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# Transformation of $\text{Co}_3\text{O}_4$ nanoparticles to $\text{CoO}$ monitored by *in situ* TEM and predicted ferromagnetism at the $\text{Co}_3\text{O}_4/\text{CoO}$ interface from first principles†

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Nanoparticles of  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$  are of paramount importance because of their chemical properties propelling their applications in catalysis and battery materials, and because of their intriguing magnetic properties. Here we elucidate the transformation of  $\text{Co}_3\text{O}_4$  nanoparticles to  $\text{CoO}$  into nanoscale detail by *in situ* heating in the transmission electron microscope (TEM), and we decipher the energetics and magnetic properties of the  $\text{Co}_3\text{O}_4/\text{CoO}$  interface from first principles calculations. The transformation was found to start at a temperature of 350 °C, and full conversion of all particles was achieved after heating to 400 °C for 10 minutes. The transformation progressed from the surface to the center of the nanoparticles under the formation of dislocations, while the two phases maintained a cube-on-cube orientation relationship. Various possibilities for magnetic ordering were considered in the density functional theory (DFT) calculations and a favorable  $\text{Co}_3\text{O}_4/\text{CoO}$  {100}/{100} interface energy of 0.38 J m<sup>-2</sup> is predicted for the lowest-energy ordering. Remarkably, the DFT calculations revealed a substantial net ferromagnetic moment originating from the interface between the two antiferromagnetic compounds, amounting to approximately 13.9  $\mu_{\text{B}}$  nm<sup>-2</sup>. The transformation was reproduced *ex situ* when heating at a temperature of 400 °C in a high vacuum chamber.

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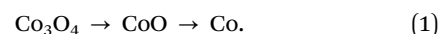
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## 1. Introduction

$\text{Co}_3\text{O}_4$  nanocrystals are materials of great importance to many applications. Cobalt oxide nanoparticles and their reduced derivatives are used as catalysts in the well-known Fischer–Tropsch process for the production of hydrocarbon fuels, but are also considered as catalysts for water splitting.<sup>1–4</sup> Furthermore, cobalt oxide is one of the most frequently used materials in Li-ion batteries<sup>5,6</sup> powering cell phones and other electronic equipment, and is used in gas sensors as well.<sup>7</sup> Understanding the reduction process and its mechanism at the nanoscale is essential for controlling the nanoparticle properties in these applications. The reduction of  $\text{Co}_3\text{O}_4$  under different chemical and physical conditions has been extensively investigated, as will be discussed in more detail below. A two-stage reduction

process has been reported by many researchers,<sup>8–10</sup> where spinel  $\text{Co}_3\text{O}_4$  first transforms to rock salt  $\text{CoO}$  and subsequently to elemental  $\text{Co}$ ,



Elemental  $\text{Co}$  adopts the hexagonal close packed (hcp) crystal structure in the bulk phase, but adopts the face centered cubic (fcc) structure with a lattice parameter of 0.354 nm when the particle size is less than 30 nm.<sup>11</sup> The crystal structures of  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$  are both cubic and the lattice parameter of  $\text{Co}_3\text{O}_4$  is approximately twice as large as the lattice parameter of  $\text{CoO}$ .

Fig. 1 shows their schematic structure.  $\text{Co}_3\text{O}_4$  has the spinel crystal structure. Cobalt atoms are in the interstices of the distorted fcc lattice of oxygen atoms.  $\text{Co}^{2+}$  cations occupy tetrahedral interstitial sites and  $\text{Co}^{3+}$  cations occupy octahedral interstitial sites. In contrast,  $\text{CoO}$  has a rock salt structure with  $\text{Co}^{2+}$  cations on one of the interpenetrating fcc sublattices and  $\text{O}^{2-}$  anions on the other fcc sublattice.

The thermal stability of the  $\text{Co-O}$  system has been investigated in several ways. The thermodynamic properties of both solid and liquid phases of the  $\text{Co-O}$  system were calculated by Chen *et al.*<sup>12</sup> In a study employing interatomic potentials obtained by machine

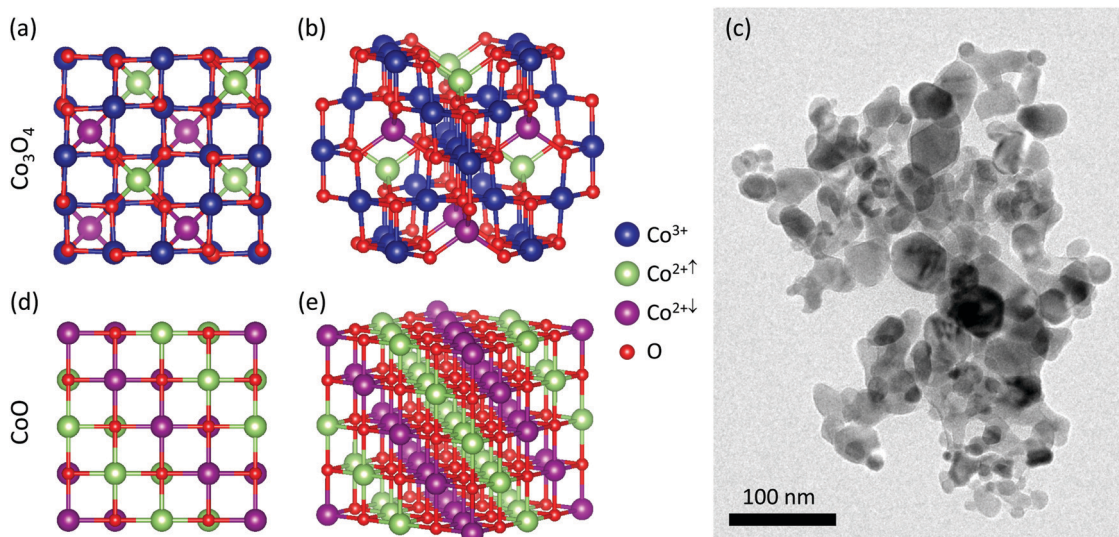
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**Fig. 1** (a and b) Crystal structure of spinel  $\text{Co}_3\text{O}_4$  with antiferromagnetic (AFM) ordering, with a [100] projection shown in (a) and a near-[110] projection shown in (b); (c) bright-field TEM overview image of the pristine  $\text{Co}_3\text{O}_4$  nanoparticles. (d and e) Crystal structure of rock salt  $\text{CoO}$  with AFM2 ordering accommodated in a  $2 \times 2 \times 2$  supercell, with a [100] projection shown in (d), and a near-[110] projection shown in (e) where the stacking of (111) spin-up Co and (111) spin-down Co atomic planes is clearly seen. Red spheres denote O atoms, and blue, green, and purple atoms denote nonmagnetic  $\text{Co}^{3+}$ , spin-up  $\text{Co}^{2+}$ , and spin-down  $\text{Co}^{2+}$  atoms, respectively.

learning, Kong *et al.* showed that only  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$  are stable compositions in the Co–O system and that the transition between cubic  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$  is reversible.<sup>13</sup> Navrotsky *et al.* calculated phase diagrams for both the bulk Co–O system and the nanoscale Co–O system, and showed that the range where the  $\text{CoO}$  phase is stable (in terms of partial oxygen pressure and temperature) is considerably narrower for 10 nm sized nanoparticles in comparison with the  $\text{CoO}$  range of stability in the bulk phase diagram.<sup>14</sup>

The reduction processes have been investigated experimentally under a  $\text{H}_2$  atmosphere<sup>4,8,10,15,16</sup> and under plasma exposure.<sup>17</sup> Ward *et al.* observed the reduction using environmental transmission electron microscopy (ETEM) under low hydrogen pressures, and found that  $\text{Co}_3\text{O}_4$  nanoparticles reduced to  $\text{CoO}$  predominantly at a temperature of 350 °C and at a hydrogen pressure of 0.1 mbar (10 Pa), while the formation of pure Co was only observed upon further heating at 450 °C at a higher hydrogen pressure of 0.3 mbar (30 Pa).<sup>18</sup> Bulavchenko *et al.* investigated the transformation at standard pressure ( $1.0 \times 10^5$  Pa) using X-ray diffraction (XRD) and reported the two-stage process, but in addition they also reported a one-step process where the  $\text{Co}_3\text{O}_4$  particles could be reduced directly to metallic Co, without intermediate formation of  $\text{CoO}$ , when the samples were exposed to pure  $\text{H}_2$ .<sup>9</sup> The standard enthalpy of reduction of  $\text{Co}_3\text{O}_4$  to  $\text{CoO}$  was reviewed and investigated experimentally by Mayer *et al.*<sup>19</sup> A detailed high-resolution study of the nanoscale structural transformation during heating under vacuum conditions in the absence of any reducing agents has not yet been performed, though. The rapidly developing *in situ* transmission electron microscopy (TEM) technique now enables the direct observation of phase transformations at atomic resolution,<sup>20</sup> which greatly benefits a detailed investigation of the reduction process.

The  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$  phases have also been extensively studied because of their interesting electronic and magnetic structures, which have been the subject of a lively debate in the literature.<sup>21–25</sup> The rock salt  $\text{CoO}$  phase undergoes a Jahn–Teller distortion at low temperature, rendering it a monoclinic phase that is still pseudo-rock-salt type.<sup>23</sup> The magnetic ground state is antiferromagnetic (AFM), where spins of equal sign are arranged in the cubic (111) planes of Co atoms, and the spin-up/spin-down alternation is along the [111] stacking direction of these Co atomic planes. This AFM type is referred to as AFM2.<sup>22</sup> The magnetic moment of the  $\text{Co}^{2+}$  atoms is approximately  $3 \mu_{\text{B}}$ <sup>21,22</sup> and the Néel temperature is  $T_{\text{N}} = 287$  K.<sup>21,26</sup> The material is a semiconductor both below and above that temperature; reported values for the band gap are about 2.5–2.7 eV.<sup>23,27</sup>

In the spinel-type  $\text{Co}_3\text{O}_4$  phase the trivalent  $\text{Co}^{3+}$  ions are nonmagnetic while the  $\text{Co}^{2+}$  ions carry a magnetic moment. At low temperature the  $\text{Co}_3\text{O}_4$  phase is antiferromagnetic (AFM) with the  $\text{Co}^{2+}$  ions following conventional AFM ordering with alternating magnetic moments along the cubic axes (AFM1 ordering). The experimentally determined magnetic moment of the  $\text{Co}^{2+}$  ions is  $3.26 \mu_{\text{B}}$  and the Néel temperature is  $T_{\text{N}} = 40$  K.<sup>24</sup>  $\text{Co}_3\text{O}_4$  is a semiconductor, with reported values for the band gap varying from 0.74 eV (ref. 25) to 1.5–2.5 eV.<sup>24,28</sup>

The electronic and magnetic properties of  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$  nanoscale particles can differ dramatically from the properties discussed above for  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$  bulk compounds. That the Néel temperature of both bulk compounds is below room temperature while our experiments are performed at room temperature, does not necessarily imply that the nanoparticles under investigation in the present study will not be magnetic. In general, due to finite size effects, and surface and interface effects, the



magnetization and magnetic anisotropy of nanoparticles can be much larger than the magnetization and magnetic anisotropy of their bulk counterparts, and the Curie and Néel temperatures can vary by hundreds of degrees.<sup>29</sup> Typically, magnetic nanoparticles consist of only one magnetic domain, which explains their generally higher anisotropy in comparison with multi-domain bulk structures. Furthermore, below a critical size nanoparticles can become superparamagnetic, in which case the atomic magnetic moments in the nanoparticles will be continuously fluctuating when an external magnetic field is absent but respond with high levels of magnetization when an auxiliary magnetic field is applied.<sup>29</sup> The magnetic ordering temperature of a nanomaterial is generally lower than the bulk phase value, but this effect can be masked or reversed by crystallographic parameters or composition.<sup>29</sup> For CoO and Co<sub>3</sub>O<sub>4</sub> nanoparticles, a reduction of the Néel temperature was observed; this reduction has been found to increase with decreasing particle size.<sup>30–32</sup> At the same time, the literature on CoO and Co<sub>3</sub>O<sub>4</sub> nanoparticles reports the observation of net ferromagnetism at room temperature;<sup>32–35</sup> this net-ferromagnetic effect is generally attributed to surface effects. Room-temperature ferromagnetism has also been reported for Co<sub>3</sub>O<sub>4</sub>/CoO core/shell particles; in their case, the net-ferromagnetism was attributed to interface effects.<sup>36</sup>

The experiments performed in this work established that the Co<sub>3</sub>O<sub>4</sub> and CoO phases are in a cube-on-cube orientation relationship with respect to each other. We therefore employed density functional theory (DFT) calculations to investigate the {100}/{100} interface between the two phases. This particular interface orientation is observed in Co<sub>3</sub>O<sub>4</sub>/CoO nanocrystals in the present study, and was also described experimentally by Tung *et al.* in Co<sub>3</sub>O<sub>4</sub>/CoO core/shell nanocubes.<sup>37</sup> Various possible input magnetic configurations were considered for the DFT calculations. The interface energy of the lowest-energy {100}/{100} interface between the Co<sub>3</sub>O<sub>4</sub> and CoO phase was calculated. We also aim to answer the interesting question of whether the overall magnetism and the magnetic ordering changes when the two phases are brought into contact with each other.

In the present study, we first investigate the thermal reduction of Co<sub>3</sub>O<sub>4</sub> to CoO nanocrystals experimentally by means of *in situ* vacuum heating in the TEM. The transformation was monitored both by real-space imaging and by electron diffraction (ED) to identify the formation of new phases and their crystal structures. The reduction started at a temperature of 350 °C, and full reduction of all particles was achieved at 400 °C. During the transition, the two phases were found to be in a cube-on-cube orientation relationship. Next, the interface between Co<sub>3</sub>O<sub>4</sub> and CoO is investigated by means of DFT calculations, to calculate the interface energy of the interface and to study the effect of the interface on the magnetic properties of the multiphase configuration.

## 2. Experimental section

### Sample preparation and TEM characterization

The Co<sub>3</sub>O<sub>4</sub> nanocrystals (NCs) were purchased from Sigma-Aldrich and had a broad size distribution of 5–50 nm as shown

in Fig. 1(c). The Electron Diffraction (ED) and *in situ* TEM investigations were conducted using a TFS TalosF200X TEM operating at 200 kV with a point-to-point resolution of approximately 1.1 Å in bright-field TEM imaging mode. An overview TEM image of the pristine samples is shown in Fig. 1(c). High-resolution imaging was also conducted with a double aberration corrected TFS Spectra300 TEM, operated at 300 kV and with a point-to-point resolution of 50 pm in TEM mode, on partially transformed particles to show high resolution details of the heterogeneous nanostructures. The TEM specimens were prepared by drop casting the Co<sub>3</sub>O<sub>4</sub> solution onto a DENSsolutions MEMS heating chip containing electron-transparent 15 nm thick SiN membranes, which we will refer to as the ‘windows’ on the chip.

### X-ray diffraction (XRD)

The crystal structure of Co<sub>3</sub>O<sub>4</sub> in the pristine samples was confirmed by XRD measurements (shown in Fig. S1, ESI†). The XRD was conducted using a PW 1729 Philips diffractometer, equipped with a Cu K<sub>α</sub> X-ray source (1.79026 Å). The Co<sub>3</sub>O<sub>4</sub> powder was uniformly dispersed on an aluminum substrate for the XRD measurement.

### *In situ* TEM heating

The heating chips were subsequently mounted on a DENSsolutions single tilt heating holder. The Co<sub>3</sub>O<sub>4</sub> nanocrystals were first heated from room temperature to 900 °C with 50 °C increments to monitor their evolution with temperature. It was established that reduction took place at 350–400 °C. The transformation took place everywhere, also in areas on the heating chip that were not previously exposed to the electron beam. A control experiment was also performed where the NCs were heated to 400 °C and then cooled down gradually, to verify that the NCs did not transform into a structure other than CoO rocksalt after cooling to room temperature, which was not the case.

### *Ex situ* heating experiments

Several *ex situ* control experiments were performed. *Ex situ* heating experiments were conducted in tube furnaces under air flow, N<sub>2</sub> flow, and under vacuum. For these experiments, the complete heating chips with the sample, prepared in the same way as for the *in situ* heating experiments, were inserted in the oven. The samples heated under air and under N<sub>2</sub> flow were heated at a rate of 5 °C min<sup>-1</sup>. The samples were kept at 400 °C for 10 minutes and allowed to cool down naturally to room temperature. The samples were also heated with the heating holder in air, and with the heating holder inserted in a high vacuum chamber (Gatan pumping station Model 655), applying the same rate as in the *in situ* heating experiments. The pressure in the high vacuum chamber was approximately 1.0 × 10<sup>-7</sup> Torr. After holding the temperature at 400 °C for 10 minutes, the sample was cooled down fast to room temperature and swiftly inserted in the TEM for subsequent analysis.



### 3. Computational section

Density functional theory (DFT) calculations were employed to study the CoO/Co<sub>3</sub>O<sub>4</sub> {100}/{100} interface. First, the CoO and Co<sub>3</sub>O<sub>4</sub> bulk phases were calculated separately, to obtain bulk phase reference energies and equilibrium lattice parameters, and to establish the magnetic ground state of the bulk phases. Four multiphase supercells with various magnetic orderings for the constituent bulk phase slabs were then constructed to calculate the interface energy of four different magnetic configurations. A Bader analysis<sup>38</sup> was performed to investigate if, and how, the magnetism changes when the two phases are brought into contact.

#### Computational method

The calculations were performed using the plane-wave VASP code<sup>39,40</sup> employing the projector augmented wave (PAW) scheme<sup>41,42</sup> and the generalized gradient approximation (GGA) with the exchange–correlation functional by Perdew, Burke and Ernzerhof (PBE).<sup>43</sup> For the bulk phases, the DFT+*U* approach<sup>44</sup> was considered as well. In the DFT+*U* approach, the Hubbard *U* potential has the effect of lowering the energies of the d electron bands and as such compensates for the deficiency of standard DFT in describing strongly correlated systems. The use of hybrid functionals such as HSE06 or PBE0 was not considered as these methods are computationally prohibitively expensive for the large interface supercells considered in this work. The energy cutoff and the density of the *k*-meshes were tested to ensure energy convergence well within 2 meV per atom. All calculations were performed in reciprocal space as calculations in real space were often found not to converge properly electronically. The required cutoff energy of the wave functions found from the energy convergence tests was 700 eV, which is higher than the energy cutoffs typically reported in the literature (500–600 eV). A cutoff energy of 980 eV was used for the augmentation functions. The electronic wave functions were sampled using the Monkhorst and Pack scheme,<sup>45</sup> on 6 × 6 × 6 *k*-grids for both the conventional Co<sub>3</sub>O<sub>4</sub> unit cell and the 2 × 2 × 2 supercell of the conventional CoO unit cell that is required to accommodate the AFM2 magnetic ordering of the latter (see Fig. 1(d and e)). For the interface supercells, 6 × 6 × 1 *k*-grids were used.

All simulation cells were structurally optimized, relaxing atomic positions and lattice parameters, to yield lower-energy configurations. For the ionic relaxation loop, accumulative energy and atomic force convergence criteria of 10<sup>−5</sup> eV and 0.01 eV Å<sup>−1</sup>, respectively, were applied for the bulk phase calculations; for the interface calculations, accumulative criteria of 10<sup>−4</sup> eV and 0.01 eV Å<sup>−1</sup> were used. For all calculations, an energy convergence criterion of 10<sup>−6</sup> eV was set for the electronic convergence loop. For the spin-polarized calculations, the initial magnitude of the magnetic moment was always set to 4 μ<sub>B</sub> for the atoms carrying a magnetic moment (*i.e.*, for all Co<sup>2+</sup> atoms), and to 0 for all other atoms. The magnetic moments were not fixed but allowed to relax (to reduce in magnitude, and even to change in sign) during the electronic self-consistent calculation. The Bader analysis, performed to determine the charge distribution among

the atoms and to calculate the magnetic moments on the atoms, was carried out using the approach by Henkelman *et al.*<sup>46</sup> All calculations are valid for a temperature of 0 K and a pressure of 0 Pa. Zero-point vibration contributions have been neglected. Non-collinear magnetism has not been considered.

#### CoO and Co<sub>3</sub>O<sub>4</sub> reference phases

Most DFT calculations in the literature have been performed using the primitive cells of the cubic phases of CoO and Co<sub>3</sub>O<sub>4</sub>, while Dalverny *et al.* performed calculations on the Jahn–Teller distorted monoclinic phase of CoO.<sup>23</sup> In the present work, we performed calculations and parameter testing on the conventional unit cells as these are more representative for the interface supercells we wish to construct. For the CoO phase, input configurations with antiferromagnetic AFM1 and AFM2, ferromagnetic (FM), and nonmagnetic (NM) magnetic orderings were considered. Here, AFM1 represents the alternation of spin-up and spin-down Co (100) planes, whereas AFM2 represents the alternation of spin-up/spin-down Co (111) atomic planes as depicted in Fig. 1(d and e); we here follow the nomenclature by Deng *et al.*<sup>22</sup> For the Co<sub>3</sub>O<sub>4</sub> phase, AFM1 (as depicted in Fig. 1(a and b)), FM, and NM magnetic orderings were considered as input. All configurations were calculated both with standard DFT, *i.e.*, using the GGA-PBE exchange–correlation functional, and with DFT+*U*. In the literature reporting DFT+*U* results on CoO and Co<sub>3</sub>O<sub>4</sub> phases, in general *U*<sub>eff</sub> values between 4 and 5 eV are chosen.<sup>21–25</sup> Here, for our DFT+*U* calculations, we used an identical value of *U*<sub>eff</sub> = 4.4 eV for all Co atoms in the two compounds, as we wish not to distinguish between Co<sup>2+</sup> and Co<sup>3+</sup> when interfaces are created.

#### CoO/Co<sub>3</sub>O<sub>4</sub> supercells and interface energy

Fig. 2 shows the interface supercells with the various configurations of the magnetic orderings that were used as input for the calculations. The designation of the magnetic orderings applies to the CoO/Co<sub>3</sub>O<sub>4</sub> {100}/{100} interface simulated by a supercell of which the bottom half consists of a 2 × 2 × 4 supercell of the conventional CoO unit cell and the top half consists of a 1 × 1 × 2 supercell of the conventional Co<sub>3</sub>O<sub>4</sub> unit cell, adding up to a total of 240 atoms per interface supercell. Besides a fully nonmagnetic (NM/NM) and a fully ferromagnetic (FM/FM) input configuration, two antiferromagnetic input configurations were considered. In the antiferromagnetic configurations, the interface is formed by a bottom CoO slab that has either AFM1 or AFM2 ordering and a top Co<sub>3</sub>O<sub>4</sub> slab that is always AFM1 ordered, which results in the AFM1/AFM1 and AFM2/AFM1 configurations depicted in Fig. 2(c)–(e).

After full relaxation of the supercells, the interface energy  $\gamma_{\text{int}}$  was calculated for each of the interfaces as:

$$\gamma_{\text{int}} = \frac{E_{\text{int}}^{\text{super}} - nE_{\text{CoO}} - mE_{\text{Co}_3\text{O}_4}}{2A_{\text{int}}} \quad (2)$$

Here,  $E_{\text{int}}^{\text{super}}$  is the energy of the interface supercell;  $E_{\text{CoO}}$  and  $E_{\text{Co}_3\text{O}_4}$  are the energy of one reference unit cell of CoO and Co<sub>3</sub>O<sub>4</sub>, respectively;  $n$  and  $m$  are the number of CoO and Co<sub>3</sub>O<sub>4</sub> unit cells in the supercell; and  $A_{\text{int}}$  is the area of the interface,



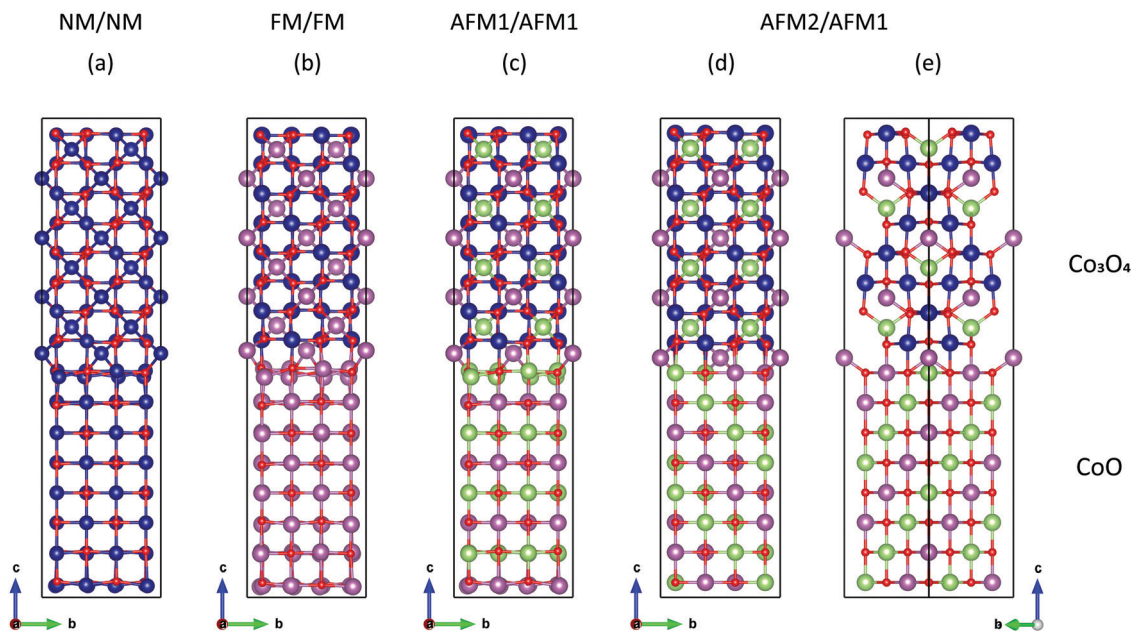


Fig. 2 Atomic models of the interface supercells with various magnetic orderings. Panels (d) and (e) both illustrate the AFM2/AFM1 configuration, showing a [100] projection in (d) and a  $[\bar{1}10]$  projection in (e). Panel (e) is included so that the AFM2 ordering in the CoO phase, *i.e.*, the antiferromagnetic ordering along the (111) direction, can be nicely seen. Red spheres denote O ions. Blue spheres denote nonmagnetic  $\text{Co}^{3+}$  ions. Purple and light green spheres denote spin-up  $\text{Co}^{2+}$  and spin-down  $\text{Co}^{2+}$  ions, respectively.

calculated from the supercell lattice vectors as  $A_{\text{int}} = |a \times b|$ . The factor of 2 in the denominator arises from the fact that due to the periodic boundary conditions that apply to plane-wave DFT calculations, the periodic interface supercells always contain two interfaces.

## 4. Results and discussion

### In situ and ex situ TEM investigations

The *in situ* heating experiments conducted on the  $\text{Co}_3\text{O}_4$  NCs were performed as described in the Experimental section. An XRD spectrum confirming the  $\text{Co}_3\text{O}_4$  phase of the pristine nanosamples can be found in Fig. S1 of the ESI†. First, the particles as dropcast on the heating chip were heated from room temperature to 900 °C with increments of 50 °C. Bright-field TEM images and selected area electron diffraction (SAED) patterns were recorded at every heating step. Fig. 3 shows TEM images of the cobalt oxide nanoparticles in two different areas at room temperature, at 400 °C, and at 800 °C. The particles agglomerated at room temperature after drying on the TEM supports. After heating at a temperature of 400 °C, the surfaces of the nanocrystals became uneven and more faceted. This indicates that particular crystallographic facets are preferentially exposed, driven by minimization of the total surface energy. As the onset of faceting coincides with the transformation to CoO, which will become clear from the SAEDs in Fig. 4, this is possibly caused by CoO NPs having more distinct facet-dependent surface energies than  $\text{Co}_3\text{O}_4$  NPs. In addition, stronger diffraction contrast also appeared on the particles, which we attribute to the phase

transformation to CoO as also evidenced by the SAED results of Fig. 4 and Fig. S2 (ESI†). At 800 °C, the particles coalesced and fused as is clear from the bottom-right panel in Fig. 3, which corroborates the results of the SAED patterns showing fewer but stronger peaks at temperatures of 600 °C and higher (Fig. S2 of the ESI†).

While bright-field TEM imaging provides information about changes in morphology and in the size of the NCs, the SAED patterns uniquely identify the crystal structure of the NCs during the heating experiments. Fig. S2 of the ESI† shows the diffraction patterns (DPs) recorded during the whole heating process. At room temperature and after heating at temperatures of up to 300 °C, the SAED patterns corresponded to the  $\text{Co}_3\text{O}_4$  crystal structure. Upon annealing at 350 °C, however, the patterns started to change, and after keeping the sample at 400 °C for 10 minutes, only three rings remained that are indicative of the highly symmetric CoO phase.

In Fig. 4, a comparison is shown between the SAED patterns at 20 °C (left) and at 400 °C (right). The rings in the DPs were indexed and found to correspond to the  $\text{Co}_3\text{O}_4$  phase and to the CoO phase, respectively. Table S2 (ESI†) shows the corresponding lattice spacings of the rings in both diffraction patterns. Fig. S3 (ESI†) shows the integrated DPs at 20 °C, 350 °C, 400 °C and 400 °C after 10 minutes, clearly showing the transformation as well. From 350 °C onwards, peaks corresponding  $\text{Co}_3\text{O}_4$  started to disappear or became weaker, whereas a new peak corresponding to the (002) reflection of CoO appeared. Finally at 400 °C, only peaks corresponding to CoO were found, indicating that the transformation of the NPs was complete. Clearly, the SAED patterns show that the transformation to CoO took place from 350 °C onwards and was completed after heating to 400 °C for



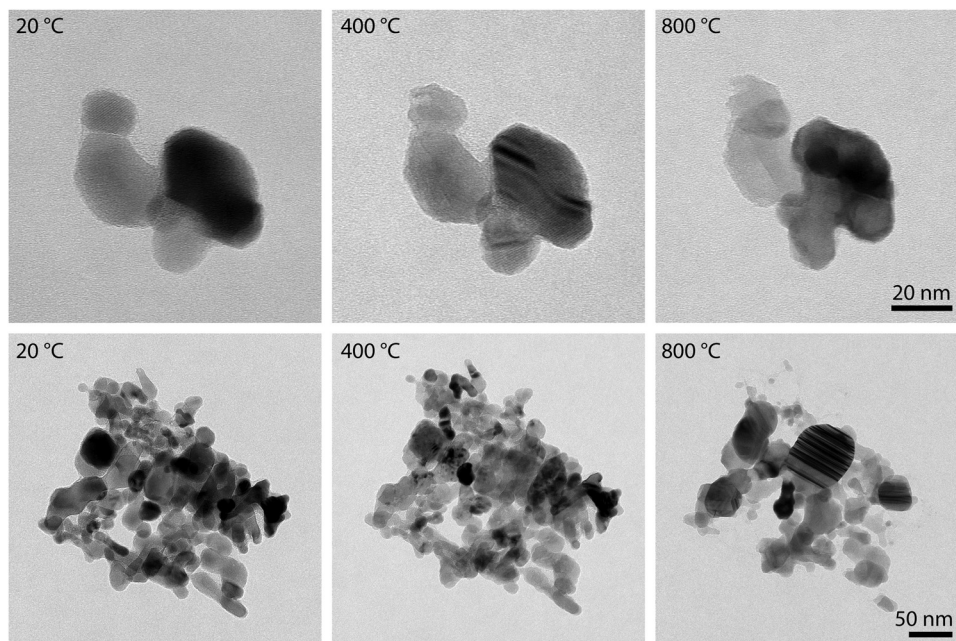


Fig. 3 Bright-field TEM images of (initially)  $\text{Co}_3\text{O}_4$  NPs at room temperature, at 400 °C and at 800 °C. The surfaces of the NPs become uneven at 400 °C, while diffraction contrast increases.

10 minutes. Above 400 °C, the rings in the DPs did not change any more, indicating no further reduction. From 600 °C onwards, there are fewer spots on the rings due to coalescence and alignment of the nanocrystals, which consequently became larger and fewer in number.

Four *ex situ* reference experiments were conducted for comparison with the *in situ* heating experiments. *Ex situ* heating was conducted in a tube oven in air (1), in a tube oven under  $\text{N}_2$  flow (2), using the heating holder while kept in ambient air outside the TEM (3), and using the heating holder in a high

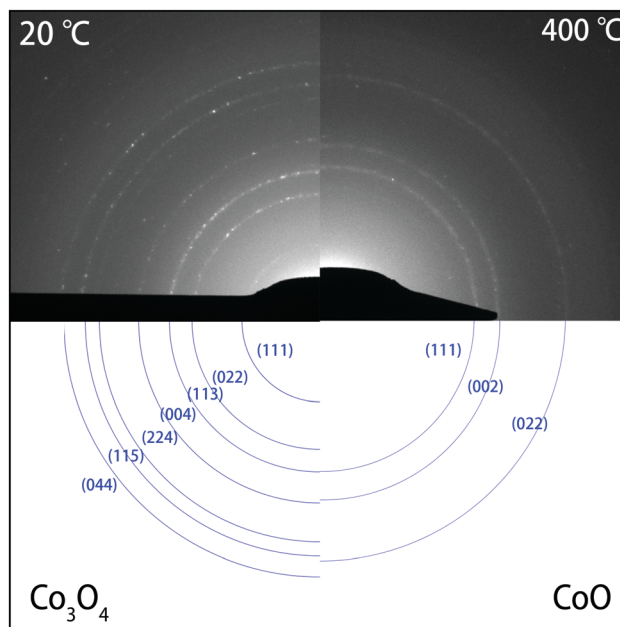


Fig. 4 SAED patterns (top) of  $\text{Co}_3\text{O}_4$  NPs before heating at 20 °C (left), and after heating for 10 min at 400 °C (right). At 20 °C, the diffraction rings in the DP corresponded to the  $\text{Co}_3\text{O}_4$  phase. After heating at 400 °C, only three rings remained that correspond to the highly symmetric CoO phase. The rings in the experimental SAED patterns (top) are indexed in blue (bottom). Please note that the  $(hkl)$  indexing of the diffraction rings refers to reflections at  $\{hkl\}$  families of lattice planes. The complete DPs are shown in Fig. S2 of the ESI.†

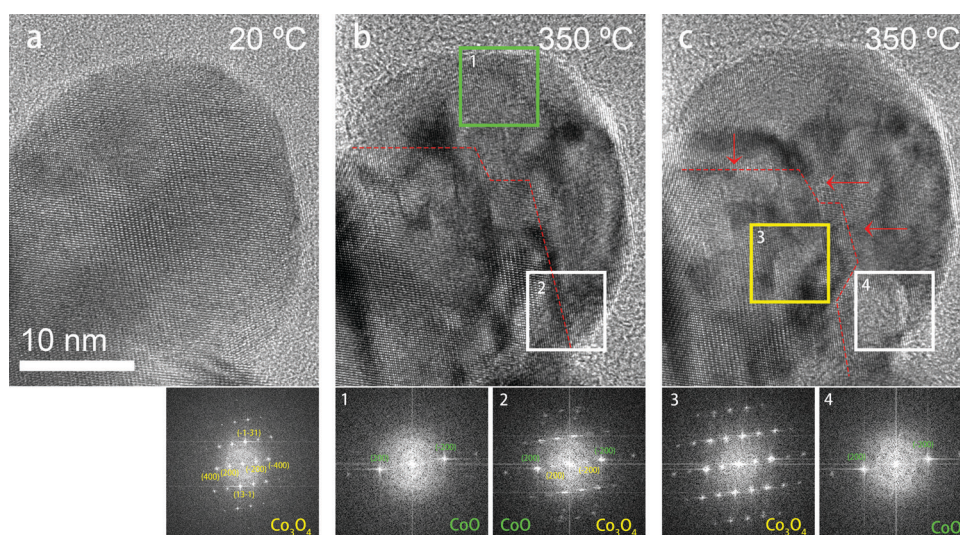


vacuum chamber (4). The results are shown in Fig. S4 (ESI<sup>†</sup>). The SAED patterns after heating in the vacuum chamber clearly indicate the CoO structure, showing that the phase transformation to CoO also took place *ex situ* under low pressure conditions. The SAED patterns after heating under standard pressure and under N<sub>2</sub> flow still show the Co<sub>3</sub>O<sub>4</sub> structure, *i.e.*, the transformation did not take place under these *ex situ* conditions, which implies that the transformation from Co<sub>3</sub>O<sub>4</sub> to CoO requires a very low partial oxygen pressure. The cooling processes in the microscope is typically much faster than in regular furnaces, so that high-temperature phases might be quenched to room temperature. As an additional control experiment, the NCs were heated *in situ* from 20 °C to 400 °C (transforming completely to CoO) and subsequently cooled down very slowly to verify that no other structures than CoO are formed during cooling down. The resulting SAEDs are shown in Fig. S5 (ESI<sup>†</sup>). Both diffraction patterns show a CoO rocksalt crystal structure. High resolution TEM images (shown in Fig. S6, ESI<sup>†</sup>) also show that the particles remain in the CoO phase after heating and cooling down. Consequently, the transformation to CoO that is observed *in situ* must be caused by the combination of elevated temperature and the very low partial oxygen pressure under vacuum conditions.

The results of the *ex situ* experiments conducted in air and under nitrogen flow are in good agreement with the Co–O phase diagrams that Navrotsky *et al.* calculated for bulk and nanoscale cobalt oxide.<sup>14</sup> For 10 nm sized anhydrous Co<sub>3</sub>O<sub>4</sub> nanoparticles, these authors predicted that the partial oxygen pressure needs to be extremely low ( $p(\text{O}_2/1 \text{ atm}) < 10^{-20}$ ) for reduction to take place at a temperature of 650 K ( $\sim 350$  °C). Consequently, during conditions of annealing *ex situ* at standard pressure either in air or under (not 100% pure) nitrogen flow, the partial oxygen pressure will not be sufficiently low for

the Co<sub>3</sub>O<sub>4</sub> NPs to be reduced. The transformation was observed, though, during heating in the *in situ* experiments and when heating *ex situ* in the high vacuum chamber. The partial oxygen pressure in these high vacuum environments is unfortunately not known but must be considerably lower than the total pressure in the column of the TEM and in the vacuum chamber, which is approximately  $1.0 \times 10^{-5}$  Pa. Therefore, as the total partial pressure (with respect to atmospheric pressure) is  $1.0 \times 10^{-10}$ , the partial oxygen pressure will be considerably lower. The thermodynamic modelling as performed by Navrotsky *et al.* is only valid for systems in equilibrium, though. From a thermodynamic point of view, vacuum annealing *in situ* in the TEM or in a high vacuum chamber is always an out-of-equilibrium condition as oxygen molecules are continuously removed from the system through the work done by the vacuum pumps, thereby driving the dissociation from Co<sub>3</sub>O<sub>4</sub> to CoO; there is no equilibrium with any gas. For a thermodynamic assessment of the reduction reaction under equilibrium conditions, we refer to the excellent review by Mayer *et al.*<sup>19</sup> and to the work of Navrotsky *et al.* who also incorporated nanosize effects.<sup>14</sup>

In Fig. 5, high-resolution TEM (HRTEM) images of a particle at room temperature and at 350 °C are shown, revealing details of the phase transformation. In Fig. 5(a), the particle is single crystalline being observed in a [013]-zone axis at room temperature. At 350 °C (Fig. 5(b) and (c)), multiple smaller areas displaying a different contrast appeared on the particle, which indicates that the particle was no longer single crystalline at this temperature. The inset images show the Fast Fourier Transforms (FFTs) of the corresponding smaller areas. The FFT images in Fig. 5(b) and (c) show that at 350 °C the central area of this particle is still in the Co<sub>3</sub>O<sub>4</sub> phase while the surface area has transformed to CoO. The area marked by the green square in Fig. 5(b) displays the CoO phase while the white area



**Fig. 5** HRTEM images of a particle imaged in a [013] projection at a temperature of (a) 20 °C; (b) and (c) 350 °C. The image in (c) was taken a few minutes after that in (b). The inset panels are the FFT pattern of the corresponding areas marked in the figure. The spots in the FFT were indexed and show the corresponding lattice planes. The planes written in green belong to the CoO phase and the yellow ones belong to the Co<sub>3</sub>O<sub>4</sub> phase. The red dashed lines mark the interfaces between two phases. The Co<sub>3</sub>O<sub>4</sub>/CoO interfaces moved inwards from the surface to the center of the nanoparticle.

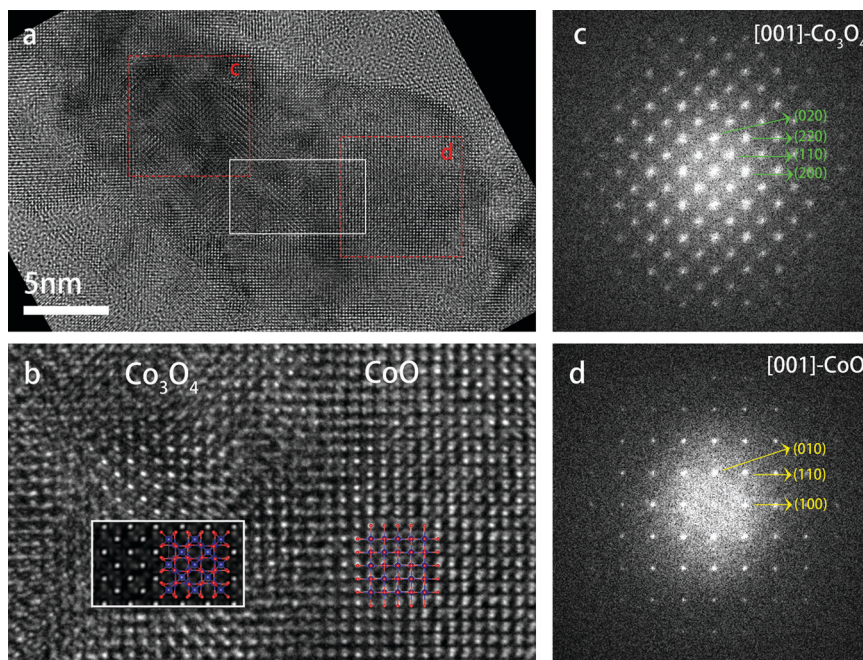


contains both  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$  phases. However, the white square area transformed to  $\text{CoO}$  after a few minutes of continued annealing (shown in Fig. 5(c)), which means that the relative fraction of the  $\text{CoO}$  phase increased during heating, while the area marked with the yellow square in Fig. 5(c) was still in the  $\text{Co}_3\text{O}_4$  phase, indicating that the transformation had not proceeded yet into the most central area of the particle. Fig. 5 also shows that at  $350^\circ\text{C}$  the spots corresponding to the (200) fringes of  $\text{CoO}$  are crystallographically aligned with the (400) fringes of  $\text{Co}_3\text{O}_4$ . This reveals that during the transformation, there is a cube-on-cube orientation relationship between the  $\text{Co}_3\text{O}_4$  parent nanocrystal and the  $\text{CoO}$  product nanocrystals.

In Fig. 6, aberration-corrected TEM (AC-TEM) images are shown of a particle that had partially transformed to  $\text{CoO}$ , where the particle is imaged in a [001] projection. The image was taken after swiftly cooling down from  $400^\circ\text{C}$  to room temperature. Fig. 6(c) and (d) are the FFT patterns indicating a central area (c) that is still in the  $\text{Co}_3\text{O}_4$  phase and an area at the edge (d) that has transformed into the  $\text{CoO}$  phase. The two phases are in a cube-on-cube orientation relationship, in good agreement with the results shown in Fig. 5. Fig. 6(b) shows a magnified HRTEM image of the central area of the particle (marked by the white rectangle in panel (a)), with the  $\text{Co}_3\text{O}_4$  phase at the left hand side and the  $\text{CoO}$  phase at the right hand side. Atomic overlays have been drawn to indicate the atomic structures. At the right hand side, the atomic columns match the  $\text{CoO}$  structure well. Very distinctively, in the  $\text{Co}_3\text{O}_4$  part of the structure there are additional columns of atoms standing out that are generating a 'diagonal' pattern that is rotated  $45^\circ$

with respect to the cubic  $\text{CoO}$  structure. These atomic columns are the  $\text{Co}^{2+}$  ions in  $\text{Co}_3\text{O}_4$ . The inset in Fig. 6(b) shows a simulated image of  $\text{Co}_3\text{O}_4$  (using QSTEM, for a thickness of  $71.3\text{ \AA}$  and a defocus value of  $10\text{ nm}$ ) where this feature is very strong, which confirms the presence of the  $\text{Co}_3\text{O}_4$  structure in the central areas of the partially transformed nanoparticles. Due to changes in thickness, and possibly some mistilt, the contrast of the  $\text{Co}_3\text{O}_4$  part in the images varies to some extent and the interfaces between both phases is not atomically sharp. This may also be caused by the fact that the TEM images are a projection of a 3D structure, while many of these particles display a core-shell structure (with a  $\text{Co}_3\text{O}_4$  core and a  $\text{CoO}$  shell), so that in projection the central part is in fact a superposition of both phases including interfaces between them. Both  $\{100\}/\{100\}$  and  $\{110\}/\{110\}$  interfaces can be distinguished where the transition seems to be gradual. An additional HRTEM image of another particle, showing very similar features, is shown in Fig. S7 of the ESI.†

In Fig. 7, HRTEM images of a larger nanoparticle are shown. At room temperature, spots corresponding to  $\text{Co}_3\text{O}_4$  (220)-lattice fringes can be clearly observed in the TEM image (panel (a)) and the corresponding FFT pattern (panel (d)). After heating to  $400^\circ\text{C}$ , spots corresponding to (331) lattice fringes appeared, and new pairs of spots also appeared that are very close to the  $\text{Co}_3\text{O}_4(440)$  spots, but which deviate by a small tilt angle and have a slightly smaller  $k$ -spacing. These pairs of spots correspond to the  $\{220\}$  lattice fringes of  $\text{CoO}$ , which implies that the surface layer of the particle was reduced to  $\text{CoO}$ , and that this layer is slightly tilted with respect to the  $\text{Co}_3\text{O}_4$  crystal



**Fig. 6** HRTEM images of a partially transformed particle. (a) Overview of the particle, the exterior and right hand side of the particle is in the  $\text{CoO}$  phase while the central part is still in the  $\text{Co}_3\text{O}_4$  phase. (b) Magnified image of the area marked by white rectangle in (a). The inset figure is a QSTEM simulated image of  $\text{Co}_3\text{O}_4$ . Atomic overlays indicate the  $\text{Co}_3\text{O}_4$  (left) and the  $\text{CoO}$  (right) crystal structures. (c) and (d) FFT patterns of the corresponding areas marked in (a), indicating the  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$  structures, respectively.





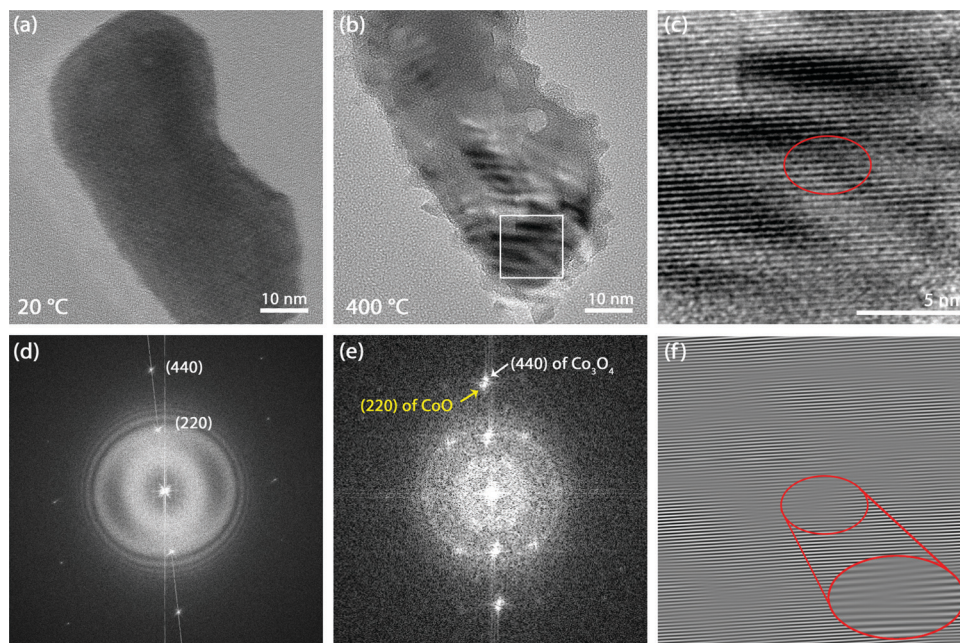
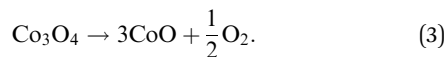


Fig. 7 HRTEM images of a particle at (a) 20 °C and (b) 400 °C. (c) Magnified image of the area marked in (b); (d) and (e) are the FFTs of (a) and (c), respectively; (f) Inverse FFT image of the (220)-spots in (e). The inset at the bottom-right shows an enlarged view of the dislocation at the center of panel (f).

lattice at the interior of the NP. Similarly small mistilts between the two phases were reported by Ward *et al.*,<sup>18</sup> who studied the reduction of Co<sub>3</sub>O<sub>4</sub> nanoparticles in a chemically reducing H<sub>2</sub> atmosphere. Combining the result of Fig. 5 and 6, both phases are observed from 350 °C to 400 °C, which is in good agreement with the result of the DPs. This means that the transformation started from 350 °C onwards, and progressed inwards from the surface to the center of the particles until complete conversion is achieved at 400 °C.

A moiré pattern also appears at the bottom part of the particle, shown in Fig. 7(b), which confirms the multi-layer structure. Fig. 7(f) shows the inverse FFT image of a mask applied around the (220) spots of CoO in Fig. 7(e), showing that dislocations are formed during the reduction. In Fig. 7(b), some voids displaying bright contrast appeared on the particle, which was single crystalline at room temperature before heating. The dislocations and voids are likely formed due to the release of oxygen atoms during the reconstruction of the Co<sub>3</sub>O<sub>4</sub> structure into the CoO structure. The dissociation reaction can be written as



The oxygen sublattices of Co<sub>3</sub>O<sub>4</sub> and CoO are nearly identical, both being fcc sublattices and having a very commensurate lattice parameter (Fig. 1). As 25% of the O atoms are released during reduction, the oxygen sublattice and therefore the volume of the nanoparticle itself has to reduce by about 25% (the positioning and occupation of the Co atoms in the lattices is not limiting their volume). If the shrinkage of the nanoparticle does not proceed fast enough to match the release of oxygen atoms and molecules, the formation of voids and dislocations can be expected.

### DFT study of the CoO/Co<sub>3</sub>O<sub>4</sub> interface

Density functional theory (DFT) calculations were conducted on CoO and Co<sub>3</sub>O<sub>4</sub> reference bulk phase unit cells and on CoO/Co<sub>3</sub>O<sub>4</sub> interface supercells, as described in the Computational details section. To investigate the performance of the DFT (PBE) and DFT+*U* (PBE+*U*) methods considered in this study in describing the CoO and Co<sub>3</sub>O<sub>4</sub> phases, the unit cells of these phases were calculated both with DFT and DFT+*U*. Table 1 summarizes the obtained lattice parameters and band gaps, and the relative energetic stability of the various magnetic geometries. As expected, the Hubbard *U* correction leads to

**Table 1** DFT results for the CoO and Co<sub>3</sub>O<sub>4</sub> reference bulk phases. Calculated total energies are given relative to the calculated total energy of the energetically most favorable magnetic ordering for each compound; for this, DFT (PBE) and DFT+*U* (PBE+*U*) are considered separately. The AFM1 and AFM2 orderings of Co<sub>3</sub>O<sub>4</sub> are identical due to the structure of the Co<sup>2+</sup> sublattice. The lattice parameter of Co<sub>3</sub>O<sub>4</sub> is divided by 2 to allow direct comparison with the lattice parameter of CoO. In the band gap column, 'M' stands for 'metallic' and 'HM' for 'half-metallic'; the band gap listed for the latter is the band gap found for the spin-up electrons

| Method        | Magnetism | Relative energy (meV per atom) |                                | Lattice parameter (Å) |                                | Band gap (eV) |                                |
|---------------|-----------|--------------------------------|--------------------------------|-----------------------|--------------------------------|---------------|--------------------------------|
|               |           | CoO                            | Co <sub>3</sub> O <sub>4</sub> | CoO                   | Co <sub>3</sub> O <sub>4</sub> | CoO           | Co <sub>3</sub> O <sub>4</sub> |
| DFT           | AFM2      | 0                              | —                              | 4.218                 | 4.043                          | 0.52          | —                              |
|               | AFM1      | 113                            | 0                              | 4.223                 | 4.043                          | M             | 0.31                           |
|               | FM        | 75                             | 4                              | 4.247                 | 4.046                          | HM: 1.08      | 0.16                           |
|               | NM        | 257                            | 95                             | 4.101                 | 4.014                          | M             | M                              |
| DFT+ <i>U</i> | AFM2      | 345                            | —                              | 4.246                 | 4.068                          | 1.57          | —                              |
|               | AFM1      | 0                              | 0                              | 4.295                 | 4.068                          | 0.91          | 2.14                           |
|               | FM        | 435                            | 1                              | 4.241                 | 4.069                          | 2.02          | 2.16                           |
|               | NM        | 857                            | 481                            | 4.088                 | 4.009                          | M             | M                              |



increased band gap values, and even opened up band gaps for the AFM1 and FM CoO configurations, making these configurations no longer metallic and half-metallic as predicted by PBE but semiconducting instead. Surprisingly, it was found that DFT+*U* incorrectly predicts the magnetic ground state (MGS) of CoO to be AFM1 rather than AFM2. The deviation of our results from earlier DFT+*U* findings in this regard may be related to the higher (and presumably more accurate) energy cutoff used in this work, and to the fact that we performed our calculations on conventional unit cells rather than on the primitive cells. Standard DFT did predict AFM2 to be the lowest-energy phase of CoO, in agreement with experiment. Both DFT and DFT+*U* correctly predict the MGS of Co<sub>3</sub>O<sub>4</sub> to be AFM1, although in these cases the ferromagnetic (FM) solution was found to be only slightly less favorable than AFM1. In a combined theoretical and experimental study by Qiao *et al.*, who investigated the electronic structure of Co<sub>3</sub>O<sub>4</sub> with DFT calculations for a range of *U*<sub>eff</sub> parameters for both Co<sup>2+</sup> and Co<sup>3+</sup> ions, it was shown that DFT+*U* leads to a severe distortion of the top of the valence band in Co<sub>3</sub>O<sub>4</sub> due to strong downward bending of the band edge corresponding to Co<sup>3+</sup> 3d orbitals,<sup>25</sup> which makes a sensible prediction of the electronic band gap cumbersome. The authors of that study found from their experiments that the fundamental band gap of Co<sub>3</sub>O<sub>4</sub> is substantially lower (0.74 eV) than typically reported (1.5–2.5 eV), and concluded from their DFT calculations that standard GGA-PBE without *U* correction is best capable of describing the electronic structure of Co<sub>3</sub>O<sub>4</sub>.<sup>25</sup>

In the present work we are particularly interested in a sufficiently reliable calculation of the total energies for calculating the interface energy between the two phases, and a reliable prediction of the magnetism at the interface. Considering the misidentification of the magnetic ground state for CoO and the distortion of the valence band of Co<sub>3</sub>O<sub>4</sub> when using DFT+*U*, there are no good reasons to choose DFT+*U* for the present study, and we performed the interface calculations using standard DFT only. For the (lowest-energy) AFM2 CoO and AFM1 Co<sub>3</sub>O<sub>4</sub> phases, Table 2 summarizes the electric charges and magnetic moments on the Co<sup>2+</sup>, Co<sup>3+</sup>, and O<sup>2-</sup> atoms, as obtained from standard DFT and Bader volume analysis. Values obtained for the magnetic moments are ±2.30 μ<sub>B</sub> for the Co<sup>2+</sup> ions in Co<sub>3</sub>O<sub>4</sub> and ±2.42 μ<sub>B</sub> for the Co<sup>2+</sup> ions in CoO, in agreement with previously reported values in the literature.<sup>22,24</sup>

**Table 2** Calculated properties for the lowest-energy phases of CoO and Co<sub>3</sub>O<sub>4</sub> (using GGA-PBE): magnetic ground state (MGS), lattice parameter *a*<sub>0</sub> (the lattice parameter of Co<sub>3</sub>O<sub>4</sub> is divided by 2 to allow direct comparison with the lattice parameter of CoO), net magnetic moment *M* per unit cell, and Bader volume evaluated atomic electric charge *q* and magnetic moment *m*

|                                | <i>a</i> <sub>0</sub> (Å) | MGS  | <i>M</i> (μ <sub>B</sub> ) | <i>q</i> (e)     |                  |                 | <i>m</i> (μ <sub>B</sub> ) |                  |                 |
|--------------------------------|---------------------------|------|----------------------------|------------------|------------------|-----------------|----------------------------|------------------|-----------------|
|                                |                           |      |                            | Co <sup>2+</sup> | Co <sup>3+</sup> | O <sup>2-</sup> | Co <sup>2+</sup>           | Co <sup>3+</sup> | O <sup>2-</sup> |
| CoO                            | 4.218                     | AFM2 | 0.000                      | +1.31            | —                | −1.31           | ±2.42                      | —                | 0.00            |
| Co <sub>3</sub> O <sub>4</sub> | 4.043                     | AFM1 | 0.000                      | +1.33            | +1.44            | −1.05           | ±2.30                      | 0.00             | ±0.07           |

Next, the four interface supercells with the magnetic ordering shown in Fig. 2 were fully relaxed. The interface energy of the various interfaces was calculated according to eqn (2) and using the energetically most favorable (AFM2) CoO and (AFM1) Co<sub>3</sub>O<sub>4</sub> phases as obtained from the bulk phase unit cell calculations as reference phases. Table 3 provides the calculated interface energies and the net magnetic moments of the supercells. The precise supercell dimensions of the obtained output configurations are provided in Table S1 of the ESI.†

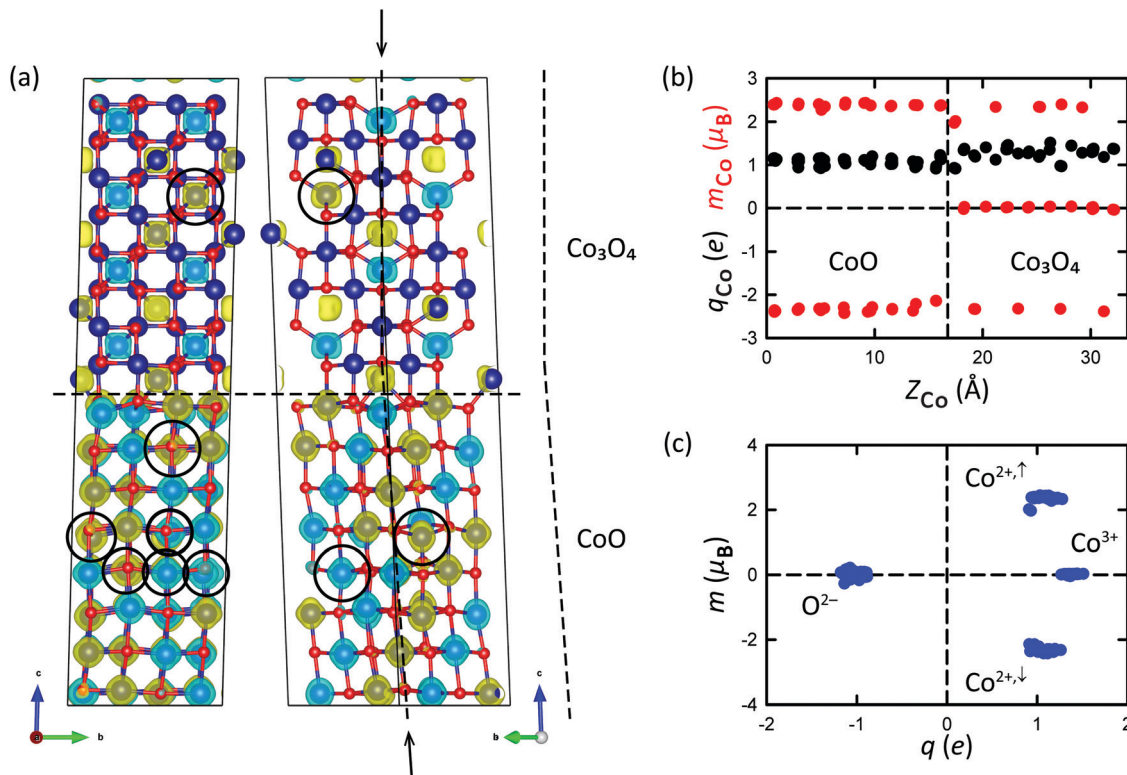
The atomic output configurations are shown in Fig. 8 and in Fig. S8 of the ESI.† The atomic models are overlaid with isosurfaces of the spin-polarization density, where yellow represents excess spin-up electron density and blue represents excess spin-down electron density. Graphs with an analysis of the Bader evaluated electric charges and magnetic moments on the atoms in the interface supercells are included as well. In Fig. 8(a), the first notable observation is that the magnetic ordering of the AFM2/AFM1 supercell at both sides of the interface is distorted. The (bottom) CoO slab of the supercell indeed displays an AFM2 ordering, and the (top) Co<sub>3</sub>O<sub>4</sub> slab an AFM1 ordering; there are, however, clearly a number of Co<sup>2+</sup> atoms whose magnetic moment changed sign during relaxation (excess spin-up electron density becoming excess spin-down electron density for these atoms, and *vice versa*), as indicated with black circles in Fig. 8(a). This can easily be seen by comparing with the input magnetic ordering displayed in Fig. 2(d and e). Remarkably, these atoms with flipped magnetic moments are found not only close to the interface, but also quite far away (at distances of up to 4 atomic layers) from the interface.

As can be seen from Table 3, the AFM2/AFM1 ordered input configuration resulted in the energetically most favorable interface configuration; *i.e.*, the two bulk components forming the interface, preferably follow the same magnetic ordering as the separate bulk phases. In absolute terms, the interface energy of 0.38 J m<sup>−2</sup> is quite favorable, in particular considering the 4.2% lattice mismatch. The NM/NM interface, with the highest total energy and an interface energy of 3.82 J m<sup>−2</sup>, is clearly unfavorable, despite the lower lattice mismatch of 2.1%; the higher energy difference is caused by the fact that here the structure is forced to be nonmagnetic while magnetic solutions are

**Table 3** Results of the DFT calculations conducted on the {100}/{100} CoO/Co<sub>3</sub>O<sub>4</sub> interface. The interface designation refers to the various magnetic and nonmagnetic input configurations depicted in Fig. 2. For each interface, the total energy *E*<sub>0</sub> with respect to the energy of the lowest-energy supercell, the calculated interfacial area *A*<sub>int</sub>, the surface energy γ<sub>int</sub> according to eqn (2), and the total net magnetic moment *M* of the supercell, are given. The lattice mismatch refers to the mismatch between the commensurate lattice parameters of the two separate bulk phases (Table 1) in the plane of the interface. All interface supercells contain the same number of atoms

| Interface | <i>E</i> <sub>0</sub> (eV) | <i>A</i> <sub>int</sub> (Å <sup>2</sup> ) | γ <sub>int</sub> (eV Å <sup>−2</sup> ) | γ <sub>int</sub> (J m <sup>−2</sup> ) | <i>M</i> (μ <sub>B</sub> ) | Mismatch (%) |
|-----------|----------------------------|---|--|---------------------------------------|----------------------------|--------------|
| AFM2/AFM1 | 0.00                       | 67.84                                     | 0.024                                  | 0.38                                  | 18.9                       | 4.2          |
| AFM1/AFM1 | 3.11                       | 63.58                                     | 0.050                                  | 0.80                                  | 6.5                        | 4.4          |
| FM/FM     | 2.76                       | 63.87                                     | 0.047                                  | 0.75                                  | 158.9                      | 4.8          |
| NM/NM     | 26.70                      | 62.78                                     | 0.239                                  | 3.82                                  | 0.0                        | 2.1          |





**Fig. 8** (a) Atomic output configuration of the lowest-energy CoO/Co<sub>3</sub>O<sub>4</sub> interface as obtained after full relaxation of the AFM2/AFM1 supercell, shown in [100] (left) and [110] (right) projection, with Co atoms represented in blue and O atoms in red, and a horizontal dashed line indicating the interface at  $Z_{rel} \approx 1/2$ . The atomic structures are overlaid with the spin-polarization density, where yellow colored isosurfaces indicate excess spin-up electron density and blue colored isosurfaces indicate excess spin-down electron density (isosurface levels are  $\pm 0.24 e \text{\AA}^{-3}$ ). Black circles indicate distortions in the AFM2 and AFM1 magnetic ordering. The supercell is skewed under the influence of the AFM2 ordering in CoO; the mistilt between the crystal lattices is indicated by black arrows and also illustrated at the right-hand side of (a). (b) Charges (black dots) and magnetic moments (red dots) on the Co atoms plotted as a function of Z-coordinate (height in the supercell). The vertical dashed line indicates the interface at  $Z_{rel} \approx 1/2$ . (c) Correlation between the charge and magnetic moments on the Co and O atoms.

preferred. Fig. 8(a) shows the atomic output configuration for the (lowest-energy) AFM2/AFM1 interface supercell. The output configurations of all interface supercells can be found in Fig. S8 of the ESI.<sup>†</sup> The charges and magnetic moments on the Co atoms in the relaxed AFM2/AFM1 supercell are shown in Fig. 8(b), where they are plotted as a function of the Z-coordinate (height in the supercell). Fig. S8(d) (ESI<sup>†</sup>) includes the charges and magnetic moments on the O atoms. The correlation between the charges on the atoms and their magnetic moments is nicely visualized in Fig. 8(c). Clearly, the CoO phase only contains  $Co^{2+}$  ions with either positive or negative magnetic moments, whereas the  $Co_3O_4$  phase also contains nonmagnetic  $Co^{3+}$  ions (Fig. 8(b)). The charges and the magnetic moments on the atoms in the supercell in general follow the same trend as the charges and magnetic moments obtained for the atoms in the CoO and  $Co_3O_4$  bulk phase compounds (Table 2). As can be seen from Fig. 8(c), the nonmagnetic  $Co^{3+}$  ions have a somewhat higher positive charge of  $+1.38e$  in comparison with the  $Co^{2+}$  ions, which carry an (either spin-up or spin-down) magnetic moment of  $\pm 2.34 \mu_B$  and have Bader charges of  $+1.09e$  (all averaged values; the  $Co^{2+}$  atoms with upward magnetic moments actually have an averaged magnetic moment that is slightly larger, namely  $+2.37 \mu_B$ , than the corresponding value for the

magnetically downwardly orientated  $Co^{2+}$  atoms, which was found to be  $-2.31 \mu_B$  on average). There is one Co layer (the Co layer closest to the interface at  $Z_{rel} \approx 1/2$ , in the  $Co_3O_4$  component of the supercell) where the  $Co^{2+}$  ions have slightly smaller magnetic moments and Bader charges of  $+1.99 \mu_B$  and  $+0.92e$ . For the  $Co^{2+}$  atoms of which the magnetic moment changed sign during relaxation, slightly larger values of the magnetic moment were found, of  $+2.42 \mu_B$  on average, at Bader charges of  $+1.05e$ .

The constituting bulk phases of the AFM2/AFM1 supercell are both AFM-type with zero net magnetic moment (Table 2). Remarkably, the formation of the interface leads to a substantial net ferromagnetic moment of  $18.9 \mu_B$  over the entire AFM2/AFM1 supercell (Table 3). The supercell as a whole is therefore ferrimagnetic. The net ferromagnetic moment that arises from the formation of the interface between the two antiferromagnetic compounds can for the largest part be retraced to the flipping of magnetic moments of  $Co^{2+}$  atoms at both sides of the interface. In total 9 ions changed the sign of their magnetic moment, 6 upwardly and 3 downwardly: in the (bottom) CoO slab, 3  $Co^{2+}$  ions changed the sign of their magnetic moment from up to down, and 5 changed their sign from down to up; and in the (top)  $Co_3O_4$  slab, one  $Co^{2+}$  ion changed its sign from down to up. The



resulting net contribution of these atoms to the magnetization of the supercell amounts to the equivalence of 3 of their upwardly orientated atomic magnetic moments, and is accompanied by a net contribution of an equal number of (unflipped) atomic magnetic moments from the  $\text{Co}^{2+}$  sublattice, where the upwardly orientated magnetic moments of three  $\text{Co}^{2+}$  atoms due to the flipping are now no longer matched and counterbalanced by originally downwardly orientated but now flipped magnetic moments. The contribution to the net magnetic moment of the entire supercell due to the flipping of magnetic moments can therefore be estimated to be  $3 \times (2.42 + 2.37) = 14.4 \mu_{\text{B}}$ . A smaller part ( $2.0 \mu_{\text{B}}$ ) of the magnetization of the supercell is caused by the difference in magnetic moment between the spin-up and spin-down  $\text{Co}^{2+}$  atoms. Note that the two  $\text{Co}^{2+}$  atoms at the interface with the smaller magnetic moments will lower the magnetization (their contribution to the net magnetization of the supercell is  $-0.6 \mu_{\text{B}}$ ). The remainder of the supercell magnetization stems from low levels of spin-polarization at the nonmagnetic  $\text{O}^{2-}$  and  $\text{Co}^{3+}$  atoms, which were found to have very small atomic magnetic moments after relaxation (of  $\pm 0.08 \mu_{\text{B}}$  and  $\pm 0.03 \mu_{\text{B}}$  on average and adding up to a net contribution of  $2.7 \mu_{\text{B}}$  and  $0.4 \mu_{\text{B}}$ , respectively). Magnetic moments can change sign as a result of the exchange interaction between magnetic moments. In the present case, apparently the broken symmetry and disorder induced by the presence of the interface causes individual magnetic moments at the interface to change in sign, which consecutively causes the adjacent magnetic moment to change in sign as well, eventually leading to flipped magnetic moments quite far away from the interface.

By analogy with the definition of the interface energy (eqn (2)), the net ferromagnetization of the supercell can be expressed per unit of interfacial area as  $13.9 \mu_{\text{B}} \text{ nm}^{-2}$ ; the larger part of the magnetization, to a value of  $10.3 \mu_{\text{B}} \text{ nm}^{-2}$ , occurs in the constituting CoO component, whereas a magnetization of  $3.6 \mu_{\text{B}} \text{ nm}^{-2}$  was found for the  $\text{Co}_3\text{O}_4$  slab. In the literature, net ferromagnetism in antiferromagnetic nanoparticles was experimentally observed to persist even at room temperature for compounds having a bulk Néel temperature below room temperature, which has generally been attributed to surface and interface effects.<sup>32–36</sup> The present calculations predict that this is indeed also the case for the  $\text{CoO}/\text{Co}_3\text{O}_4$   $\{100\}/\{100\}$  interface geometry investigated here. We suggest that a follow-up study could study experimentally whether partially converted composite  $\text{Co}_3\text{O}_4/\text{CoO}$  nanoparticles exhibit stronger ferromagnetism than pure  $\text{Co}_3\text{O}_4$  NPs or pure CoO NPs.

The second notable observation that can be made from Fig. 8(a) is that the relaxed AFM2/AFM1 supercell is clearly skewed, most likely under the influence of the directionality along  $\langle 111 \rangle$  of the antiferromagnetic ordering in the CoO phase. Please note that when both phases are nonmagnetic (NM/NM), skewing of the supercell does not occur as can be seen in Fig. S8(a) of the ESI.† (The precise dimensions of the supercells can be found in Table S1, ESI.†) As is indicated by arrows and illustrated schematically at the right-hand side of Fig. 8(a), relaxation resulted in a mistilt of approximately  $4^\circ$  between the Z-axes of the two cubic phases. We point out that a

lattice mistilt between the two phases was sometimes also observed in the experiments, as evidenced by the electron diffraction pattern of Fig. 7(e), and by the study by Ward *et al.* who reduced  $\text{Co}_3\text{O}_4$  in an  $\text{H}_2$  atmosphere. In theory, the experimentally observed mistilt could be explained from the magnetic interactions between the two phases. As explained in the Introduction, magnetism is often found for nanoparticles above the Curie or Néel temperature of their corresponding bulk phases because of size effects and surface and interface effects.<sup>29</sup> In addition, there is quite a strong magnetic field present in the electron microscope with field strengths up to 2 Tesla,<sup>47</sup> which can easily induce magnetization. Nonetheless, we consider that, whereas the skewing and mistilt observed in the simulations are most likely related to the different directionality of the magnetic ordering of the two phases, the most plausible explanation for the experimentally observed lattice mistilt is the formation of dislocations in the oxygen sublattice, as revealed by the real-space HRTEM observations.

## 5. Conclusion

The thermal reduction process of  $\text{Co}_3\text{O}_4$  nanoparticles to CoO was investigated by *in situ* heating in the TEM under vacuum conditions. The results show that transformation of the  $\text{Co}_3\text{O}_4$  NPs starts at  $350^\circ\text{C}$  and that the NPs are completely converted after heating at  $400^\circ\text{C}$  for 10 min. Upon heating to higher temperatures, up to  $900^\circ\text{C}$ , no further reduction was observed. The reaction proceeds from the surface to the center of the particle, where the parent  $\text{Co}_3\text{O}_4$  and the product CoO nanoparticles are in a cube-on-cube orientation relationship of their crystal lattices. The CoO reduced surface layer was sometimes slightly tilted with respect to the  $\text{Co}_3\text{O}_4$  interior, which is likely associated with the formation of dislocations as the volume of the NPs has to reduce by 25% due to oxygen release. The transformation did not take place during *ex situ* heating experiments conducted in air and under nitrogen flow, however the transformation was achieved *ex situ* when heating in a high vacuum chamber; vacuum conditions, equivalent to a very low partial oxygen pressure, are necessary for achieving the transformation to CoO at a temperature of  $400^\circ\text{C}$ .

The energetics and magnetic structure of the interface were investigated by density functional theory (DFT) calculations predicting a favorable  $\text{CoO}/\text{Co}_3\text{O}_4$   $\{100\}/\{100\}$  interface energy of  $0.38 \text{ J m}^{-2}$ . The antiferromagnetic orderings of the two phases at both sides of the interface, AFM2 for CoO and AFM1 for  $\text{Co}_3\text{O}_4$ , correspond to those of the lowest-energy bulk phases. It was also found, however, that the magnetic ordering is distorted as several atoms have magnetic moments with a sign that is opposite to the sign that would yield the perfect magnetic order. The distortion in the antiferromagnetic ordering takes place at the interface but also leads to flipping of magnetic moments at a considerable distance ( $\sim 1 \text{ nm}$ ) from the interface, likely due to exchange coupling. The flipping in sign of the magnetic moments leads to a considerable net ferromagnetic moment of  $18.9 \mu_{\text{B}}$  over the entire supercell, which corresponds



to a net magnetization of approximately  $13.9 \mu_B \text{ nm}^{-2}$ . We suggest that verifying experimentally whether the presence of the  $\text{Co}_3\text{O}_4/\text{CoO}$  interface indeed enhances the ferromagnetism of NPs with respect to pure  $\text{Co}_3\text{O}_4$  or pure  $\text{CoO}$  NPs, would be an interesting topic for an experimental follow-up study. Both in the experiments and in the simulations, a small mistilt between the two cubic phases was found. In the simulations, this is likely related to stress fields originating from different directionalities of the antiferromagnetic orderings in  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$ . In the experiments, this is likely due to the formation of dislocations in the oxygen sublattice during the thermal reduction. In the present work we show that the formation of an interface leads to ferromagnetism in otherwise only anti-ferromagnetic materials. Although we demonstrate this solely for the  $\text{Co}_3\text{O}_4/\text{CoO}$  interface, this effect can be expected to take place in many other transition metal oxide systems as well. The implication of the current findings is that it could be very beneficial to reduce transition metal oxide nanoparticles only partially, in order to boost ferromagnetism at their interfaces. This would be an interesting topic for an experimental follow-up study, as generating ferromagnetism simply by partial reduction would make these nanoparticles interesting to a much wider range of applications including magnetic recording media, sensing, and biomedical applications.<sup>48–50</sup>

## Author contributions

MAvH conceived the experimental part of the study. XDC performed and analyzed the *in situ* and *ex situ* heating experiments. HvG conceived the computational part of the study and performed and analyzed the DFT calculations. XDC and HvG wrote the manuscript. All authors commented on the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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