Electrostatic doping as a source for robust ferromagnetism at the interface between antiferromagnetic cobalt oxides

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Polar oxide interfaces are an important focus of research due to their novel functionality which is not available in the bulk constituents. So far, research has focused mainly on heterointerfaces derived from the perovskite structure. It is important to extend our understanding of electronic reconstruction phenomena to a broader class of materials and structure types. Here we report from high-resolution transmission electron microscopy and quantitative magnetometry a robust – above room temperature (Curie temperature $T_C > 300 \text{ K}$) – environmentally stable ferromagnetically coupled interface layer between the antiferromagnetic rocksalt CoO core and a 2–4 nm thick antiferromagnetic spinel Co$_3$O$_4$ surface layer in octahedron-shaped nanocrystals. Density functional theory calculations with an on-site Coulomb repulsion parameter identify the origin of the experimentally observed ferromagnetic phase as a charge transfer process (partial reduction) of Co$_{3+}$ to Co$_{2+}$ at the CoO/Co$_3$O$_4$ interface, with Co$_{2+}$ being in the low spin state, unlike the high spin state of its counterpart in CoO. This finding may serve as a guideline for designing new functional nanomagnets based on oxidation resistant antiferromagnetic transition metal oxides.

Functional oxide interfaces based on transition metal oxides$^1$ have been recognized for their new and exciting fundamental physics$^{2-3}$ as well as for their potential as next-generation nanoelectronic materials. They are associated with a wide variety of interesting physical phenomena, such as superconductivity, ferroelectricity, ionic conduction and magnetism. Given the success that has been achieved in finding novel properties for technological applications in systems such as perovskite-type LaAlO$_3$/SrTiO$_3$ oxide interfaces$^4$, it becomes important to also find further promising material combinations and structure types that may exhibit exotic properties. For example, a surprising lamellar ferromagnetic order at intergrowths of antiferromagnetic (AFM) haematite (Fe$_2$O$_3$) and para/antiferromagnetic (PM/AFM) ilmenite (FeTiO$_3$) has been reported$^5,6$. The charge imbalance at the interface has been identified as a source of this phenomenon, very often accompanied by local distortions. This can induce charge transfer processes and change the bond-angles between ions. These effects modify the competing ferromagnetic (FM) and AFM interactions (super–exchange, and double exchange) in antiferromagnets as described by the so called Goodenough-Kanamori-Anderson (GKA) rules$^7$. For instance a distortion (bond-angle change) and charge transfer can turn the AFM 180° magnetic ion-oxygen-magnetic ion superexchange of partially filled 3d $e_g$ ($d_{xy}, d_{xz}$) or $t_{2g}$ ($d_{xy}, d_{yz}, d_{xz}$) orbitals into ferromagnetic (double) exchange. Consequently, tuning the relative magnitudes of competing magnetic interactions via strain control at interfaces opens a promising route to create new types of magnets.

The interesting question arises if ferromagnetic order can be stabilized between two simple antiferromagnets like CoO and Co$_3$O$_4$, both of which are antiferromagnets with ordering temperatures $T_N = 291 \text{ K}$ and 40 K, respectively$^8,9$. In nanostructured AFM materials$^{10}$ pairing of the two mutually compensating ferromagnetic sublattices is broken due to surface rearrangement, which leads to the presence of “uncompensated” and often “frustrated” surface moments and the consequent magnetic reconstruction$^{11}$. Several examples of weak antiferromagnetism in nanoparticulate Co$^{12-13}$ and Co$_3$O$_4$$^{14-17}$ materials have been reported in the literature based on these explanations, though the irregular shapes and the relatively wide size distributions of nanoparticles have made a detailed analysis of the origin of the observed ferromagnetic response very difficult. In contrast, nearly perfect antiferromagnetic CoO nanocrystals with octahedron shapes and different average sizes, as reported in

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Ref. 18, should allow the origin of the room temperature ferromagnetism to be identified. These crystalline CoO octahedra have eight (111) crystal facets stabilized by a thin CoO/Co$_3$O$_4$ shell, which forms naturally by surface oxidation in air$^{19-21}$, and is thermodynamically more stable than CoO. The uncompensated magnetic moments in the ~3 nm thick AFM Co$_3$O$_4$ surface layer have been assumed as a likely source of the observed ferromagnetism. However, the origin of a quasi two-dimensional long-range ferromagnetic order persisting in a temperature range where the AFM CoO and Co$_3$O$_4$ bulk phases are paramagnetic is not understood.

Here, we demonstrate that the atomically sharp interface between the crystalline ~3 nm thick spinel-type CoO$_2$/Co$_3$O$_4$ surface layer and the crystalline CoO (rocksalt structure) is the source of the ferromagnetism observed up to 400 K. The octahedron-shaped nanocrystals with edge lengths between 40 and 150 nm, have a heavily strained epitaxial CoO/Co$_3$O$_4$ interface that forms at the eight (111) facets, offering quasi-2D ferromagnetic interfaces stable even in the paramagnetic regime of the antiferromagnetic CoO (T > 291 K). Using a combination of magnetometry, transmission electron microscopy and density functional theory (DFT) we obtain quantitative results confirming that an electronic reconstruction accompanied by a considerable interlayer compression of the CoO oxide (111) layer spacing at the interface to the Co$_3$O$_4$ surface coating explains the ferromagnetic order and its stability. One may note that such an enhanced T$_C$ in a quasi 2D interface is remarkable, since lower dimensionality in in general expected to lead to enhanced thermal fluctuations and a reduced ordering temperature$^{22}$. Consequently, our results show that the occurrence of magnetic order in these octahedron-shaped nanocrystals can be attributed to the changes of bond-angles and valence states at the (111) CoO/Co$_3$O$_4$ interface, which modify the relative strengths of the inherent ferromagnetic double exchange and antiferromagnetic superexchange.

CoO crystallizes in the cubic rocksalt-structure, Fm$ar{3}$m (O$_h^8$), above the Neél temperature T$_N$ = 291 K, in which alternating layers of (111) Co planes with opposite magnetization directions are separated by oxygen planes. The Co$^{2+}$ ions occupy the octahedral sites formed by the face-centered-cubic (FCC) arranged O$^2-$ ions. Below T$_N$ the magnetic order induces a transition to a monoclinic phase (C2/m (C$_2$$_h$))$^2$. This results in a distorted octahedral crystal field with a spin S = 3/2 and an unquenched orbital moment of approximately L = 1 (L/S = 0.7)$^8$ in the antiferromagnetically ordered state. AFM CoO has a very high magnetocrystalline anisotropy constant of $\sim 2.7 \times 10^6$ J cm$^{-3}$, which is comparable to that of the hard magnet samarium-cobalt$^{20}$. In thin CoO layers the single ion magnetic anisotropy energy (MAE) density was found to change from 4.8 meV/atom to -1.6 meV/atom upon diluting or compressing along the CoO(100) plane and has been related to a large change of electronic occupation of the s$_{\alpha}$ and t$_{2g}$ orbital states$^{27}$. In principle, an ideal CoO crystal slab in a (111) orientation could show two contributions: a vanishing total magnetization for an even number of Co layers and the magnetization of a single Co$^{2+}$ monolayer for an odd number of Co layers. On the other hand, the modified crystal field symmetry at the surface due to a missing or relaxed O$^{2-}$ surface layer changes the octahedral (O$_h$) symmetry dramatically, can quench the orbital momentum and can consequently modify the spin only magnetic moment S = 3/2 with $\mu_S = g_S \sqrt{S(S+1)} \mu_B = 3.9 \mu_B$. Unfortunately, such ideal surface layers cannot be stabilized due to their high polarity. As shown for Co (111) films grown on Ir(100), nature circumvents the polarity problem by an appropriate surface reconstruction, that is, by switching from the rocksalt type to wurzite-type stacking near the surface, which turns out to become metallic at the interface in ultrahigh vacuum$^{28}$. Co$_3$O$_4$ crystallizes in the normal spinel structure with the general formula [A]$^{2+}$[B$_2$]$^{3+}$[Co$_{2}$]$^{3+}$[Co$_{2}$]$^{3+}$[O]$_4$. Co$^{2+}$ ions (“B” sites, 3d$^5$, spin S = 0) occupy octahedral sites and Co$^{3+}$ ions occupy the tetrahedral (“A”) sites formed by O$^{2-}$ species yielding an S = 3/2 state. The Co$^{2+}$ ions on the A site are antiferromagnetically ordered below 40 K, namely, each ion at a tetrahedral site “A” is surrounded by four nearest neighbor A sites with an antiparallel magnetic moment. The [Co$^{3+}$]$^{3+}$ ions on the B site are in the low spin (LS) S = 0 state, i.e., diamagnetic.

Cobalt oxide octahedron-shaped nanocrystals (Fig. 1a) prepared by colloidal chemistry (described in the Methods section) offer the possibility to study changes in interface structure, electronic properties and competing magnetic interactions. X-ray powder diffraction, neutron diffraction and X-ray photoemission spectroscopy measurements revealed that the major constituent of these nanocrystals was CoO with a rocksalt structure at room temperature and confirmed the absence of metallic (Co$^0$) cobalt. High-resolution TEM measurements revealed the CoO-Co$_3$O$_4$ core-shell structure of the nanoparticles. Figure 1a shows a bright-field TEM image of the as-synthesized CoO nanocrystals deposited on an amorphous carbon support film. The observed morphologies of the nanocrystals, which take the form of hexagons, rectangles and rhombi in 2D projection, originate from 3D octahedral particle shapes (confirmed using electron tomography) whose crystal facets are determined by the underlying cubic crystallographic structure (see the scheme in Fig. 1b). The average edge lengths of the octahedron-shaped nanocrystals were determined to be 40 ± 8 nm and 75 ± 10 nm from bright-field TEM images. In the following, these samples are referred to as S-40 nm and S-75 nm, respectively.

Magnetic characterization of the CoO nanocratahedra was performed using a SQUID magnetometer under zero-field cooling (ZFC) and field cooling (FC) conditions. The measured field-dependent magnetization M(H) showed clear hysteresis loops (Fig 1c,d) at T = 300 K and 5 K, with characteristics of ferromagnetic behavior, superimposed on the expected paramagnetic (T = 300 K) and antiferromagnetic (T = 5 K) linear field-dependent response of CoO and Co$_3$O$_4$. The saturation magnetization M$_S$ = 1.58 Am$^2$/kg (Co metal: 163.6 Am$^2$/kg), the remanent magnetization M$_R$ = 0.261 Am$^2$/kg, and the coercivity H$_C$ = 35.7 mT measured at 300 K for the S-75 nm sample (Fig. 1c) unambiguously indicate a ferromagnetically ordered component in the nominally purely paramagnetic state above the Néel temperature T$_N$ = 291 K of CoO, which forms the core of every octahedron. Another unambiguous proof for the interfacial coexistence of FM and AFM components is the observation of an exchange bias field H$_{EB}$ at lower temperatures, seen as the horizontal and vertical shift of the hysteresis after field cooling (FC) relative to the ZFC M(H) loop (Fig 1d). The temperature-dependence of the exchange bias field H$_{EB}$ and of the coercive field H$_C$ for samples S-40 nm and S-75 nm (Fig. S1) shows that H$_{EB}$ vanishes above T$_N$ = 291 K as expected, while the coercive field $\mu_B$H$_C$ is still larger than about 30 mT. A detailed summary of the variation in Ms, MR and HC with temperature for the ZFC and FC M(H) experiments is given in Supplementary Tables T1 and T2. In addition, K-edge X-ray absorption spectra, neutron diffraction studies, and temperature dependent susceptibility measurements confirmed the absence of metallic cobalt and the existence of crystalline antiferromagnetic CoO with T$_N$ = 291 K and a thin shell of Co$_3$O$_4$ with a finite-size-effect reduced T$_N$ = 20 K$^8$.

The reduced – mass normalized - saturation magnetization M$_S$ measured for the smaller octahedra S-40 nm (2.81 Am$^2$/kg at 5 K and 2.60 Am$^2$/kg at 300 K) in comparison to the S-75 nm octahedra (1.72 Am$^2$/kg at 5 K and 1.55 Am$^2$/kg at 300 K) suggests that a surface or interface contribution is the origin of the ferromagnetic response. To support this analysis, we have calculated the expected magnetization of ferromagnetic single and double surface or interface layers of Co$^{2+}$ ions. The number of these Co$^{2+}$ cations at the apexes, edges, surfaces, and interfaces was estimated for a given size and shell thickness of a CoO-Co$_3$O$_4$ core-shell octahedron, by making use of the geometrical relationship between the rocksalt-spinel crystal structures and the octahedral morphology. For an octahedral
particle with eight 111 facets (Fig. 2b), where the number of atoms along the 111 facet is \( n \), the number of Co\(^{2+} \) cations at the apexes is 6, at the edge is \( 12(n - 1) \), at the surfaces is \( 8(n^2 - 4)/2 \), and in the inside volume is \( (2n^2 - 1)/3 \). Taking the typical magnetic moment \( \mu = (4.8 \pm 0.4)\mu_B \) for Co\(^{2+} \), we calculate the saturation magnetization \( M_S \) for one layer (blue curves) of surface Co\(^{2+} \) cations (see Fig. 2a), while the red curves show the calculated values of \( M_S \) for a double-layered interface of Co\(^{2+} \). The red curves intersect the measured \( M_S \) (black solid and dashed lines for 300 K and 5 K) for the S-40 nm sample at a size range of 38–45 nm, while for S-75 nm the intersection occurs at a size range of 60–80 nm. The striking match between the measured and calculated saturation magnetization must therefore be associated with interfacial ferromagnetic long-range order, and not surface-derived ferromagnetism.

In order to understand the reason for the appearance of this interfacial long-range ferromagnetic order, we have also performed high-angle annular dark field (HAADF) imaging. Figure 3a shows an atomically resolved HAADF image of the edge of a typical cobalt oxide octahedron, oriented along the [110] direction. In HAADF imaging, the recorded contrast arises primarily from Rutherford and thermal diffuse scattering. Under our experimental conditions, the HAADF intensity scales to a good approximation with the atomic number \( Z \) and the specimen thickness, since the area of interest is sufficiently thin. A distinct core-shell contrast variation with different atom-column configurations is appreciated. Figure 3b shows an enlargement of the interface area outlined by a dashed-square in Fig. 3a, in which a (111)-type interface and (002)-type interfaces between CoO and Co\(_3\)O\(_4\) (delineated by dashed lines) can be identified. The core region (A) corresponds to a [110] atomic column projection of the rocksalt CoO structure, while the shell region (B) corresponds to a [110] atomic column projection of the normal spinel Co\(_3\)O\(_4\) structure. The bright contrast corresponds to cobalt cation columns, whose scattering strength is greater than that of oxygen anions. For more precise atomic lattice information, we have analyzed the intensity variation and lattice spacing in different HAADF images. The rectangular a–b area shown in Fig. 3b was selected for intensity profile analysis (not shown) and indicates a clear intensity variation that reflects structure and chemistry differences across the interface boundaries. By using the CoO core as a reference, we measured variations of the (111)-plane lattice spacing in the CoO/Co\(_3\)O\(_4\) interface region. The measurements (red data points in Fig. 3c) revealed a progressive decrease in lattice spacing from the core to the surface by as much as 8%, suggesting the presence of large strain in the interface region. Within experimental accuracy, we find that the Co\(_3\)O\(_4\) plane spacing (235 pm) is bulk-like and stays unchanged. Only the CoO (111) spacing is strongly compressed at the interface and relaxes towards the core within three to four layers to its respective bulk value.

To shed more light on the underlying mechanisms DFT+U calculations were performed considering two different terminations of Co\(_3\)O\(_4\) at the interface: one with exclusively octahedral Co (named B-layer) and one with a mixed octahedral, tetrahedral layer. The calculated lattice spacings (blue data points in Fig. 3c) match very well the experimentally measured ones confirming that the interlayer distances on the CoO side of the interface are strongly reduced, while on the Co\(_3\)O\(_4\) side it is close to the bulk-value. The very good agreement between the theoretical and experimental interlayer distances shown in Fig. 3d for the B-layer model unambiguously identifies that the latter is realized at the interface.
Below the side view of the relaxed structure from DFT + U calculations (Fig. 3d), Fig. 3e) shows the spin density and orbital polarization of the heterostructure. Red and blue contours denote antiparallel orientations of magnetic moments. Besides the antiferromagnetically ordered octahedral Co$^{2+}$ in CoO and tetrahedral Co$^{2+}$ in Co$_3$O$_4$, a striking feature is the noticeable spin density at the Co$^{3+}$ sites (we note that no spin density is observed in bulk Co$_3$O$_4$ – not shown here). While the total contribution of the red and blue lobes at Co$^{3+}$ in the inner layers sums up to a relatively small spin magnetic moment of 0.05 $\mu_B$, individual octahedral Co-sites at the interface adopt a considerable magnetization of 0.4–0.8 $\mu_B$ (for details see Methods). This high magnetic moment signals a valence change from Co$^{3+}$ towards Co$^{2+}$ at the interface. Most importantly, these sites are in a low spin (LS) state, unlike Co$^{2+}$ in the CoO part of the superlattice. The latter are in a high spin (HS) state with magnetic moments of 2.58 $\mu_B$ (close to the value of 2.64 $\mu_B$ in bulk CoO). Thus, the interface magnetism originates from a change in oxidation state at the octahedral sites with a LS state, which is clearly distinct from the HS state in bulk CoO.

By making use of the interface atomistic information obtained from the HAADF image analysis and the DFT + U calculations, it is possible to draw conclusion about the atomic interface structure of the two cobalt oxides. As mentioned above in bulk rocksalt CoO, Co$^{2+}$ cations occupy octahedral sites in a lattice of FCC O$^{2-}$ ions. In contrast, in bulk normal spinel Co$_3$O$_4$, Co$^{3+}$ cations populate half of the octahedral sites, while Co$^{2+}$ cations populate one-eighth of the tetrahedral sites in an FCC lattice of O$^{2-}$ ions. The two structures can be epitaxially matched at the (111) facets of the FCC sublattice of host O$^{2-}$ ions, when the bulk lattice mismatch of about 5% (4.261 Å for CoO: JCPDS card no. 48-1719 and 4.084 Å for Co$_3$O$_4$: JCPDF card no. 42-1467) can be accommodated by strain. Such “flexible” accommodation of cobalt cations to form different oxides has also been observed in other transition metal oxide systems. Consequently, one can construct rocksalt/spinel (111)-type interfaces. In this model, the interfacial oxygen plane is adjacent to octahedral Co$^{3+}_{\text{oct}}$ (S = 3/2) in CoO and octahedral Co$^{3+}_{\text{oct}}$ (S = 0) in Co$_3$O$_4$. To understand the appearance of ferromagnetism we can compare the interface structure to an inverse spinel structure, which is typical for example for ferrimagnetic Fe$_3$O$_4$. The difference between ((Co$^{3+}$)$_{\text{CoO}}$(Co$^{2+}$)$_{\text{CoO}}$)O$_2$$^-$ and ((Fe$^{3+}$)$_{\text{Fe}_3}\text{O}_4$(Fe$^{2+}$)Fe$^{3+}$)O$_2$$^-$ is the valence of the cobalt and iron cations in their respective tetrahedral and octahedral environments. In Fe$_3$O$_4$, magnetic superexchange (SE) and double exchange (DE) interactions between iron cations and their inequivalent neighbors proceed via the same oxygen anion. The Fe$^{3+}_{\text{Tet}}$ and Fe$^{3+}_{\text{Oct}}$ cations are coupled ferromagnetically through double exchange (DE). However, the two Fe$^{3+}_{\text{Tet}}$ and Fe$^{3+}_{\text{Oct}}$ cations are coupled antiferromagnetically through superexchange (SE), such that their moments of $\pm 5\mu_B$ cancel. An unpaired moment of 4 $\mu_B$ on the Fe$^{3+}_{\text{Oct}}$ cation site remains. Consequently, Fe$_3$O$_4$ exhibits ferrimagnetic behavior with a high Curie temperature $T_C = 858$ K. In Co$_3$O$_4$, on the other hand, the weak tetrahedral-tetrahedral (T-T) AFM interactions between the Co$^{2+}_{\text{Tet}}$ cations lead to antiferromagnetism with a low ordering temperature $T_N$ of $\sim 20–40$ K. Consequently, a ferromagnetic order with a high Curie temperature can be stabilized at the interface if magnetic moments are present at both the octahedral and the tetrahedral sites. Such a scenario was previously explained by a transition from a normal to inverse spinel in CoO$_4$ nanoparticles by Chen et al. and by Serrano et al. at the surfaces of nanoparticles on TiO$_2$. On the other hand, our results demonstrate a rather different mechanism of formation of Co$^{3+}_{\text{Oct}}$ at the interface with an unanticipated low spin state of $S = 1/2$. In the study of Serrano et al., a weak FM signal was attributed to surface reduction of Co$^{3+}_{\text{Oct}}$ to Co$^{2+}_{\text{Oct}}$, whereas complex magnetic interactions involving T-T (Co$^{2+}_{\text{Tet}}$-Co$^{3+}_{\text{Tet}}$), O-O (Co$^{2+}_{\text{Oct}}$-Co$^{2+}_{\text{Oct}}$), and T-O could occur, in analogy to that in Fe$_3$O$_4$. Here, we suggest that it is possible to achieve long-range ferromagnetic order with a high Curie temperature due to the coupling of Co$^{3+}_{\text{Oct}}$ (S = 3/2 and 1/2) and Co$^{2+}_{\text{Tet}}$ cations on both sides of the epitaxial interface, as shown in Fig. 3d) and e). Our experimental and computational results indicate that robust ferromagnetic order can occur at (111) interfaces between CoO and Co$_3$O$_4$ above the highest Neel temperature of the antiferromagnets. To understand that such a behavior was not observed in previous Co oxide thin film studies, one may consider lateral size effects in the nanocrystallites. These may be important to prevent the formation of strain-releasing misfit dislocations at the interface – as has also been found in the growth of nanowires with heavily strained semiconductor heterostuctures. It will be interesting to investigate in the future, if defect-free CoO/Co$_3$O$_4$ interfaces could be stabilized in laterally extended epitaxial thin films despite the large strain observed in the CoO interface layers.

In summary, the present rocksalt/spinel-type system provides a fascinating oxide interface, in which electrostatic doping can induce changes of competing magnetic interactions (SE and DE) at the
Besides the antiferromagnetic alignment of octahedral Co\textsuperscript{2+} blue contours denote antiparallel orientations of magnetic moments. The significant spin polarization in the interface Co\textsubscript{3}O\textsubscript{4} signaling the interface plane (dashed line) of O\textsubscript{2} (blue dots) in Co\textsubscript{3}O\textsubscript{4} on the right to octahedral Co\textsuperscript{2+} tetrahedral Co\textsuperscript{2+} Co\textsubscript{3}O\textsubscript{4} (111) heterostructure obtained from the DFT calculations.

Methods
CoO nano-octahedra were obtained using the hot-injection thermodecomposition of cobalt acetate (Sigma-Aldrich, 98%), (2.66 and 4 mmol) (dissolved in 5 ml of ethanol) in trioctylamine (Aldrich, 90%) (25 ml, 57.18 mmol) and oleic acid (Aldrich, 90%) (5.12 and 8 mmol) at 170 °C and then left to reflux (at T = 300 °C) for two hours. Once cooled to room temperature, the nanocrystals were obtained by centrifugation, washed several times and stored in ethanol. Repeated syntheses confirm the reproducibility of the final products.

Figure 3 | STEM-HAADF image of a single octahedral cobalt oxide nanocrystal. (a), Atom-column-resolved STEM-HAADF image of the edge of a [1–10]-oriented cobalt oxide nanocrystal acquired in STEM mode at 80 kV using a probe size of ~0.1 nm. The core region A and the shell region B exhibit contrast characteristic of [1–10]-oriented CoO and Co\textsubscript{3}O\textsubscript{4} respectively. (b), Enlargement of the interface area: (111)-type interface between a CoO core and the Co\textsubscript{3}O\textsubscript{4} shell. (c), Measured (111) (red dots) and calculated (blue dots) lattice plane spacings as a function of spacing number near the interface. “d00” denotes the spacing indicated by the dashed line in b. (d), Side view of the relaxed geometry of the CoO/Co\textsubscript{3}O\textsubscript{4} (111) heterostructure obtained from the DFT + U calculations. The interface plane (dashed line) of O\textsubscript{2} (red dots) connects octahedral Co ions (blue dots) in Co\textsubscript{3}O\textsubscript{4} on the right to octahedral Co\textsuperscript{3+} ions in CoO on the left. Co\textsuperscript{2+} and Co\textsuperscript{3+} are denoted by blue/yellow polyhedra. As discussed in the text, electronic reconstruction in the interface Co\textsubscript{3}O\textsubscript{4} layer reduces the S = 0 [Co\textsuperscript{3+}]\textsuperscript{4μ}\textsuperscript{2-} to low spin [Co\textsuperscript{2+}]\textsuperscript{μ}\textsuperscript{2}. (e), Spin density of the CoO/Co\textsubscript{3}O\textsubscript{4} (111) heterostructure obtained from the DFT + U calculations. Red and blue contours denote antiparallel orientations of magnetic moments. Besides the antiferromagnetic alignment of octahedral Co\textsuperscript{2+} in CoO and tetrahedral Co\textsuperscript{3+} in Co\textsubscript{3}O\textsubscript{4}, note a considerable spin density at the Co\textsuperscript{2+} sites in the inner Co\textsubscript{3}O\textsubscript{4} layers (not present in bulk Co\textsubscript{3}O\textsubscript{4}). A key feature is the significant spin polarization in the interface Co\textsubscript{3}O\textsubscript{4}, signaling the reduction of octahedral Co\textsuperscript{3+} to Co\textsuperscript{2+} sites in an unanticipated low spin state (S = 1/2) – the corresponding sites are emphasized by the arrow.
