ABSTRACT
Cobalt nanoparticles play an important role as a catalyst in the Fischer-Tropsch synthesis. During the reaction process, cobalt nanoparticles can become oxidized leading to the formation of two phases: CoO rock-salt and Co₃O₄ cubic spinel. Experimentally, it is possible to evaluate the phase change and follow the catalyst degradation by measuring the magnetic moment, as each material presents a different magnetic structure. It is therefore important to develop a fundamental description, at the atomic scale, of cobalt and its oxide phases which we have done here using density functional theory with the Dudarev approach to account for the on-site Coulomb interactions (DFT+U). We have explored different U values, ranging from 0 to 5 eV, and found that U = 3.0 eV describes most appropriately the mechanical properties, as well as the electronic and magnetic structures of Co, CoO and Co₃O₄. We have considered a ferromagnetic ordering for the metallic phase and the antiferromagnetic structure for the oxide phases. Our results support the interpretation of the catalytic performance of metallic cobalt as it transforms into its oxidized phases under experimental conditions.

KEYWORDS
Materials chemistry, cobalt oxides, cobalt metal, spinel, density functional theory, on-site Coulomb correction.

1. Introduction
Supported cobalt nanoparticles play an important role as catalysts in the Fischer-Tropsch synthesis (FTS), which is a surface polymerization reaction producing hydrocarbon chains from syngas (mixture of H₂ and CO). Recent investigations have concentrated their efforts on the link between the optimum performance of the nanoparticles and their structure. Other investigations have focused on the deactivation of the cobalt nanoparticles by oxidation from water and related this process to the size of the nanoparticles. Indeed, H₂O, a by-product of FTS, has an important effect on the deactivation of cobalt-based FT catalysts. Claeyss and co-workers showed a correlation between the cobalt nanoparticle’s size and its deactivation, which is a consequence of complex re-oxidation mechanisms leading to the formation of the inactive cobalt oxide phase (CoO). To track the deactivation process and the phase change, Claeyss and collaborators used a magnetometer and reduced tricobalt tetroxide (Co₃O₄) to metallic cobalt. The phase change modifies the magnetization, thereby generating a signal in the magnetometer. The initial Co₃O₄, which also has potential applications in several fields of catalysis, was reduced stepwise to CoO and then to metallic Co. This process led to a change from an antiferromagnetic to a ferromagnetic structure. The opposite process, i.e., Co oxidation, would lead to CoO before forming Co₃O₄. Therefore, a description of the Co oxidation to CoO and then Co₃O₄ is crucial for understanding and designing the properties of the catalyst nanoparticles.

A key to controlling the FTS process on Co-based catalysts is to understand the catalyst and active species, where computational modelling can help to explain any structure-activity relationships. Previous theoretical studies have investigated independently the metallic cobalt and oxide phases, but a common protocol to describe accurately all three materials is required, i.e., a common computational setup for representing the electronic and mechanical properties. Thus, the goal of this investigation is to determine a common computational methodology, based on the Density Functional Theory (DFT) to describe accurately the electronic and geometric structures of Co, CoO, and Co₃O₄.

DFT commonly underestimates the band gap and magnetic moment of materials where the valence electrons are highly localized, such as Co metal and Co oxides. Here, we therefore adopt the DFT+U method to describe correctly the electronic and geometric properties of Co, CoO and Co₃O₄. DFT+U is a correction of the pure DFT method, where the U parameter is a Hubbard-like potential added to the Kohn-Sham DFT Hamiltonian. DFT+U usually provides accurate results for 3d transition metal oxides, hence the use of this method in our investigation. We have considered several U parameters, ranging from 0 to 5 eV, in order to calculate the lattice parameters, the band gaps, the total magnetic moments, and the bulk moduli of the materials, following the procedure used in previous works.

2. Computational Methods
We have carried out the calculations using the Vienna Ab-initio Simulation Package (VASP), which solves the Kohn-Sham equations in a periodic framework. All calculations were spin-
polarized and we have employed the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)\(^{32}\) as the density functional. The long-range dispersion interactions were described by the semi empirical method of Grimme (DFT-D)\(^{32}\). We have considered the dispersion effects for modelling these metallic and ionic bulk phases, as we expect in future work to study the catalytic properties of the surfaces of these materials, where this correction plays a major role.\(^{33-44}\)

We have used the Dudarev approach\(^{22}\) to describe the d electrons of the metal atoms, in the DFT+U\(^{45}\) scheme, as implemented in the VASP software. Note that the U used in this investigation is the effective Hubbard U\(_{\text{eff}}\) = U – J where J is considered equal to zero. The core electrons up to and including the 3p levels of Co and the 1s of O were considered as frozen states and the projected augmented wave method (PAW)\(^{46}\) was used to evaluate the interaction between the core and the valence electrons. To determine the number of plane-waves required, we have run energy convergence tests and found that 500 eV is sufficient to properly describe the three materials, i.e. Co, CoO, and Co\(_3\)O\(_4\). The geometry optimizations were performed using the conjugate gradient technique with an ionic convergence criterion of 0.01 eV/Å. Both the shape and the volume of the cell were allowed to change to obtain the ground state lattice. The reciprocal space was sampled by a 21 × 21 × 21 mesh of k-points for both Co and CoO bulks, while for Co\(_3\)O\(_4\) an 8 × 8 × 8 mesh of k-points was used.

**Cobalt.** Metallic cobalt (Co) has three crystal structures: hexagonal close-packed (hcp) (α-phase), face centred cubic (fcc) (β-phase) and primitive cubic phase (ε-phase). Under room conditions, the hcp cobalt is more stable than the fcc phase, while above 450 °C the β-phase becomes the most stable structure.\(^{37}\) Additionally, it has been observed that the FTS is facilitated by an hcp Co catalyst.\(^{48-50}\) Thus, we discuss only the catalytically important cobalt hcp phase, whose primitive unit cell is shown in Fig. 1a.

**Cobalt oxide.** Metal monoxides such as CoO have a rock-salt NaCl crystal structure (R3m) and the most stable magnetic ordering below its Néel temperature is the antiferromagnetic type II (AF-II). In the AF-II ordering, the metal atoms located on the (111) plane present a ferromagnetic ordering, while the metal atoms on two adjacent planes have an antiferromagnetic arrangement.\(^{31,52}\) In the solid state calculations, this magnetic ordering cannot be represented as there is a geometrical frustration in the CoO crystal structure. Thus, to investigate the AF-II structure, we have considered a rhombohedral four-atom unit cell (R3m space group) (Fig. 1b), which is equivalent to the geometry used in previous theoretical studies where the authors investigated the electronic and magnetic structures of CoO.\(^{53,54}\)

**Tricobalt tetroxide Co\(_3\)O\(_4\).** The mixed oxidation state cobalt oxide has a normal spinel structure with a formula unit represented as (A)[B]\(_2\)O\(_4\), where A and B represent Co\(_{2+}\) and Co\(_{3+}\), respectively. The magnetically active Co\(_{2+}\) are located in the tetrahedral site. Co\(_{3+}\) are located in the octahedral site, leading to a complete occupation of the low energy t\(_{2g}\) orbitals and therefore those atoms do not have a permanent magnetic moment.\(^{55}\) Below the Néel temperature (~40 K), the stable magnetic structure is the collinear antiferromagnetic ordering of the spins within the tetrahedral sites.\(^{35-37}\) Figure 1c shows the crystal structure of Co\(_3\)O\(_4\) and its magnetic ordering where neighbouring Co\(_{2+}\) have opposite orientated high-spin states (S = 3/2).

### 3. Results

**3.1. U Parameters Fitting**

The calculated values of the lattice parameter for Co, CoO, and Co\(_3\)O\(_4\), as a function of U values, are shown and compared with previous experimental studies in Table 1. The c/a ratio for Co, which is defined as the ratio of the lattice parameters c and a, increases from 1.616 to 1.801 for a range of U values between 0.0 and 4.0 eV, then it falls to an average of 1.587 at U = 4.5 and 5.0 eV. The calculated values are close to the experimental one obtained from the X-ray bond's method, c/a = 1.623,\(^{38}\) with the highest percentage error of 12 %. (Fig. 2).

The cell lattice of the CoO cubic cell ranges from 4.259 to 4.349 Å as a function of U (Table 1), which is in good agreement with the experimental value (4.26 Å).\(^{39,56}\) Indeed, we have a maximum percentage error of only 2.1 % for U = 1.5 eV (Fig. 2).

Table 1 Calculated lattice parameters (c/a) for Co and (a) for the cubic cells of CoO and Co\(_3\)O\(_4\) for different U values.

| U/eV | c/a  | Co   | a/Å  | Co\(_3\)O\(_4\) |
|------|------|------|------|-----------------|
| 0.0  | 1.616| 4.272| 8.053|                 |
| 0.5  | 1.616| 4.259| 8.063|                 |
| 1.0  | 1.618| 4.259| 8.067|                 |
| 1.5  | 1.621| 4.349| 8.070|                 |
| 2.0  | 1.624| 4.260| 8.077|                 |
| 2.5  | 1.632| 4.308| 8.080|                 |
| 3.0  | 1.658| 4.286| 8.085|                 |
| 3.5  | 1.789| 4.282| 8.088|                 |
| 4.0  | 1.801| 4.281| 8.093|                 |
| 4.5  | 1.581| 4.279| 8.096|                 |
| 5.0  | 1.592| 4.276| 8.099|                 |

**Experiments**

| U/eV | c/a  | Co   | a/Å  |
|------|------|------|------|
| 1.623\(^{38}\) | 4.26\(^{39,52}\) | 8.086\(^{61}\) |
while the O-Co$_{2+}$-O angles keep the same value upon bulk optimization.

### 3.1.2. Mechanical Properties

We have calculated the bulk modulus for each of the three materials as a function of the U value (Table 2). The calculated bulk moduli for pure Co are all in the same order as the experimental values and the bulk modulus derived using $U = 2.5$ eV is within the range of experimental values (19165–199.666) (Fig. 2). The bulk modulus of CoO was reported experimentally to be 181 GPa$^{68}$ and subsequently confirmed by shock and static experiments to be 179 GPa$^{67}$. Our best agreement with the experimental results was again found for $U = 2.5$ eV, where we calculated a value of 182 GPa (Fig. 2). Our result using DFT-D3 + $U$ is close to the one obtained using hybrid functionals (214.92 GPa)$^{70}$.

The bulk modulus of the Co$_3$O$_4$ material was evaluated experimentally to be 189 GPa$^{69}$, which is similar to the PBE+$U$ value (192 GPa)$^{71}$ calculated by Chen et al.$^{71}$ However, our derived values using DFT+$U$ range from 232 to 249 GPa and therefore overestimate the experimental values (191–199.6$^{65,66}$, 179–181$^{67,68}$, 189$^{69}$).

![Figure 2. Lattice parameter, bulk modulus, magnetic moment, and band gap as a function of the U parameter for Co, CoO and Co$_3$O$_4$. For Co, the calculated lattice parameter is the c/a ratio. The dashed lines represent the experimental values.](https://journals.sabinet.co.za/content/journal/chem/)

| U/eV | Bulk modulus/GPa |
|------|------------------|
|      | Co      | CoO     | Co$_3$O$_4$ |
| This work |        |        |             |
| 0.0  | 211     | 164    | 249         |
| 0.5  | 211     | 145    | 244         |
| 1.0  | 211     | 165    | 244         |
| 1.5  | 208     | 188    | 242         |
| 2.0  | 205     | 150    | 239         |
| 2.5  | 198     | 182    | 239         |
| 3.0  | 176     | 157    | 237         |
| 3.5  | 107     | 156    | 236         |
| 4.0  | 126     | 155    | 235         |
| 4.5  | 186     | 133    | 233         |
| 5.0  | 218     | 133    | 232         |

Experiments: 191–199.6$^{65,66}$, 179–181$^{67,68}$, 189$^{69}$.
mate the Co₃O₄ compressibility as the bulk modulus represents the resistance to fracture of a materials. The smallest percentage error was found for U = 5.0 eV (22.75 %) (Fig. 2).

From our calculations (Table 2 and Fig. 2) we note that the value of U = 2.5 eV gives the best agreement with the experimental results for both Co and CoO materials. Concerning CoO, our calculated values are generally overestimating the bulk modulus compared to the experimental result (189 GPa). However, our calculations are based on a perfect and pure single crystal, whereas the presence of impurities and defects, which are difficult to control in experimental samples, may play a key role in influencing the bulk modulus. Thus, if our calculations of the bulk modulus for CoO are correct, as suggested by the excellent agreement with experiment for Co and CoO, then the non-perfect nature of the experimental CoO material makes it less resistant to fracture, compared to the perfect material considered in our calculations.

3.1.3. Electronic Structure

We show in Table 3 the magnetic moment per Co atom and the band gap as a function of the U value for Co, CoO and Co₃O₄ buks.

We note an increase of the magnetic moment in line with the d-correlation for metallic Co, from 1.58 to 2.04 µB. The best agreement with the experimental value (1.72 µB) is found for U = 1.5 eV. However, for the range of U = [0.5–3] eV, the percentage error is relatively small, at less than 5.5 % (Fig. 2), in good agreement with previous GGA+U reports.

The calculated magnetic moment per Co atom in the oxides also increases with the U parameter. In the case of CoO, it is underestimated by ~1 µB compared to the experimental values. The disparity with experiment is attributed to the inaccurate description of the angular momentum of Co²⁺, which is not totally quenched by the crystal field. We could have increased the U parameter to agree better with the experimental magnetization value, but that would have compromised the accuracy of the lattice parameters and the band gap. However, our calculated magnetic moments fall in the range of previous theoretical studies (2.63–2.74 µB).

The poor treatment of the Co²⁺ angular momentum is also reflected in Co₂O₃. The values in Table 3 are equivalent for all the Co²⁺ and we should bear in mind that the magnetic moment indicates the absolute value and may be negative or positive depending on the spin orientation. Experimental magnetic moment measurements of the Co³⁺ atom have indicated a value of 3.26 µB in Co₂O₃, which is ~0.5 µB larger than our calculation using U = 5.0 eV. Singh et al. used DFT+U (U = 4.4 eV for the Co²⁺ ions and 6.4 eV for the Co³⁺ ions) to derive a magnetic moment of Co²⁺ of 2.71 µB. They have also employed hybrid functional calculations, which calculated a value of 2.66 µB. Walsh et al. also used DFT+U (U = 2.0 eV) and reported a similar value for the Co²⁺ magnetic moments, i.e. 2.52 µB.

We therefore consider that any U parameter bigger than 3 eV describes as accurately as is possible the magnetic moment of CoO and Co₂O₃.

Similarly to the magnetization, the band gap (Table 3) increases with the U parameter. In the case of CoO, Kurmaev et al. found a value of 2.60 eV using synchrotron-excited oxygen X-ray K-emission spectroscopy. Forti et al. used DFT+U (U = 4.0 eV), including spin orbit coupling (SOC), to calculate a band gap of 2.81 eV, which is very close to our calculated value (2.82 eV), indicating the negligible effect of SOC in this material.

The accepted experimental band gap values found in the literature for Co₂O₃ ranges from 1.6 to 3.0 eV. However, infrared optical spectroscopy has found a band gap of 0.76 eV whereas the use of long-lived photoexcited carrier dynamics of d-d excitation measured an optical band gap of 0.82 eV. There are also discrepancies in previous theoretical band gap calculations of Co₂O₃. Lima used hybrid calculations, which led to a band gap of 0.72 eV in agreement with the experimental study made by Qiao et al. (0.76 eV) and with our result (for U = 1.0 eV). They found that SOC was not essential for the description of Co₂O₃. However, another study made by Walsh et al. using DFT+U (U = 2.0 eV) determined a band gap of 1.23 eV. The discrepancies between the different studies concerning the Co₂O₃ band gap shows that the description of this property is still under debate.

To determine the U value that describes correctly the geometry of the three materials, we have considered a percentage error cut off of 2.5 % as a good estimation of the cell lattice. We note from Fig. 2 that for Co, CoO and Co₂O₃, the percentage error to describe the bulk geometry is smaller than 2.5 % for the range of U values [0, 3] eV and U = [4.5, 5] eV. The accuracy of the bulk modulus is compromised for Co₂O₃ but U ≥3.0 eV provides a suitable description for the rest of the materials.

A U value of ~3.0 eV also describes adequately the magnetic moment of the three materials and the band gap of both CoO and Co₂O₃. As we will consider a system containing pure Co and its oxides in future investigations, we need to determine one U value that describes, with an acceptably small percentage error, the properties of the three materials at the same time. We will therefore ensure that the formation energies of the cobalt oxide phases are in good agreement with experiment results. Thus, an effective increment of the on-site Coulomb repulsion in the Co d electrons by 3 eV is a fair compromise to investigate the physical and chemical properties of Co and its oxides, although a single U value cannot describe accurately all the properties of the three solids.

3.2. Electronic and Mechanical Properties for U = 3 eV

We have adopted U = 3 eV to describe and discuss in more detail the electronic structure, elastic constants, and mechanical properties of Co, CoO and Co₂O₃.

We have determined the interatomic distances for the three materials and found the Co-Co distance in metallic Co to equal 2.427 Å, which is comparable to previous experimental findings (2.497 Å). In the CoO bulk, we have determined a Co-O distance of 2.142 Å, which is in agreement with previous reports.
In Co₃O₄, the Co³⁺-O and Co²⁺-O distances are 1.920 and 1.937 Å, respectively, which is comparable to a previous theoretical investigation⁶⁴ (Co³⁺-O = 1.926 Å and Co²⁺-O = 1.929 Å), whereas another theoretical study determined the following distances: Co³⁺-O = 1.93 Å and Co²⁺-O = 1.94 Å.⁸¹ Our calculated Co³⁺-O and Co²⁺-O distances are also in good agreement with the experimental result (Co³⁺-O = 1.923 Å and Co²⁺-O = 1.928 Å) reported by Liu et al.⁹⁰

In Fig. 3, we show the total and projected density of states (DOS) of Co, CoO and Co₃O₄ materials. The asymmetric up and down spin channels show the ferromagnetic characteristic of metallic cobalt, where the shift of the band centre in the minority spin towards higher energies has also been observed in previous theoretical studies.⁴⁷,⁹¹

The total magnetization of CoO is zero as the DOS of the up and down spin channels are symmetric (Fig. 3). Indeed, the three unpaired electrons of each cobalt atom in the four-atom unit cell present an antiferromagnetic ordering as shown in (Fig. 1b). We note that the valence band is composed by the Co 3d orbitals and O 2p orbitals, while the contribution of anion orbitals to the conduction band is negligible. Similar results were shown by Archer et al.⁹² and Wdowick et al.⁵² who used DFT+U methodology to show the hybridization of the Co 3d orbitals with the O 2p orbitals in the valence band, while the conduction band is composed only by Co 3d. More precisely, the valence band maximum is mainly composed by the O 2p orbitals and the Co t₂₈ orbitals, while the conduction band minimum is dominated by the Co 3d orbitals.

We have also computed the Jₑ coupling between the nearest Co neighbours (Equation 1), where S = 3/2 and Eₐₚ and Eₚₘ are the total energies of the antiferromagnetic and ferromagnetic structures, respectively. Our J value (15.69 meV) is double the

Figure 3 Electronic density of states (DOS) of Co, CoO and Co₃O₄. Colour key: for each material, the total DOS is represented by a black line. The blue line corresponds to the projected density of state (PDOS) of metallic Co 3d orbitals. The red, the green, and the yellow lines represent the PDOS of Co e and e, Co t₂ and t₂₈, O 2p, orbitals.
one determined by Deng et al. (8.00 meV), who used $U = 5.1$ eV and $J = 1.0$ eV to describe the rocksalt CoO bulk.

$$J_1 = \frac{1}{2} \times \frac{1}{4} \times \frac{1}{4} \times (E_{FM} - E_{AFM})$$

(1)

In the case of Co$_3$O$_4$, we note from Fig. 3 that the DOS is mainly constituted of the Co$^{3+}$ d-orbitals, for the band energies between $-1.5$ and $-0.5$ eV. Moreover, it is equally formed by the d-Co$^{3+}$, d-Co$^{2+}$ and 2p O orbitals between $-0.5$ eV and the Fermi energy. In the conduction band, the Co$^{3+}$-d orbitals are less dominant and the contribution of O p orbitals and Co$^{2+}$-d orbitals is negligible, in good agreement with previous experimental and theoretical investigations, which have also demonstrated that the Co$^{3+}$ d-orbitals prevail in the valence band.\textsuperscript{64,71,94} Additionally, from the projection of the Co$^{3+}$ orbitals, we noted that the valence band is composed of t$_{2g}$ orbitals and the conduction band is composed of e$_g$ orbitals. The symmetrical plot of the Co$^{3+}$ DOS confirms that all the t$_{2g}$ orbitals are filled with six electrons, while the e$_g$ orbitals are empty. Thus, our computational results validate the magnetic structure: $S = 0$ (t$_{2g}$ e$_g$), showing that the Co$^{3+}$ atom in spinels has the same behaviour regardless whether it occupies the tetrahedral or octahedral position.\textsuperscript{95}

In Co$_2^+$, the down spin states of the t$_2$ orbitals are located in the valence band, while the spin-up states are located in the conduction band (Fig. 3). We observe that most of the e orbitals are located at a higher energy than the t$_2$ orbitals and both alpha and beta states are located in the valence band, but at different energies (non-symmetric plot). These show the magnetic configuration of Co$^{2+}$ to be $S = 3/2$ (t$_2^1$ t$_2^3$), which confirms that the magnetization in the Co$_2$O$_4$ bulk comes from the Co$^{2+}$ atoms with their unpaired electrons, which is in good agreement with the study made by Chen et al.\textsuperscript{71} It also suggests that the magnetic properties of this atom in a spinel do not depend on the cation filling the octahedral holes.\textsuperscript{95}

We have next computed the J$_1$ exchange coupling between the nearest Co$^{3+}$ neighbours (Equation 2):

$$J_1 = \frac{1}{2} \times \frac{1}{4} \times \frac{1}{4} \times (E_{AFM} - E_{FM})$$

(2)

where $S = 3/2$ and $E_{AFM}$ and $E_{FM}$ are the total energies of the antiferromagnetic and ferromagnetic structures, respectively. In this work, we determined a value of $J_1 = -4.28$ meV, which is close to the value reported in a previous experimental investigation.\textsuperscript{56} Another theoretical investigation made by Chen et al.\textsuperscript{71} reported a value of $-5.0$ meV using hybrid functionals. However, the same authors determined a value of 0.1 meV using DFT+U as their $U_{eff}$ parameter is larger than ours: they chose $U_{eff} = 4.4$ eV.\textsuperscript{56} We have therefore chosen this latter value to describe the electronic and magnetic structures, and the elastic constants of the three materials. We have shown, from the DOS plots that metallic cobalt is ferromagnetic, while both cobalt oxides, CoO and Co$_3$O$_4$ present an antiferromagnetic structure. In Co$_2$O$_4$, the magnetization comes from the Co$^{2+}$ atoms as they have unpaired electrons and the neighbouring Co$^{3+}$ atoms have their highest spin states (S = 3/2).\textsuperscript{96} $U = 3.0$ eV also describes correctly the crystal structure of Co$_3$O$_4$, with a distortion along two different axes is 14.1 GPa larger for magnetite, indicating that the cobalt spinel is slightly easier to deform in this direction compared to Fe$_3$O$_4$.

### Conclusion

We have studied the mechanical and electronic properties of Co, CoO and Co$_3$O$_4$ considering $U$ values ranging from 0 to 5 eV. The calculated bulk properties, i.e. cell parameter, bulk modulus, magnetic moment, and band gap for all the materials were in fair agreement with previous theoretical and experimental studies for $U = 3.0$ eV. We have therefore chosen this latter value to describe the electronic and magnetic structures, and the elastic constants of the three materials. We have shown, from the DOS plots that metallic cobalt is ferromagnetic, while both cobalt oxides, CoO and Co$_3$O$_4$ present an antiferromagnetic structure. In CoO, the metal atoms belonging to the same (111) plane have a ferromagnetic ordering, while the metal atoms on two adjacent (111) planes present an antiferromagnetic ordering. In Co$_3$O$_4$, the magnetization comes from the Co$^{3+}$ atoms as they have unpaired electrons and the neighbouring Co$^{3+}$ atoms have opposite high-spin state (S = 3/2).\textsuperscript{56} $U = 3.0$ eV also describes correctly the band gaps of both CoO and Co$_3$O$_4$ materials. Finally, the calculated elastic constants are in fair agreement with previous theoretical and experimental studies, except for the $C_{13}$ and $C_{36}$ of metallic Co.

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