and ferric iron oxides present seven crystalline phases, the more common are $\alpha$-$\text{Fe}_2\text{O}_3$ (hematite), $\gamma$-$\text{Fe}_2\text{O}_3$ (maghemite), $\text{Fe}_3\text{O}_4$ (magnetite) and $\text{Fe}_{1-x}\text{O}$ (wustite); the less commonly found are the $\beta$- and $\epsilon$-$\text{Fe}_2\text{O}_3$ phases and the low-temperature rhombohedral structure of magnetite. Thanks to their fascinating properties, all of these oxides have been widely investigated by chemists, engineers, and physicists. These phases have been used successfully in many applications; e.g., magnetite nanoparticles have been used in cancer diagnosis and therapy [1], drug delivery vehicles [2], and in water remediation [3]. Magnetite thin films lend themselves to room temperature applications in the construction of different devices such as tunneling magnetoresistance, giant magnetoresistance and magnetic random-access memory devices [4]. Maghemite is used in magnetic resonance imaging [5], magnetic recording media [6], fabrication of biocompatible magnetic fluids [7], and electrochromic devices [8]. Hematite nanostructures have been explored in the development of electrochromic devices [8], as cathodes in lithium batteries [9], and in the construction of photoelectrochemical systems to produce hydrogen from water using solar radiation [10]. Thin films of wustite/maghemite have been used in solar radiation filters [11].
1.1. Nanostructures of Iron Oxides

Hematite exhibits a rhombohedral structure which is antiferromagnetic below its Morin transition ($T_M$) of about 260 K. Between this temperature and the Néel temperature ($T_N$) of about 948 K, it exhibits a weak ferromagnetic behavior. The weak ferromagnetic behavior is due to a slight disorder of the spin axis from exact antiparallelism. The dependence of the particle size on $T_M$ has been studied, and it was found that the $T_M$ is lower for smaller particles; however, $T_M$ is strongly dependent on the sample preparation method, lattice defects, and the incorporation of water and OH groups into the hematite structure [12]. The magnetic properties of this phase are strongly related to the morphology and size of the nanoparticles. The coercivity ($H_c$) ranges from 31 to 530 Oe [13-16], and remanent magnetizations ($M_r$) are from 0.6 to 16 emu/g [13-16]. The higher $H_c$ and $M_r$ are associated with greater sizes; otherwise, small particles of hematite with different morphologies above the blocking temperature ($T_b$) acquire a single magnetic domain behavior showing superparamagnetic properties [13, 17].

Magnetite and maghemite are ferrimagnetic, and both crystallize in the inverse spinel cubic structure. At ambient conditions, these phases are thermodynamically less stable than hematite [18]; despite this, it has been found that for smaller nanocrystals of maghemite, the stability increases. This can be inferred because its surface energy is lower than that of hematite [19]. Maghemite is an insulator with an energy gap of 2 eV, while magnetite is a Fe$^{2+}$-Fe$^{3+}$ mixed valence metal. Magnetite has a Curie temperature ($T_C$) of 860 K, while the $T_C$ is 900 K for maghemite. Furthermore, magnetite shows an order-disorder transition at the Verwey transition $T_V$, at about 120 K, in which the electrical conductivity decreases by almost two orders of magnitude [20]. According to Verwey, below $T_V$ magnetite exhibits an orthorhombic structure, although other researchers argue for a monoclinic structure [20]. The absence of the structural transition for magnetite nanoparticles smaller than 10 nm and the observation of the nonexistence of $T_V$ have been reported [21].

Wustite is an antiferromagnet; with a $T_N$ of about 200 K, it crystallizes in the rock salt structure. The iron deficiency in wustite leads to the formation of vacancies located on interstitial, tetrahedral sites clustered around Fe$^{3+}$ ions [22]. Wustite exhibits semiconductor properties. Thermoelectric measurements record a drop in the thermoelectric power taking place below 120 K, and a change in the sign from positive to negative is observed [23]. Wustite is metastable, yielding metallic iron and magnetite; this metastability has been used to prepare mixed-phase nanoparticles with both composition and magnetic properties controlled by the fabrication technique [24, 25]. In order to stabilize the wustite phase with controlled stoichiometry, the nanoparticles have been capped with organic ligands [24-26].

1.2. Other Ferrites

Ferrites have the general formula of $MFe_2O_4$, where $M$ can be one or more metal atoms with different ratios between them; they crystallize in the inverse spinel structure. A great variety of metal ferrite nanoparticles has been reported in the literature. Very important properties can be found, such as in CoFe$_2$O$_4$, which exhibits light-induced changes in the coercive field; this property, called photomagnetism, may be used in the fabrication of hybrid data storage [27]. The superparamagnetic properties of nanoparticles cover a broad range of
particle sizes of ferrites such as MgFe₂O₄ [28], Ni₀.₂₀Zn₀.₄₄Fe₂.₃₆O₄ [29], NiFe₂O₄ [30], and MnFe₂O₄ [31]. In order to satisfy the current technological demands, other ferrites such as BiFeO₃ [32] and ferrites with more complex compositions, such as the Mg₀.₅₅xCuₓZn₀.₄₅O(Fe₂O₃)₀.₉₇ [33] and Ba₁₋ₓSrₓFe₁₂O₁₉ compounds [34] are extensively studied because of their ferroelectric, ferroelastic, and ferromagnetic properties.

2. PREPARATION OF IRON OXIDE NANOSTRUCTURES

2.1. Synthesis of Nanoparticles

Iron oxide nanoparticles have been synthesized by a variety of techniques. The most commonly used methods for the preparation of hematite, maghemite, magnetite, wustite, and other ferrite nanoparticles are: co-precipitation [27, 28, 35], the polyol process [36, 37], thermal decomposition of metal-organic compounds [3, 24, 26], microemulsion [29, 32, 38], hydrothermal synthesis [13-17], aerosol pyrolysis [39], high energy ball milling [25, 31], sol-gel [6, 40], and some vacuum methods such as sputtering have also been used for the preparation of core-shell nanoparticles [41]. Obtaining nanoparticles with a controlled size, morphology, and composition is the main challenge for all the techniques mentioned above; also, a simple, reliable, and cheap process is needed for large-scale syntheses. Figure 1 shows a comparison of the size distribution of iron oxide nanoparticles prepared by different techniques.

![Figure 1](image-url)  
**Figure 1.** Size distribution of iron oxides nanoparticles obtained by different preparation methods. Very narrow distributions are seen in smaller particles prepared by thermal decomposition and microemulsion. Nanoparticles prepared by co-precipitation and sputtering shows spread size distributions.
Co-precipitation methods are simple methods of synthesizing magnetite and other ferrite nanoparticles from ferric and ferrous salts such as nitrates, chlorides, sulfates, perchlorates, etc. With the appropriate ratios of the precursor salts, it is possible to obtain narrow size distribution of spherical nanoparticles [27, 28, 35]. As an alternative method, the polyol process uses polyols such as ethylene glycol; polyols are high-boiling solvents, reducing agents, and stabilizers that control the growth and prevent the aggregation of nanoparticles. This method is useful for the preparation of dispersed magnetite nanoparticles with tailorable size and tuneable magnetic properties [36, 37]. The thermal decomposition at appropriate conditions yields monodispersed nanocrystals in one reaction without a further size-selection process; large scale amounts of material are available because inexpensive reagents can be used [26]. With this method, wustite, magnetite, and maghemite nanoparticles have been prepared [24, 26]. In the microemulsion method, co-precipitation occurs in the aqueous phase of water-in-oil emulsions controlling the particle size and size distribution in the desired proportions. Particles of a great variety of ferrites including magnetite, nickel zinc and bismuth ferrite have been successfully prepared by this method [29, 32, 38]. The hydrothermal method involves high-temperature aqueous solutions at high vapor pressures; this technique is very effective to control the size and shape of nanocrystals. The hydrothermal syntheses of nanorods, nanotubes, nanocubes, and rhombohedral crystals of maghemite and hematite have been reported [13-17]. Aerosol pyrolysis is a technique that involves a series of reactors with a temperature gradient. In these reactors the aerosol droplets travel following the next step in the processes: evaporation of the solvent, solute condensation within the droplet, drying, and the thermolysis of the precipitated particle. This method is useful for obtaining particles of predictable shape, size and composition; maghemite hollow spheres have been prepared by this method [39]. By ball milling, the mechano-synthesis of nanostructures is promoted by the mechanical activation of the chemical reactions involved in the formation of the oxides. Wustite nanoparticles from metallic iron and hematite have been prepared by this method [25]. The sol-gel process uses metallic alkoxides as precursors; it allows the preparation of ceramic nanoparticles of a great variety of compounds, including ellipsoidal single-crystalline nanoparticles of hematite and polycrystalline spherical nanoparticles of hematite. With a proper reduction-reoxidation process, magnetite and maghemite nanoparticles that retain their shape can be obtained [6].

2.2. Thin Film Growth

Iron oxide thin films of hematite, maghemite, magnetite and wustite have been prepared by a variety of techniques including chemical vapor deposition (CVD) [42, 43], sputtering [4, 10, 11, 44], sol-gel [8, 45], pulsed laser deposition (PLD) [46, 47, 48, 49], molecular beam epitaxy (MBE) [50, 51], and spray pyrolysis [52, 53]. The quality of the film depends on the technique of growth and diverse operating parameters. For physical techniques such as PLD and sputtering, the most important parameters are target-substrate distance, chamber pressure, substrate temperature, deposition time, oxygen partial pressure, laser energy density, laser frequency, and the power of the RF or DC source [37]. For the chemical techniques, the most important parameters that affect the quality and properties of iron oxide films are the type of chemical precursors, deposition rate, carrier gas pressure, substrate temperature, precursor temperature, and annealing temperature. MBE is a technique that grows films with excellent
Thin films of magnetite, maghemite, and hematite have been successfully prepared by PLD [46, 47, 48]. Using different substrates, hematite targets, vacuum pressure, and substrate temperatures from 623 to 773 K, the formation of thin films exhibiting the maghemite or magnetite phases has been observed [46, 47, 48]. Hematite films have been prepared by using oxygen at working pressures ranging from 2 to 7 Pa [46]. PLD allows the preparation of smooth films at reasonable deposition rates with a controlled phase; the only drawback of this technique is that only small areas can be coated. As an alternate method, sputtering is a technique that allows depositing iron oxide films on large areas; films of iron oxides have been prepared on soda-lime glass of 60×30×3 mm³ at residual pressures of 700 Pa. In order to change the reflectance properties, these films were heated in a reducing atmosphere of H₂ and N₂, yielding mixed phase films of maghemite and wustite. These films have been successfully used as solar radiation filters for saving energy in warm weather [11]. Sputtered magnetite films have been prepared at room temperature by introducing an external RF power; without this, mixed phase films of Fe₂O₃ and Fe₅O₄ are obtained [44]. Saturation magnetizations ranging from ~70 to ~440 emu/cm³ were reported for magnetite films prepared at different substrate temperatures with different thicknesses; higher magnetizations are obtained for films prepared at substrate temperatures higher than 523 K and thicker than 10 nm [4, 44]. Additionally, wustite films have been prepared by DC magnetron sputtering; these films exhibit large $M_s$ and low temperature $H_c$ [54]. This unusual behavior is attributed to the existence of 16:5 spinel type defect clusters coherently embedded in the FeO matrix [54].

Hematite thin films have been obtained by CVD using iron (III) tert-butoxide at substrate temperatures ranging from 623 to 673 K, while magnetite films can be prepared at 773 K. Intermediate temperatures yield films crystallized with both phases [43]. In addition, films crystallized in the cubic $\beta$-Fe₂O₃ phase have been obtained by CVD using iron (III) acetylacetonate as a precursor at temperatures ranging from 623 to 673 K; these films were studied for electrochromic applications [42]. Using spray pyrolysis techniques, hematite films were prepared by spraying aqueous solutions of iron (III) chloride at 773 K [52]. While iron (III) chloride dissolved in methanol sprayed at 633 K yields maghemite/hematite films, the formation of maghemite is promoted under a reducing atmosphere promoted by the organic solvent [53]. The spray deposition of iron (II) sulfate onto glass substrates has not yielded films of iron oxides [52]. Using the sol-gel method, hematite films have been formed at annealing temperatures of 623 to 873 K in air [8, 45]; annealing at 873 K in nitrogen/hydrogen atmosphere yields metallic iron films, and with a subsequent heat treatment at the same temperature in nitrogen, the generation of maghemite is observed [45].

3. Characterization Techniques for Iron Oxides Nanostructures

3.1. Magnetic and Electrical Properties

The vibrating sample magnetometer (VSM) and the superconducting quantum interference device (SQUID) magnetometer are used to measure the magnetic properties of
materials. SQUID magnetometers are very sensitive; they are used to measure extremely small magnetic fields, based on the properties of electron-pair wave coherence and Josephson junctions. In a VSM, a sample is placed in a uniform magnetic field, and the sample is vibrated sinusoidally. The magnetic flux generated by the vibrating sample induces a current, which is proportional to the magnetization of the sample. The electrical properties of films are usually measured by the Van der Pauw method; this is useful for the determination of resistivity and the Hall parameters of films of arbitrary shape.

Experimentally and theoretically, the relationship between the size and the magnetic properties of nanoparticles has attracted much attention [3, 5-6, 13, 15, 21, 27-28, 37-39]. It has been found that nanoparticles smaller than a critical size (~40 nm) present a variety of size-dependent behaviors [3]; e.g., the cooperative phenomenon in ferromagnetism is no longer observed, and the particles behave like single domains, showing magnetic susceptibilities higher than the bulk, and the superparamagnetic behavior appears. The size of superparamagnetic nanoparticles can be obtained from the slope of their magnetization loop near zero magnetic field; for samples with a wide size distribution, the major contribution comes from the largest particles. Therefore, the upper limit of the magnetic size ($D_m$) is given by [17]:

$$D_m = \left[ \frac{18 k_B T}{\pi \chi_i \rho M_s} \right]^{1/3}$$

where $k_B$ is the Boltzmann constant, $T$ the temperature, $\chi_i$ the initial magnetic susceptibility ($\chi_i = \frac{dM}{dH}$)$_{H \to 0}$, $\rho$ the density of the nanoparticle and $M_s$ the saturation magnetization. Additionally, it is frequently observed that the saturation magnetization decreases for smaller particles; this is due to the increase of spin order effects at the particle surface, which yields smaller net magnetic moments.

The correlation between the superparamagnetic properties of ferrite nanoparticles and size is related to the size dependence of the magnetocrystalline anisotropy energy ($E_A$) in the nanoparticles. According to the Stoner-Wohlfarth theory, $E_A$ of a single domain particle is approximated by [28]:

$$E_A = KV \sin^2 \theta$$

where $K$ is the magnetocrystalline anisotropy constant, $V$ is the volume of the nanoparticles, and $\theta$ is the angle between the direction of field-induced magnetization and the easy axis of the nanoparticles. This anisotropy is the energy barrier that prevents the change of magnetization direction [28]. When $E_A$ is comparable with thermal activation energy ($k_B T$), the magnetization direction is moved away from the easy axis by thermal activation or an external magnetic field. The coercivity of nanoparticles is closely related to $E_A$. At a constant temperature below $T_B$, $H_c$ corresponds to the magnetic field strength at which the magnetic field provides the required energy in addition to $k_B T$ to overcome the magnetic anisotropy. Hence, $H_c$ of nanoparticles increases with nanoparticle size; in addition, the $H_c$ is affected by the shape anisotropy contribution, since high changes in $H_c$ have been reported for iron oxide nanoparticles with different aspect ratios, such as nanorods, nanocubes, ellipsoidal, spherical and polyhedral shaped nanoparticles [6, 13]. Table 1 shows some characteristics of iron oxide nanoparticles with a variety of shapes and sizes, the effects of the size on the coercive field, saturation magnetization, and remanent magnetization as explained above is seen in these data which were extracted from the literature.

Typically, the magnetization of magnetite films is not easily saturated because of the localized antiphase boundaries (APB) present in the films [51]; however, some films reach their saturation magnetization easily, see figure 2. Sputtered magnetite films prepared at optimal conditions on Si (100) and MgO (100) substrates showed saturated magnetization loops, while those prepared at coarse conditions are not easily saturated [4, 44]. The
observation of $M_s$ lower than the bulk value (~477 emu/cm$^3$) can be due to the presence of other phases at the interfaces between the substrate and to the presence of voids between the grains and APB.

Table 1. Particle size, shape and magnetic parameters determined at room temperature of different iron oxide nanoparticles reported in the literature

<table>
<thead>
<tr>
<th>Iron oxide</th>
<th>Particle size (nm)</th>
<th>Shape</th>
<th>$M_s$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
<th>$M_r$ (emu/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite Fe$_3$O$_4$</td>
<td>4</td>
<td>spherical</td>
<td>31.8</td>
<td>12</td>
<td>0</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>11.5</td>
<td>spherical</td>
<td>60.1</td>
<td>34</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>47.7</td>
<td>spherical</td>
<td>65.4</td>
<td>156</td>
<td>16.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-150</td>
<td>spherical</td>
<td>75.6</td>
<td>323</td>
<td>18.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-200</td>
<td>tubes</td>
<td>60.9</td>
<td>340.2</td>
<td>18.6</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>9-12</td>
<td>rodlike</td>
<td>-</td>
<td>250</td>
<td>0.02</td>
<td>[16]</td>
</tr>
<tr>
<td>Hematite α-Fe$_2$O$_3$</td>
<td>215x28</td>
<td>rodlike</td>
<td>-</td>
<td>46.94</td>
<td>2.754x10$^{-3}$</td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>-400</td>
<td>rhombohedral</td>
<td>-</td>
<td>99.21</td>
<td>1.657x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-230</td>
<td>rhombohedral</td>
<td>-</td>
<td>77.75</td>
<td>1.043x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>rodlike</td>
<td>-</td>
<td>31</td>
<td>1.6x10$^{-3}$</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>cubes</td>
<td>-</td>
<td>10</td>
<td>6.1x10$^{-4}$</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>cubes</td>
<td>8.6</td>
<td>106</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>roughly spherical</td>
<td></td>
<td>72*</td>
<td>200*</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maghemite γ-Fe$_2$O$_3$</td>
<td>4.6</td>
<td>roughly spherical</td>
<td>55*,**</td>
<td>510*</td>
<td></td>
<td>[5]</td>
</tr>
<tr>
<td></td>
<td>2.7</td>
<td>spherical</td>
<td>48*,**</td>
<td>680*</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-200</td>
<td>tubes</td>
<td>42.7</td>
<td>342.2</td>
<td>13.56</td>
<td>[14]</td>
</tr>
</tbody>
</table>

*The measurement was made under non-saturated magnetic hysteresis loops.
**Determination at a temperature of 5 K.

Electrical resistivity measurements in magnetite films prepared by different techniques reveal that the metal-insulator transition in the films is dependent on the deposition conditions and the film thickness; $T_v$ estimations lie between 75 and 165 K for magnetite films prepared by different methods [4, 44, 47, 48, 49]. Figure 3 shows the temperature dependence of the electrical resistivity ($\rho$) for magnetite films prepared by different authors using PLD. For all samples, the semiconductor like behavior can be observed at lower temperatures; however, at higher temperatures of around 100 K, abrupt decreases of $\rho$ are observed. From this abrupt change of $\rho$, the $T_v$ values are measured. The difference of $T_v$ for films with respect to the bulk value (~120 K) has been associated with the residual strain of lattice mismatch between the substrate and the film. However, the lowest value (~75 K), which differs substantially from the bulk, is due to the presence of Fe$_3$O$_4$ [44]. Pure magnetite exhibits magnetoresistance (MR); this is defined as $MR = [R(H) - R(0)]/ R(0)$, where $R(0)$ is the resistance at zero magnetic field ($H$) and $R(H)$ is the measurement at the applied field. Typical MR measurements with respect to temperature show a peak close to $T_v$ [48]. For sputtered films
with magnetic fields in the range of 1-5 T [44], the MR remained around 8% to 10% at
diverse temperatures; for comparison, MR up to 16% in a magnetic field of 7.7 T was observed for a magnetite single crystal near \( T_v \) [49]. The small MR values exhibited in sputtered magnetite films have been attributed to the intergranular transport of spin polarized electrons.

Figure 2. Magnetization hysteresis curves measured at 300 K for magnetite films prepared by sputtering and PLD on different substrates at various deposition conditions. Films deposited at optimal conditions with appropriate thicknesses display clear saturation magnetizations such as the sputtered films prepared by Soeya et al. and Hong et al. [4, 44]. The difference in the magnetization saturation values is due to the difference in the deposition temperature. Films deposited at room temperature show a \( M_s = 190.6 \) emu/cm\(^3\) [44], while the films deposited at 573 K show a \( M_s \) of 430 emu/cm\(^3\) [4].

Figure 3. Electrical resistivity as a function of temperature for magnetite films with different thickness prepared by PLD for different authors. For comparison, the resistivity of single crystal magnetite is included.
3.2. Optical Properties

The optical properties of iron oxides are very important for designing electrochromic devices, photoelectrochemical generation of hydrogen, solar radiation filters, etc. [8, 9, 10, 11]. Magnetite and wustite show thermally induced electronic transitions assigned to intervalence charge transfer; for this reason they exhibit absorption in the visible and near-IR region [55]. Maghemite and hematite are insulators and do not present any absorption in the near-IR region. The oxidation process of magnetite nanoparticles to maghemite has been monitored by the loss of optical absorption in the near-IR region [55]. For hematite films, the direct optical band gap determined through Tauc plots ranges from 2.0 to 2.7 eV [43, 52, 53], while the indirect transition energy is around 1.9 eV [52]. Direct band gaps of 1.73 and 1.97 eV are reported for amorphous and β-Fe₂O₃ films, respectively [42]. The band gap of bulk maghemite is 2.0 eV [54], while maghemite nanoparticles exhibit an energy gap of 2.47 eV due to the quantum confinement effects [56].

3.3. Mossbauer Spectroscopy and X-Ray Photoelectron Spectroscopy (XPS)

Mossbauer spectroscopic studies of iron oxide nanostructures have been extensively reported. One group reported a study on the iron oxides, noting that there was difficulty in guaranteeing complete stoichiometry [57]. Similar studies have been conducted on nanoparticle iron oxides as part of a composite system with polymers [58], while yet another study was directed at the iron oxides and their stability against further oxidation [41]. Mossbauer studies have been reported for nanoparticles and thin films of several of the polymorphic phases such as hematite [9, 17, 40], maghemite [5, 39], magnetite [21, 24, 50] and wustite [24, 54], and other ferrites, as well as nanoparticles of iron oxides that have been coated with other oxides [35, 38]. Additionally, Mossbauer studies have shown the evidence of the presence of an amorphous, spin-glass like phase due to spin frustration at the FeₓO/Fe₃O₄ interface [24].

X-ray photoelectron spectroscopy (XPS) has been widely used for determination of the composition and chemical states of many systems, including magnetite films [44], hematite films [8, 52], iron oxide nanotubes [14], crystals synthesized using copolymer micelles [59], and the production of iron oxide nanoparticles by laser precursors [60]. Nanoparticles of maghemite made by electrodeposition also have been studied by X-ray photoelectron spectroscopy [61]. The Fe 2p₁/₂ and Fe 2p₃/₂ orbitals can be used for the study of the iron oxide phases such as magnetite, hematite, and wustite. However, there is a wide deviation in the published values at the NIST XPS-Database [62]; e.g., wustite presents a variation of 1.1 eV in the Fe 2p₁/₂ peak, while magnetite exhibits a difference of 1.5 eV in the same orbital, which lies at around 710.4 eV [62]. Despite this, XPS is a powerful characterization technique used to determine the purity of magnetite films; e.g., the features that distinguish magnetite from maghemite are the broadening of the Fe 2p₁/₂ and Fe 2p₃/₂ peaks and the absence of a satellite line located at ~718 eV [44].
REFERENCES

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