Electronic properties of single-layer CoO$_2$/Au(111)

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Abstract
We report direct measurements via angle-resolved photoemission spectroscopy (ARPES) of the electronic dispersion of single-layer (SL) CoO$_2$. The Fermi contour consists of a large hole pocket centered at the $\Gamma$ point. To interpret the ARPES results, we use density functional theory (DFT) in combination with the multi-orbital Gutzwiller Approximation (DFT+GA), basing our calculations on crystalline structure parameters derived from x-ray photoelectron diffraction and low-energy electron diffraction. Our calculations are in good agreement with the measured dispersion. We conclude that the material is a moderately correlated metal. We also discuss substrate effects, and the influence of hydroxylation on the CoO$_2$ SL electronic structure.

1. Introduction
Layered bulk crystals based on hexagonal CoO$_2$ [1–3] display intriguing electronic and phononic properties that arise from the quasi-two-dimensional (quasi-2D) nature of the atomic layers. For example, when the CoO$_2$ layers are interleaved with H$_2$O, Na$^+$, and H$_3$O$^+$, superconductivity is observed at transition temperatures $T_c$ of approximately 4–5 K [1, 2], and the nearly 2D character of the CoO$_2$ layers is understood to be a key aspect of these superconducting properties [1, 4–6]. Similarities to the high-$T_c$ copper oxides are also notable. In both cases, a strong anisotropy between the in-plane and out-of-plane directions is key to the materials’ electronic properties [7–10]. Atomic layers that intervene between oxide layers play, in both cases, a complex role that goes beyond simple doping to determine the special many-body physics of the whole system [11–13] (although the superconducting phases certainly also have a critical dependence on doping [14–16]).

Given that the complex electronic properties of these bulk systems arise as quasi-2D physics in weakly interacting, atomically thin oxide layers, it is natural to ask whether any of the interesting electronic properties of the bulk persist in the single-layer (SL) limit. The electronic properties of a SL material can differ in important ways from those of layered bulk parent compounds. For example, among the transition metal dichalcogenides, the band dispersion [17, 18] and electronic correlations [19, 20] can be significantly modified in the SL limit.

A method has recently been developed for epitaxially fabricating rotationally aligned SL CoO$_2$ islands on Au(111), Pt(111), and Ag(111) substrates [21, 22]. So far, the SL system has been studied in the context of applications to catalysis [23]. Here we investigate the electronic properties of the SL, which—to the best of our knowledge—have not yet been studied experimentally, although a recent theory paper has predicted that the SL might manifest 2D ferromagnetism and undergo a superconducting...
transition at $T_C = 25–28$ K [24]. Besides laying the groundwork for new directions in the very active field of 2D-materials research, our study aims to clarify our understanding of layered CoO$_2$-based compounds.

2. Methods

Our growth procedure is based on the synthesis method that has been previously described by Walton et al [21]. It consists of two steps, performed in-situ in a vacuum chamber with a base pressure of low-$10^{-10}$ mbar. First, we evaporate elemental Co while simultaneously exposing the sample to O$_2$ at a chamber pressure of $(6 \times 10^{-7})$ mbar. In this step, the sample temperature is ca. 380 K. This forms SL CoO on the Au(111) substrate. We use a growth rate of approximately one monolayer CoO per hour. We then stop depositing Co and increase the local O$_2$ pressure, using a moveable O$_2$ doser that we bring to within a few mm of the sample face: with this we further oxidize the CoO for two hours, to form CoO$_2$. The sample temperature is in this second step is ca. 325 K and the chamber pressure is $4 \times 10^{-6}$ mbar, but the local pressure at the sample face is presumably much higher (likely as much as two orders of magnitude). The full procedure results in SL CoO$_2$ islands [21].

Electronic structure measurements were made by angle-resolved photoemission spectroscopy (ARPES) at the SGM3 beamline of the ASTRID2 Synchrotron Light Source in Denmark [25]. Incident light is linearly polarized in the direction parallel to the scattering plane; the angle between analyzer axis and incident light axis is 50°. Sample quality and coverage were assessed in situ via a combination of x-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and scanning-tunneling microscopy (STM). The sample was at room temperature during STM characterisation [26], while it was at (30 ± 5) K during XPS, LEED and ARPES measurements. The width of the Fermi edge in the ARPES measurements (fitted from projected bulk continuum states of the Au substrate) was approximately 80 meV.

In order to interpret the ARPES measurements, a precise knowledge of structural parameters is crucial. Previous studies of SL CoO$_2$ on noble metal (111) surfaces [21, 22, 27] have used STM and XPS to obtain structural information about the SL. However, XPS is a rather indirect method of assessing structure. STM does provide structural information, but mainly only about the top layer of atoms, and it is limited in its scope to local measurements, so it is not an optimal probe of average atomic structure over macroscopic areas. Here we use x-ray photoelectron diffraction (XPD) as a direct, high-resolution probe of the local geometric structure around each chemically distinct type of emitter, averaged over the area of the beam spot. Measurements were made at the Super-ESCA beamline at Elettra, the synchrotron radiation facility in Trieste, Italy [28]. Here the incident light is linearly polarized in the horizontal plane, where also the electron energy analyser lies, at an angle of 70° with respect to the photon beam. The overall energy resolution was below 100 and 200 meV in the energy range from 650 to 1150 eV photon energy, respectively. The high resolution spectra of O 1s and Co 2p core levels were measured in normal emission conditions and the binding energy was normalized to the Fermi level of the Au substrate. Sample cleanliness, layer quality and order where checked with XPS and LEED prior to the XPD measurements.

XPD patterns are constructed by collecting XPS spectra across a range of polar ($\theta$) angles, from 70° (normal incidence in the configuration of Super-ESCA) to normal emission, and azimuthal angles ($\phi$) across a range of 130°, with an angular resolution in the order of 1°. More details can be found in [29, 30]. For the measurements in this study, the sample was at room temperature.

In the peak fitting analysis of the resulting data, the photoemission intensity $I(\theta, \phi)$ of each component is extracted from every XPS spectrum by the use of a Doniach–Sunjic fitting function [31] with Shirley background subtraction. From this we obtain the modulation function $\chi$, defined as:

$$\chi = \frac{I(\theta, \phi) - I_0(\theta)}{I_0(\theta)},$$

where $I_0(\theta)$ is the average intensity for an azimuthal scan at polar angle $\theta$. The XPD pattern is a projection of the modulation function for a particular peak. We compare measured XPD patterns to multiple scattering simulations for trial structures that are generated using the program package electron diffraction in atomic clusters [32]. The agreement between measured and simulated XPD patterns is then quantified, via calculation of a reliability factor $R$ that is defined as the sum of the normalised mean-square deviation of the experimental ($\chi_{ex}$) and theoretical ($\chi_{th}$) modulation functions,

$$R = \frac{\sum_i (\chi_{th,i} - \chi_{ex,i})^2}{\sum_i (\chi_{th,i}^2 + \chi_{ex,i}^2)}.$$  

for each emission angle $i$. By this definition, an $R$-factor of 0 corresponds to perfect agreement, while an $R$-factor of 1 indicates uncorrelated data [33]. (Anti-correlated data give an $R$-factor of 2.) Values of $R$ less than 0.3 are generally taken to indicate relatively good agreement (e.g. [29]). We take the confidence interval $\Delta R$ of the minimized $R$ value to be $\Delta R = R_{\text{min}} \sqrt{2/N} \sim 0.01$ [29, 30], with $N \approx 250$ being the ratio of the solid angle of the measurements to the solid-angular resolution.

3. Results

3.1. Electronic structure determination

ARPES measurements acquired with photon energy $h\nu = 89$ eV are presented in figure 1 for SL CoO$_2$. 

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with a sample coverage of approximately 70%, as determined by in-situ STM (see [26]). Figure 1(a) shows the APRES spectrum along cuts through the high-symmetry points \( \Gamma, M, \) and \( K \) of the CoO\(_2\) Brillouin zone (BZ). The Au(111) surface state at \( \Gamma \) is faintly visible—presumably deriving from exposed regions of the Au(111) substrate—and so are the sharp, highly dispersive features of the bulk Au(111) \( sp \)-band, which cross the Fermi level near \( M \) and along the \( \Gamma K \) cut [34]. In figure 1(b), the electron dispersion from figure 1(a) is reproduced with the Au features highlighted: the Au surface state and bulk bands are overlaid with orange dashed lines as guides to the eye, and the projected bulk band continuum is shaded orange. Several observed features are not associated with the Au(111) substrate, and we attribute these to the electronic structure of SL CoO\(_2\). At first glance, the adlayer band structure shows a metallic character and seems to consist of one band around 1.5 eV binding energy \( E_B \) (mostly visible between \( \overline{M K} \)), and at least two bands close to the Fermi level, at less than 1.0 eV in binding energy. Of these bands close to the Fermi level, the lower one appears to exhibit energy minima at approximately \( E_B = 0.6 \) eV at \( \overline{M} \) and approximately \( E_B = 0.5 \) eV close to \( K \). (As we will see below, however, the actual dispersion is more complicated than this.) A Fermi level crossing at \( k_F = (0.67 \pm 0.03) \) \( \AA^{-1} \) in the \( \overline{\Gamma M} \) direction is marked with a white arrow in the figure. In the \( \overline{\Gamma K} \) direction, the band crosses the Fermi level at approximately \( k_F = (0.69 \pm 0.05) \) \( \AA^{-1} \) (black arrow). To identify the Fermi level crossing, the band dispersion near the Fermi level was determined by fitting energy distribution curves (EDCs) to Gaussian-broadened Lorentzians convoluted with the Fermi function, within a range of about 100 meV below the Fermi level. The EDC fits were also found to agree well with Gaussian fits to momentum distribution curves within the same energy range. The bands appear to flatten close to the Fermi level, creating the impression of kinks in the dispersion; this will be further discussed below. The Fermi contour corresponding to the measured dispersion is presented in figure 1(c). The overlaid orange hexagon marks the Au(111) surface BZ (SBZ), which is slightly larger than the CoO\(_2\) BZ (red hexagon). The high-symmetry directions in figure 1(a) are marked with black dashed lines, and the high-symmetry points are labeled. The Au(111) surface state creates a small ring around \( \Gamma \), and the large, faint hexagonal feature with its vertices at approximately the \( \overline{M} \) points of CoO\(_2\) arises from Au bulk states. Between these, the SL CoO\(_2\) forms a distorted, rounded hexagon centered around \( \Gamma \); by referencing the dispersion in panel (a), one can see that this is a large hole pocket. The relative sizes and rotations of the BZs are calculated on the basis of LEED measurements, and a representative measurement is presented in figure 1(d). Diffraction spots forming two rotationally aligned hexagons arise from the SL CoO\(_2\) (red arrow) and the Au(111) substrate (yellow arrow). By using the known in-plane Au(111) lattice parameter of 2.88 Å [35], the in-plane lattice parameter of the SL CoO\(_2\) is determined to (3.12 ± 0.03) Å, which is within the range of values (2.8–3.3 Å) previously reported on the basis of STM measurements [21, 27].

3.2. Core level data

The O 1s spectrum is displayed in figure 2(a). The main component (dark red) occurs at a binding energy of \( E_B = (529.0 \pm 0.1) \) eV (binding energies are referenced to the measured Fermi level). An additional hydroxyl component (bright red) is also present, as expected from previous studies [23, 27, 36]. Similarly to what is reported in the earlier-published results, this OH peak is shifted (2.05 ± 0.05) eV towards higher binding energy relative to the main O peak. Fester et al, attribute the presence of this component to a partial hydroxyl overlayer formed by H bonding to O at the top of the CoO\(_2\) SL (i.e. the side of the SL away from the interface.
with the Au(111) substrate). They suggest that the hydroxylation results from dissociative adsorption of H₂O or H₂ rest gas in the vacuum chamber [27]. The main O peak contains photoemission intensity from unhydroxylated emitters at both the top and the bottom of the layer. These components are known to be very closely separated in energy [36] and cannot be resolved.

Figure 2(b) shows the Co 2p spectrum. It is dominated by a large peak with several closely spaced minor components. The complexity of this spectrum attests to the presence of more than one oxidation state of Co. Freestanding CoO₂ might be naïvely expected to exhibit the Co³⁺ oxidation state; however, we instead observe a Co⁴⁺ oxidation state—fitted here with an asymmetric main peak (blue) at a binding energy of E₈ = 778.7 eV—consistent with previously published findings [21, 27]. The (3 + δ)⁺ oxidation state is presumably due to charge transfer from adsorbates (or possibly from the substrate, but see discussion below). We surmise that such charge transfer stabilises the SL; however, the possible mechanism for such stabilisation is beyond the scope of the present work. Some areas of CoO have failed to further oxidize in the second step of the growth procedure, and this is manifest in the persistent presence of a set of peaks arising from the Co²⁺ oxidation state. Co⁴⁺ has a high-spin configuration that generates a complex peak structure with multiplet splitting and shake-up satellites [39-42]. Here we fit it with just two components, aside from the Co²⁺ main component at E₈ = (780.4 ± 0.1) eV (dark green in the figure): a shake-up satellite, labelled ‘II’ (dark brown), separated from the main peak by (5.7 ± 0.1) eV, and peak ‘I’ (light green), which arises from multiplet splitting and is fixed to a separation of 2.1 eV from the main peak [41]. While the intensities and locations of these two peaks are in relatively good agreement with related peak structures previously identified in the literature [40-42], our fitting here is phenomenological and does not attempt to capture the details of the complex peak structure of the Co³⁺ spectrum.

Note that this makes it difficult for us to estimate the precise amount of the less-oxidized CoO that remains on this particular sample after the second oxidation step; however, it does not impact the modulation of the Co⁴⁺ component, which is only associated with photoemission from fully oxidized CoO₂.

We identify an additional weak satellite peak (‘III,’ shown in light brown) at (10.3 ± 0.1) eV higher binding energy than the Co⁴⁺ peak. The position and the intensity of this satellite are similar to what has been seen in diverse related compounds such as CoOOH, Co(OH)₂, and Co₃O₄ [40, 41, 43], though its physical interpretation remains uncertain. Finally, a negligible amount of unoxidized Co metal remains, even after the full growth procedure, and leads to the small peak shown in red in figure 2.

3.3. Crystalline structure determination

XPD results are presented in figure 3. The experimental data are shown in orange, superimposed on the grayscale best-fit multiple-scattering simulations. Figure 3(a) shows the diffraction pattern of the unhydroxylated O 1s core level peak obtained with a photon energy of hν = 650 eV. This photon energy was chosen so that the photoelectron kinetic energy would be less than 150 eV, to enhance the cross section for backscattering of photoelectrons from the underlying structure and thus the sensitivity of the

The Co 2p⁹/₂ spectrum for bulk metallic Co is known to display an asymmetric main peak together with surface and bulk plasmon peaks [44]. Here, the plasmon satellites are excluded from the metallic Co fit, due to the very small amount of metallic Co found to be present. The binding energy is set to match the value reported by Walton et al [21], in their measurements of Co metal on Au(111), and the peak shape is asymmetric with both the shape and location similar to what is measured by Walton et al [21].
measurement to emitters in the top layer of O atoms. By contrast, in figure 3(b) a higher photon energy of $h\nu = 900$ eV was used, favouring the forward scattering of photoelectrons and enhancing sensitivity to emitters in the bottom layer of O atoms. The resulting modulation function is, in this latter case, highly dependent on the structure above the bottom layer of O—the arrangement of Co atoms and of O atoms at the top of the layer. The diffraction pattern arising from the Co 2$p^3$ core level, acquired from the $(3 + \delta)$ peak with photon energy $h\nu = 1150$ eV, is shown in figure 3(c). Here, again, forward scattering is favoured. From these three data sets, we obtain the out-of-plane parameters of the crystal lattice from the best-fit structural model to the XPD data, keeping the in-plane parameter in the simulation fixed to the result from LEED We note that LEED gives sharp diffraction spots, consistent with the presence of well-aligned rotational domains of CoO$_2$. We start by assuming that SL CoO$_2$ has a crystalline structure related to the CdI$_2$ type, in accordance with previous predictions [21]. The CdI$_2$ structure, however, has only three-fold symmetry. We therefore assume that the nearly six-fold symmetry of the XPD patterns derives from the presence of exactly two domains in the sample, and these are related to each other by mirror symmetry (equivalent to 60° in-plane rotation).

The R-factor for the simulations presented in figures 3(a)–(c) is shown at the bottom right of each panel. The low values in each case indicate good agreement between the measurement and the simulation. $z_1$ and $z_2$ were determined by optimizing $R$ for all three simulations simultaneously, with the assumption that CoO$_2$ is present on the sample in two equally distributed orientations rotated with respect to one other by 60°. The results suggest a slightly smaller distance between Co and top O atoms ($z_1 = (0.95 \pm 0.10)$ Å) than between Co and bottom O atoms ($z_2 = (1.00 \pm 0.10)$ Å). The uncertainties in $z_1$ and $z_2$ are rough estimates of our confidence in identifying the minimum $R$ value across all three data sets shown in figure 3. (Within these uncertainties, the average $R$ value for the three simulations falls mostly within $\Delta R$, as defined above, of the minimized value.) Our values of $z_1$ and $z_2$ are consistent with the asymmetric structure proposed by Walton et al [21]. In a qualitative sense, such an asymmetry is not unexpected, considering that one side of the layer is at the interface with the substrate, while the other side is hydroxylated and at the interface with vacuum. However, the range of our uncertainty does also permit the possibility that $z_1 = z_2$, which would not affect any of the conclusions we draw in the present study [26]. The atomic structure derived from the XPD simulations is shown from top and side views in figure 3(d), and from an oblique view in figure 3(e). A hexagonal layer of Au atoms corresponding to the unreconstructed (111) surface is shown in figure 3(e) for illustrative purposes, even though the actual XPD simulations do not include the substrate. Because of the lattice mismatch between the SL and the Au(111) substrate, there are many different adsorption sites on the substrate surface, and thus there is no simple geometric relationship between the emitters in the SL CoO$_2$ and the Au(111); this justifies neglect of the Au(111) in the simulations.

Previously published work has found that adsorbed H at the top of the SL assumes a partially disordered ‘labyrinth’ structure [27]. In the present study, we observe weak modulation of the hydroxylated O 1s core-level peak: this might arise from small structural changes associated with hydroxylation. However, it is small compared with the modulation of the non-hydroxylated component, and we have not been able to analyse it successfully.

3.4. Electronic structure simulations

Here we analyse the electronic structure of the CoO$_2$ SL. To take into account the electron-correlation effects, we utilize the density functional theory
in combination with the multi-orbital Gutzwiller Approximation (DFT+GA) method [45–47]. Specifically, we have utilized the implementation of [47, 48], using the DFT code Wien2k [49], employing the Local Density Approximation (LDA) and the standard 'fully localized limit' form for the double-counting functional [50]. Our calculations were performed using a 24 × 24 k-point grid and setting the product of the smallest atomic-sphere radius times the largest plane-wave momentum (called RKmax in Wien2k) to 9. As in reference [51], we set the Hund’s coupling constant to J = 0.9 eV, while we set the screened Hubbard interaction parameter to U = 6 eV.

In our calculations we do not artificially break the spin symmetry. Within DFT+GA, the many-body effects originating from fluctuating local moments (paramagnetism) are encoded in a self-energy correction, whose influence on the band structure of our system is explained below.

For band structure calculations we employed the measured lattice constant from LEED (a = (3.12 ± 0.03) Å) and the out of plane distances from XPD (z₁ = (0.95 ±0.1) Å and z₂ = (1.00 ±0.1) Å). In the supplementary material (available online at stacks.iop.org/2DM/8/035050/mmedia) [26] we also show that small changes in the out-of-plane parameters—within the precision of XPD measurements—lead to band structures that are also consistent with the ARPES data. In particular, this includes the inversion-symmetric lattice structure with z₁ = z₂ = 1.0 Å.

In figure 4(a) we compare the DFT and the DFT+GA bands with the dispersion measured by ARPES. Note that in figure 4 the theoretical Fermi level of the pure SL is shifted by approximately 90 meV above the calculated value, as such shift results in a more satisfactory agreement with the experiments. In the supplemental material we argue, based on DFT calculations, that this energy shift may be caused by the adsorption of H atoms on the SL [26]. We observe that the correlation effects captured by DFT+GA improve the agreement with the experiments considerably compared to bare DFT.

Within the multi-orbital GA framework, the correlation effects on the band structure (figure 4(b)) are encoded in a linear momentum-independent self energy, Σ(ω), for the Co 3d electrons, represented as follows [47, 52]:

$$\Sigma(\omega) = -\left[1 - \frac{Z}{Z} + \Sigma_0, \right]$$ (3)

where 1 is the identity matrix, Z is the so-called 'matrix of quasi-particle weights' Z (whose eigenvalues measure the degree of correlation of the corresponding degrees of freedom) and Σ₀ is the frequency-independent component of the self-energy matrix (inducing interaction-driven d-electron on-site level shifts). The Co 3d manifold is generated by one one-dimensional A₁ irreducible representation and two two-dimensional E representations. From standard group-theoretical considerations [48] it follows that Z has a non-degenerate A₁ eigenvalue Z₁ and two two-fold degenerate E eigenvalues Z₁,E, Z₂,E.

Based on our calculation, Z₁,E ≈ 0.68, Z₁,E ≈ 0.72 and Z₂,E ≈ 0.82. The fact that they are appreciably smaller than 1 indicates that the SL CoO₂ system is a moderately-correlated metal [52]. In figure 4(b) we show the Co 3d spectral weight of the bands, resolved with respect to the corresponding p₃m₁ point symmetry-group representations. As expected, the correlation effects are particularly important for capturing the experimental behavior of the d-electron bands, such as those at low binding energy close to the K-point, which have predominantly A₁ character. However, the d-electron correlations considerably influence the whole band structure, including the O 2p band (because of hybridization effects).

4. Discussion

Key questions in 2D-materials research are how the electronic properties of SL systems differ from those of related 3D (bulk) compounds, and how those properties are affected by the environment—for example, by the presence of the substrate, or by adsorbates. Here we consider these questions for the case of SL CoO₂.

4.1. Influence of Au(111) substrate

The Au(111) substrate plays a role in catalyzing the growth of CoO₂ and in stabilizing the SL [22, 23].

![Figure 4](image-url)

(a) Band structure of SL CoO₂ calculated with DFT+GA (solid lines) and DFT (dashed lines), superimposed on measured ARPES spectra. The inset shows the corresponding SBZ of Au(111) (CoO₂) in orange (red) and the DFT+GA constant energy contour (black) in comparison with ARPES. The theoretical Fermi level is shifted by 90 meV above the calculated value (see discussion in the main text). (b) Orbital character of the d-electron degrees of freedom within DFT+GA (Z₁ in red, Z₁,E and Z₂,E in blue).
Furthermore, as discussed above, the Au(111) substrate introduces an asymmetry in the out-of-plane direction—not only by interacting directly with the SL, but also by inhibiting hydroxylation at the bottom of the layer. (Full hydroxylation of the top and bottom of the layer—i.e. synthesis of SL Co(OH)$_2$ on Au(111)—has been shown to be possible in the presence of ‘high’ pressures (i.e. $\sim 10$ mbar) of H$_2$O vapor \cite{23}; however, to our knowledge, hydroxylation at the bottom of the SL on Au(111) does not occur due to the presence of chamber rest gas alone.)

Nevertheless, despite the impact it has on structure, the Au(111) substrate appears to have a weak influence on the electronic properties of the SL. The most important observation in this regard is the fact that calculations neglecting the substrate agree well with the measured ARPES spectra. It is also interesting to observe that the splitting between the two O 1s XPS peaks, which derive from photoemission from the top and the bottom of the layer, is so small that it cannot be resolved by our measurements. If the interaction were strong between the substrate and the oxygen atoms at the bottom of the layer, one might expect to see a significant peak shift, similar to what has been observed for MoS$_2$/Au(111) \cite{29}, and which we do not see in the present case.

### 4.2. Hydroxylation

To estimate the amount of hydrogen present, we note that in the O 1s core level of figure 2(a) the hydroxyl component accounts for 43% of the combined intensity of the two peaks. We assume that there is attenuation of the photoemission intensity from the bottom O layer (due to an inelastic mean free path of $\lambda=5.3$ Å \cite{53, 54}) but that the presence of H does not attenuate the photoemission intensity. Furthermore, we assume that hydroxylation happens only at the top of the CoO$_2$ layer \cite{27}, and that each H is bonded only to a single O. This results in a value of 57% hydroxylated O at the top of the layer. Note, however, that there is a rather high level of uncertainty in this estimate, depending on the validity of our several assumptions. Also, this rough estimate does not take into account the persistence of local regions of CoO after the second oxidation step: these certainly persist into account the persistence of local regions of CoO$_2$; thus, our estimate represents only a lower bound for the extent of hydroxylation in our sample. Our findings appear roughly consistent with those of previous studies, which have shown that hydroxylation of the CoO$_2$ layer is approximately $\frac{2}{3}$ (i.e. two out of every three O atoms at the top of the layer hydroxylated) after storage in UHV conditions for several hours \cite{27}. Indeed, the sample that generated the XPS data shown above was stored under UHV conditions for a few days before the measurements in figure 2 were acquired.

By contrast, the samples that generated the ARPES data above were stored in UHV conditions for only a few hours before they were measured. They might, therefore, be less hydroxylated than the samples measured with XPS. However, on the basis of the existing literature we would not expect the level of hydroxylation to be less than approximately $\frac{1}{3}$, as this is the lower bound previously observed in freshly-grown samples \cite{27}. The measured Fermi contour in figure 1 is $(70 \pm 3\%)$ filled, which indicates a charge transfer to the SL of $(0.40 \pm 0.06)e$ per unit cell (by contrast with undoped CoO$_2$, whose Fermi contour would be half-filled). Thus, the amount of hydroxylation that we estimate using XPS would likely be sufficient to generate the charge transfer that we observe in ARPES, even without charge transfer from the Au(111) substrate.

An obvious question is what influence the hydroxylation has on the electronic dispersion. Importantly, the calculations shown in figure 4—which do not include hydroxylation—successfully reproduce most of the main features of the band structure. This is consistent with what one might expect on the basis of previous work \cite{27}, which has shown that the H ions are not well ordered on the surface. In this case, the OH groups would be likely to shift and broaden the band structure, as we see in our data, rather than to impact the bare-band dispersion. Nevertheless, there could, of course, be some level of weak ordering of the H ions, and we consider the implications of this for the band dispersion in the supplementary material \cite{26, 55–59}.

### 4.3. Comparison of SL CoO$_2$ with related bulk materials

In light of the apparently weak impact of the substrate on the electronic dispersion, and the likelihood of little if any charge transfer from the substrate, it seems reasonable to consider our CoO$_2$ system as approximately ‘2D.’ Here, then, we discuss the electronic structure of this 2D material in relation to analogous layered bulk systems, such as Na$_2$CoO$_2$ and Na$_x$CoO$_2$·yH$_2$O. This is a particularly interesting point of consideration, because the superconducting and magnetic properties of the layered bulk materials have been interpreted as arising from the pseudo-2D nature of the weakly interacting CoO$_2$ atomic layers: the layers are partially isolated from one another in bulk materials by interleaving layers of Na$^+$, H$_2$O, and H$_2$O$^+$ \cite{1, 2, 4–6}. (We note that superconductivity would not be expected in our samples, because of the proximity effect of the Au(111) substrate.)

The electronic dispersion of the SL is remarkably similar to that of related layered bulk materials \cite{11, 60–64}. The large hole pocket around $\Gamma$ is the most obvious feature of the bulk dispersion, and this is true for the SL, as well. Discussion in the literature has surrounded the question of why six small hole pockets that are predicted to cross the Fermi
level along $\overline{TK}$ in the bulk dispersion \cite{60,61} are not observed experimentally at any doping level \cite{11,62,63,65}. Our results are similar to those of ARPES studies of the bulk, in that no hole pockets rise above the Fermi level along $\overline{TK}$. However, we do note that there are hole pockets just below the Fermi level, and that the measured Fermi contour of the SL exhibits diffuse, elongated intensity in the $\overline{TK}$ direction, due to the presence of these shallow states located in close vicinity to, and leaking some intensity across, the Fermi level.

Comparing the properties of the bulk and the SL, it is worth pointing out that there are some structural differences between our samples and the stacked layers of similar bulk systems. The in-plane lattice constant we have identified here, 3.12(3) Å, is larger than that reported for the bulk (2.8222(15) Å \cite{66}). The O height above Co as reported for the bulk (e.g. 0.91 Å for NaCoO$_2$ \cite{60}) is within the range of the uncertainty of our measurements of the SL, but the bulk layer would be expected to be symmetrical around the Co plane, whereas our results agree with earlier suggestions that the SL is likely to be asymmetrical around the Co plane \cite{21}.

4.4. Kinks and electron-phonon coupling

A final point of interest relates to electron-phonon coupling, a topic relevant to superconductivity. Several studies of related bulk CoO$_2$-based materials identify kinks in the bands that cross the Fermi level \cite{62,63,67}. In the case of the SL, although at first glance the data in figure 1(a) do appear to exhibit kinks at both band crossings, we do not find any decisive indication that such kinks definitely occur. As can be seen from figure 4, the sharp downturn in the filled band dispersion just below the Fermi level along the $\overline{TK}$ direction seems adequate to explain the shape of the band there, in agreement with Qian et al \cite{64}. Along the $\overline{TM}$ we were not able to convincingly fit any kink in the dispersion, so the situation here remains somewhat unclear.

5. Conclusions

Using XPD, we have determined the crystalline structure of SL CoO$_2$ on Au(111), finding good agreement with previous predictions. We have reported the electronic structure on the basis of ARPES measurements and DFT+GA calculations. Our calculations describe the ARPES data well, and indicate that SL CoO$_2$ is characterized by moderate electronic correlations. We have observed significant hydroxylation at the top of the layer, and found that the main effect of the H impurities is a shift of the Fermi level. Our calculations, which are based on freestanding SL CoO$_2$, reproduce the ARPES data well, consistent with a conclusion of weak interaction between the SL and the Au(111) substrate.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

\cite{[1] Takada K, Sakurai H, Takayama-Muromachi E, Izumi F, Dilanian R A and Sasaki T 2003 Nature \underline{422} 53
[2] Sakurai H, Ihara Y and Takada K 2015 Physica C \underline{514} 378
[3] Raveau B and Seikh M M 2015 Z. Anorg. Allg. Chem. \underline{641} 1385
[4] Lorenz B, Cmaidalka J, Meng R L and Chu C W 2003 Phys. Rev. B \underline{68} 132504
[5] Milne C J, Argyriou D N, Chemseddine A, Aliouane N, Veira J, Landsgezell S and Alber D 2004 Phys. Rev. Lett. \underline{93} 247007
[6] Wang C H, Chen X H, Luo J L, Liu G T, Lu X X, Zhang H T, Wang G Y, Luo X G and Wang N L 2005 Phys. Rev. B \underline{71} 224515
[7] Nakamura Y and Uchida S 1993 Phys. Rev. B \underline{47} 8369
[8] Terasaki I, Sasago Y and Uchino K 1997 Phys. Rev. B \underline{56} R12685
[9] Basov D N, Woods S I, Katz A S, Singley E J, Dynes R C, Xu M, Hinks D G, Homes C C and Strongin M 1999 Science \underline{283} 49
[10] Sugiuira K, Ohta H, Nakagawa S I, Huang R, Ikuhara Y, Nomura K, Hosono H and Koumoto K 2009 Appl. Phys. Lett. \underline{94} 152105
[11] Yang H B et al 2005 Phys. Rev. Lett. \underline{95} 146401
[12] Raghuv S, Thomale R and Geballe T H 2012 Phys. Rev. B \underline{86} 094506
[13] Takahata K, Iguni Y, Tanaka D, Itoh T and Terasaki I 2000 Phys. Rev. B \underline{61} 12351
[14] Saha R K, Klimczuk T, Foo M L and Cava R J 2003 Nature \underline{424} 527
[15] Foo M L, Wang Y, Watauchi S, Zandbergen H W, He T, Cava R J and Ong N P 2004 Phys. Rev. Lett. \underline{92} 247401
[16] Rybicki D, Jeurkutat M, Reichhardt S, Kapusta C and Haase J 2016 Nat. Commun. \underline{7} 11413
[17] Kuc A, Zibouche N and Heine T 2011 Phys. Rev. B 83 245213
[18] Zha Z X, Cheng Y C and Schwingenschlögl U 2011 Phys. Rev. B 84 153402
[19] Feng J et al 2018 Nano Lett. 18 4497
[20] Xi X, Zhao L, Wang Z, Berger H, Forró L, Shan J and Mak K F 2015 Nat. Nanotechnol. 10 765
[21] Walton A S, Fester J, Bajdich M, Arman M A, Osiecki J, Knudsen J, Vojvodic A and Lauritsen J V 2015 ACS Nano 9 2445
[22] Fester J, Bajdich M, Walton A S, Sun Z, Plessow P N, Vojvodic A and Lauritsen J V 2017 Top. Catal. 60 503
[23] Fester J, Makoveev A, Grumelli D, Gutzler R, Sun Z, Rodríguez-Fernández J, Kern K and Lauritsen J V 2018 Angew. Chem. 130 12069
[24] Nguyen D L, Hsing C R and Wei C M 2019 Nanoscale 11 17052
[25] Hoffmann S V, Sandergaard C, Schultz C, Li Z and Hofmann P 2004 Nucl. Instrum. Methods Phys. Res. A 523 125430
[26] See supplementary material for information on coverage estimates, discussion of the fitting procedures for XPS and XPD data, and additional discussion about the role of hydroxylation and lattice parameters in the theory calculations
[27] Fester J, Walton A, Li Z and Lauritsen J V 2017 Phys. Chem. Chem. Phys. 19 2425
[28] Baraldi A, Comelli G, Lizzit S, Kiskinova M and Paolucci G 2003 Surf. Sci. Rep. 49 169
[29] Bana H et al 2018 2D Mater. 5 035012
[30] Bignardi I et al 2019 Phys. Rev. Mater. 3 014003
[31] Doniach S and Sunjic M 1970 J. Phys. C: Solid State Phys. 3 285
[32] de Abajo F J G, Van Hove M A and Fadley C S 2001 Phys. Rev. B 63 075404
[33] Woodruff D P 2007 Surf. Sci. Rep. 62 1
[34] Takeuchi N, Chan C T and Ho K M 1991 Phys. Rev. B 43 13899
[35] Maeland A and Flanagan T B 1964 Can. J. Phys. 42 2364
[36] Fester J, Sun Z, Rodríguez-Fernández J, Walton A and Lauritsen J V 2018 J. Phys. Chem. B 122 561
[37] Heimann P, van der Veen J and Eastman D 1981 Solid State Commun. 38 595
[38] Moulder J F, Stickle W F, Sobol P E and Bomben K D 1992 Handbook of X-ray Photoelectron Spectroscopy Chastain J (Eden Prairie, MN: Physical Electronics Division, Perkin-Elmer Corporation)
[39] Frost D, McDowell C and Woolsey I 1974 Mol. Phys. 27 1473
[40] Chuang T, Brundle C and Rice D 1976 Surf. Sci. 59 413
[41] Biesinger M C, Payne B P, Grosvenor A P, Lau L W, Gerson A R and Smart R S 2011 Appl. Surf. Sci. 257 2717
[42] Kim K S 1975 Phys. Rev. B 11 2177
[43] Yang J, Liu H, Martens W N and Frost R L 2010 J. Phys. Chem. C 114 111
[44] Grosvenor A P, Wik S D, Cavell R G and Mar A 2005 Inorg. Chem. 44 8988
[45] Deng X Y, Wang L, Dai X and Fang Z 2009 Phys. Rev. B 79 075114
[46] Ho K M, Schmalian J and Wang C Z 2008 Phys. Rev. B 77 073101
[47] Lanatà N, Yao Y X, Wang C Z, Ho K M and Kotliar G 2015 Phys. Rev. X 5 011008
[48] Lanatà N, Yao Y, Deng X, Dobrosavljević V and Kotliar G 2017 Phys. Rev. Lett. 118 126401
[49] Schwarz K and Blaha P 2003 Comput. Mater. Sci. 28 259
[50] Anisimov V I, Aryasetiawan F and Lichtenstein A I 1997 J. Phys. Condens. Matter 9 767
[51] Lanatà N, Tsung-Han L, Yong-Xin Yao V S and Dobrosavljević V 2019 npj Comput. Mater. 5 30
[52] Bünemann J, Gebhard F and Thul R 2003 Phys. Rev. B 67 075105
[53] Tougaard S 2019 Quases-Tougaard, Ver. 7.0. software package for characterizing surface nanostructures by analysis of electron spectra (available at: www.quases.com/)
[54] Shinotsuka H, Tanuma S, Powell C J and Penn D R 2015 Surf. Interface Anal. 47 871
[55] Kresse G and Furthmüller J 1996 Comput. Mater. Sci. 6 15
[56] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758
[57] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[58] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
[59] Demaison J, Herman M and Lievin J 2007 Int. Rev. Phys. Chem. 26 391
[60] Singh D J 2000 Phys. Rev. B 61 13397
[61] Lee K W, Kunes J and Pickett W E 2004 Phys. Rev. B 70 045104
[62] Hasan M Z et al 2004 Phys. Rev. Lett. 92 246402
[63] Arakane T, Sato T, Takahashi T, Ding H, Fujii T and Asamitsu A 2008 Physica B 403 1086
[64] Qian D, Wray L, Hsieh D, Viciu L, Cava R J, Luo J L, Wu D, Wang N L and Hasan M Z 2006 Phys. Rev. Lett. 97 186405
[65] Yang H B et al 2004 Phys. Rev. Lett. 92 246403
[66] Amatucci G G, Tarascon J M and Klein L C 1996 J. Electrochem. Soc. 143 1114
[67] Geck J et al 2007 Phys. Rev. Lett. 99 046403