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Two-photon photoemission from CoO layers on Ir(1 0 0)

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Abstract

Two-photon photoelectron spectroscopy is used to study the unoccupied electronic states of cobalt oxide layers on Ir(1 0 0). For thicker layers of (1 0 0) orientation the conduction band minimum is found 2 eV above the Fermi level. Layers with (1 1 1) orientation and thickness ≤4 bilayers show a peak around 3.4 eV energy and no evidence for the conduction band minimum. This is attributed to the metallic character of thin CoO(1 1 1) layers.

Keywords: cobalt oxide, electronic states, work function, two-photon photoemission

(Some figures may appear in colour only in the online journal)

1. Introduction

Transition-metal oxides cover a wide range of crystal structures and oxidation states. They can be metals or insulators and the magnetic properties may show ferro-, ferri-, or antiferromagnetic behavior. The theoretical description is challenging due to localized and strongly-correlated electrons. Experiments have to deal with demanding sample preparations due to the variety of oxidation states and crystal structures. Studies of the electronic structure usually require well-ordered surfaces prepared under ultrahigh-vacuum conditions. Electron spectroscopies can only be applied to insulating oxides, if they are prepared as thin films on a metallic substrate.

With respect to the electronic structure CoO is classified as a charge-transfer insulator [2] with an antiferromagnetic order. The understanding of the electronic excitations of localized and strongly-correlated electrons is of particular interest for theory and experiment. The details of the description of exchange and correlation by various theoretical models yield band gaps between 2.3 and 3.6 eV [3–12]. Calculated unoccupied band structures show a strongly dispersing parabolic band at Γ formed by Co 4s states and a flat band arising from Co 3d t 2g states near the conduction band minimum (see figure 1). The relative position of these bands depends on the treatment of exchange and correlation [3, 4, 6, 8, 10, 12]. A recent study of the electronic structure of the CoO(1 0 0) surface reports no surface state in the fundamental band gap [13]. Photoemission studies of the occupied states focused on CoO in the rock-salt structure with (1 0 0) surface orientation [14–19]. Information on the unoccupied electronic states is available from bremsstrahlung isochromat spectroscopy (inverse photoemission) and x-ray absorption [20]. In combination with photoemission this study reports the band gap to be 2.5 ± 0.3 eV in good agreement with optical absorption measurements [21]. The combination of photoemission and inverse photoemission yields the correct band gap energy defined as the minimum energy required to remove one electron from the valence band and add it to the conduction band. Optical techniques transfer one electron directly from occupied to unoccupied states. This energy might be below the band gap energy, if the electron and hole are bound in an excitonic state. No distinct exciton lines below the fundamental band gap were identified [22] which is attributed to the flat bands of CoO near the band edges [23]. The downshift of the absorption spectrum relative to the single-particle excitation spectrum is explained by excitonic and local field effects [23].
Figure 1. Band structure of CoO showing the valence band maximum (VBM) and conduction band minimum (CBM) [3]. Fermi energy $E_F$ and vacuum level $E_{Vac}$ are estimated from experiment (see text). Arrows indicate two-photon photoemission processes for two different photon energies.

step the electron is excited from the conduction band to an energy above the vacuum level and leaves the surface. Two different scenarios are possible: (i) If the electron is bound in an exciton, the final state has a hole in the valence band which is identical to the case of photoemission induced by the simultaneous absorption of the two photons. No information on unoccupied states is obtained. (ii) If the electron and hole are decoupled, e.g., by decay of the initial exciton into a lower excited state [24], the second photon just removes the electron from the conduction band. No information on occupied states is obtained. The two situations can be distinguished by changing the photon energy: The electron is emitted by two photons in the first scenario and by only one photon in the second. This difference is reflected by corresponding changes in the kinetic energy of the emitted electrons upon change of photon energy [25]. Photon energies above 4.5 eV were used to excite the two-photon photoemission spectra. These photon energies are well above the optical band gap (see figure 1) and the photons may be absorbed in the oxide layer with sufficient probability [22, 23]. The photon energies are below the work function of all surfaces studied to exclude one-photon photoemission, but still provide access to a large energy range of unoccupied states.

The following section gives a short description of the sample preparation and the essential experimental details. Then we discuss the two-photon photoemission results from thick layers of CoO(1 0 0) on Ir(1 0 0). Measurements from layers of CoO with (1 1 1) orientation are presented afterwards. Finally, we show results for monolayers of Co on Ir(1 0 0) with various amounts of oxygen. The paper is wrapped up with a summary and conclusions.

2. Experiment

Ultrathin layers of CoO were epitaxially grown on Ir(1 0 0) following the recipes and notation given in [1, 26, 27]. The layer thickness was determined from the amount of evaporated Co monitored by a quartz microbalance. The thickness is given in monolayers (ML) for the epitaxial (1 0 0) structures and for CoO(1 1 1) in bilayers (BL) which contain 86.6% as many Co atoms per unit area as a (1 0 0) monolayer [1]. The sample preparation was checked by low-energy electron diffraction (LEED) which indicated epitaxial growth of CoO layers with the desired structures. All measurements were performed at a sample temperature of 90 K.

Two-photon photoemission (2PPE) experiments used the frequency-tripled output of a Ti:sapphire oscillator running at a repetition rate of 86 MHz. The pulse length was ≈55 fs. The angle between the p-polarized laser beam and electron analyzer was fixed at 80°. Photoelectron spectra were recorded in normal emission using an Omicron EA 125 HR spectrometer with seven channeltron detectors at an angular resolution of 1.4°. The energy resolution was 34 meV for the CoO(1 0 0) measurements and 68 meV otherwise. For details of the experimental setup see [28].

3. Results

3.1. CoO(1 0 0)

Figure 2 shows the two-photon photoemission spectra for 4 and 20 ML of CoO(1 0 0) on Ir(1 0 0). All spectra were normalized to the same peak height. The photon energies used were 4.51 and 4.65 eV (solid and dashed lines in figure 2). The data are plotted on the intermediate-state energy scale obtained by subtracting the photon energy from the measured final-state energy (see arrows in figure 1). Spectra for different photon energies are almost indistinguishable. This proves that the observed peaks correspond to unoccupied states above the Fermi level $E_F$. For both thicknesses a main peak around 2 eV is observed. The peak width is 0.25 eV for 4 ML and 0.35 eV for 20 ML. The broader peak width might be attributed to poorer film quality for the thicker film which showed some intensity at $(2 \times 2)$ spot positions in LEED. This is in agreement with the more Gaussian peak shape for the 20 ML films typical for inhomogeneous broadening while the lineshape for the 4 ML films is better described by a Lorentzian characteristic for lifetime broadening. The lifetime deduced from the Lorentzian linewidth would correspond to ≈5 fs. This value seems rather small for the conduction band minimum on an insulator. The high intensity of the two-photon photoemission signal points to a high population in the intermediate state which can only be accumulated during long lifetimes. This discrepancy can be resolved by considering, that linewidths obtained in energy-resolved spectroscopy include also contributions from quasi-elastic scattering [29, 30]. The flat 3d bands near the conduction band minimum (figure 1) facilitate scattering processes with negligible energy exchange. For the 4 ML film electrons might also couple to conduction bands of the metallic
Figure 2. Two-photon photoemission spectra for 4 and 20 ML of CoO(1 0 0) on Ir(1 0 0). The spectra are normalized to the same peak height and plotted as function of intermediate-state energy relative to the Fermi level $E_F$. Solid and dashed lines are for 4.51 and 4.65 eV photon energy, respectively.

Therefore, the values might not readily be comparable to our results for 4 ML of CoO on Ir(1 0 0).

The spectra in figure 2 show besides the main peaks some minor peaks. The minor peak at 3.80 eV for 4 ML has a binding energy of 1.18 eV with respect to the vacuum level. Image-potential states are candidates for surface states close to the vacuum level. On metals they are found in the energy range 0.85 below the vacuum level [38]. At the surface of a dielectric with a dielectric constant $\varepsilon$ the binding energy should be reduced by a factor $(\varepsilon - 1)/(\varepsilon + 1)^2$ [38]. For cobalt oxide $\varepsilon$ is 10.9 at 90 K [39] and the reduction factor amounts to 0.7. Binding energies below 0.85 eV are observed for thin CoO monolayers (see section 3.3) and for NiO [40]. Therefore, the minor peak 1.18 eV below the vacuum level cannot be an image-potential state. An assignment of the minor peak to areas of lower coverage with a $\varepsilon(10 \times 2)$ reconstruction (see following section 3.2) is a plausible interpretation. The LEED pattern of the 4 ML film showed some (12 × 12) spots characteristic for lower coverages [1]. Consistent with this interpretation is the absence of this peak for the 20 ML film in figure 2. Instead a shoulder of the main peak is observed around 2.5 eV. A possible assignment would be the flat band arising from Co 3d $t_{2g}$ states above the conduction band minimum formed by the Co 4s states at $\Gamma$ (see figure 1). The band structure calculations report various values for the energy difference between these states [3, 4, 6, 8, 10, 12] which are compatible with the 0.5 eV difference in peak energy found in our experiments. The low intensity of the minor peak relative to the main peak could be attributed to a reduced dipole matrix element and photoionization cross section for 3d states compared to 4s states. In addition, higher excited electrons would collect at the conduction band minimum and the second photon would sample an increased electron population from the state at the lowest energy.

The work function can be determined from the low-energy cutoff of the spectra (not shown in figure 2). We obtained values around 5 eV (see table 1) in good agreement with a report of 4.9 eV for cleaved bulk CoO(1 0 0) [41]. Calculated data around 3.5 eV are available only for 1 and 2 monolayers on Ag(1 0 0) [42] which are significantly lower than our values. The striking discrepancy to our results cannot be explained by the smaller layer thickness or different substrate in the calculations compared to experiment. The theoretical work finds almost the same work function for 2 ML NiO on Ag(1 0 0) as for CoO. Two-photon photoemission experiments report values around 4.4 eV for the work function for 2–4 ML NiO [40] in agreement with measurements on cleaved NiO(1 0 0) surfaces [41]. Apparently, the calculated work functions [42] are systematically lower than the experimental values for CoO and NiO on Ag(1 0 0). Also the calculated increase of the work function by ≈0.1 eV from 2 to 5 ML for NiO [42] is at variance with the constant values found in experiment [40].

3.2. CoO(1 1 1)

Two-photon photoemission spectra taken with a photon energy of 4.65 eV for CoO layers in (1 1 1) orientation are shown in figure 3. The spectra show the actual number of
counts as a function of intermediate-state energy. The work function is obtained from the energy of the low-energy cutoff by adding the photon energy of 4.65 eV. The assignment of the observed peaks to intermediate states was checked by using different photon energies as illustrated in figure 2 for CoO(1 0 0). The number of counts of the peaks is relatively low. For CoO(1 0 0) the intensity is about two orders of magnitude higher as can also be seen from the negligible statistical noise in figure 2 compared to figure 3. For low thicknesses a single peak is observed around 3.4 eV. For thicker films a second weaker peak appears at lower energies. We note that the energy of all peaks is significantly larger than 2 eV which was assigned to the conduction band minimum on CoO(1 0 0). Around 2 eV no peak is observed for CoO(1 1 1) even for thicker layers where the band gap of CoO should have developed and the influence of the metallic substrate has minimized. The CoO(1 1 1) spectra show a distinct Fermi edge at an intermediate-state energy of 4.65 eV in figure 2 indicating a metallic surface. On CoO(1 0 0) no Fermi edge is observed. For CoO(1 1 1) layers a wurtzite termination at the surface has been reported which is characterized by a metallic surface [43, 44]. For film thicknesses up to 4 BL the metallic nature of the surface and interface may hinder the development of the full band gap of CoO. The presence of a density of states at $E_F$ for CoO(1 1 1) layers would reduce the lifetime of excited electrons. This explains the low two-photon photoemission signal compared to the one from CoO(1 0 0) layers. The assignment of the 3.4 eV peaks cannot be made on the basis of bulk band structure calculations (see figure 1), because no band gap is observed. Information from band structure calculations for the specific surface structures would be needed. Calculations for the CoO(1 1 1) bilayer on Ir(1 0 0) with a c(10x2) reconstruction concentrate on structural aspects and unfortunately give no information on the electronic structure [45]. Photoemission results for CoO(1 1 1) on Au(1 1 1) [46] and Pt(1 1 1) [47] are consistent with our observations: A metallic behavior is found for thicknesses up to 3 BL on Au(1 1 1). Above 5 BL no intensity is detected at the Fermi energy and the valence band maximum is located 1 eV below $E_F$ indicating the development of bulk CoO. For 6 ML CoO(1 1 1) on Pt(1 1 1) the valence band maximum is found <0.1 eV above the one of CoO(1 0 0) [47]. Valence band features for both surfaces are very similar indicating the development of bulk CoO above that layer thickness. Scanning tunneling spectroscopy on thicker three-dimensional islands of CoO(1 1 1) on Pt(1 1 1) also show a band gap between −0.4 and +0.5 eV, while 1 and 2 ML are metallic [48].

Work functions close to 6 eV are obtained which are about 1 eV higher than for CoO(1 0 0). An explanation of this large difference is the oxygen termination of the polar CoO(1 1 1) surface [49] in contrast to the non-polar CoO(1 0 0) termination. For CoO(1 1 1) on Au(1 1 1) a work function around 3.7 eV has been reported [46]. This striking discrepancy to the values close to 6 eV on Ir(1 0 0) can only be understood if the structure and morphology of CoO(1 1 1) are different for the two substrates. Indeed an Auger electron diffraction study for a 7 BL CoO(1 1 1) film on Au(1 1 1) finds a bulk-like termination and does not mention a wurtzite stacking in the top layer [50].

### 3.3. CoO monolayer

One monolayer of Co on Ir(1 0 0) can bind various amounts of oxygen. The resulting structures are characterized by

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**Table 1.** Data extracted from the two-photon photoemission spectra of this work.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Co layers</th>
<th>Work function</th>
<th>Main peak</th>
<th>Minor peak</th>
<th>STS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO(1 0 0)</td>
<td>4 ML</td>
<td>4.98</td>
<td>2.13</td>
<td>3.80</td>
<td>—</td>
</tr>
<tr>
<td>CoO(1 0 0)</td>
<td>20 ML</td>
<td>5.17</td>
<td>2.00</td>
<td>2.52</td>
<td>—</td>
</tr>
<tr>
<td>CoO(1 1 1)</td>
<td>1 BL</td>
<td>5.85</td>
<td>3.51</td>
<td>—</td>
<td>4.83</td>
</tr>
<tr>
<td>CoO(1 1 1)</td>
<td>2 BL</td>
<td>6.01</td>
<td>3.36</td>
<td>—</td>
<td>3.38</td>
</tr>
<tr>
<td>CoO(1 1 1)</td>
<td>3 BL</td>
<td>5.95</td>
<td>3.44</td>
<td>2.94</td>
<td>—</td>
</tr>
<tr>
<td>CoO(1 1 1)</td>
<td>4 BL</td>
<td>5.91</td>
<td>3.62</td>
<td>3.10</td>
<td>—</td>
</tr>
<tr>
<td>(2 × 2)</td>
<td>1 ML</td>
<td>5.18</td>
<td>2.36</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(3 × 3)$_I$</td>
<td>8/9 ML</td>
<td>5.55</td>
<td>3.15</td>
<td>2.55</td>
<td>3.5</td>
</tr>
<tr>
<td>(3 × 3)$_II$</td>
<td>8/9 ML</td>
<td>5.80</td>
<td>3.65</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>c(10 × 2)</td>
<td>0.9 ML</td>
<td>5.85</td>
<td>3.51</td>
<td>—</td>
<td>4.83</td>
</tr>
<tr>
<td>c(8 × 2)</td>
<td>0.9 ML</td>
<td>6.21</td>
<td>4.03</td>
<td>3.49</td>
<td>4.15</td>
</tr>
</tbody>
</table>

**Note:** All energies in eV. Additional information from scanning tunneling spectroscopy [57, 58] is included for comparison.

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**Figure 3.** Two-photon photoemission spectra from CoO(1 1 1) layers on Ir(1 0 0) taken with a photon energy of 4.65 eV. The spectra are offset for clarity. The spectra are plotted as function of intermediate-state energy relative to the Fermi level $E_F$. 

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different surface reconstructions illustrated in figure 4 [26]. The $c(8 \times 2)$ structure is similar to the $c(10 \times 2)$ structure with an additional oxygen layer between the Ir substrate and the cobalt layer [1]. Figure 5 shows two-photon photoemission spectra from monolayers of Co on Ir(1 0 0) with increasing oxygen content from bottom to top taken with a photon energy of 4.65 eV. The $c(10 \times 2)$ reconstruction is the stoichiometric cobalt oxide and is identical to the 1 BL case of the preceding section. For comparison we included the spectrum for the clean Ir(1 0 0)(1 × 1) surface. With increasing amount of oxygen in the top layer the work function (low-energy cutoff) increases. The final value at an oxygen to cobalt ratio of 2 is higher than the work function determined for the polar CoO(1 1 1) surfaces of several bilayers thickness. For CoO monolayer structures on Pd(1 0 0) field emission resonances were measured [51], which are compatible with a work function increase with oxygen content as observed in this work for CoO on Ir(1 0 0).

The $(2 \times 2)$ surface with the lowest work function has the highest intensity at the low-energy cutoff which is formed by secondary electrons or hot electrons excited by the femtosecond laser pulses. The intensity of the peaks is similar to the situation for the CoO(1 1 1) surfaces and about two-orders of magnitude lower than for CoO(1 0 0). This would be in agreement with the reduced lifetime of the observed states due to the metallic nature of the surface. The metallic character of the surfaces is evident from the observation of a Fermi edge up to the highest oxygen contents.

The $(2 \times 2)$ surface shows a peak around 2.4 eV. Considering the low coverage and low oxidation state [26] this peak cannot be related to the conduction band minimum of CoO. Instead it should be classified as an adsorbate-induced surface state in the band gap of the projected bulk band structure of Ir(1 0 0) which ranges from 2.4 to 10.8 eV in a fully-relativistic calculation [52]. The spectrum from the clean Ir(1 0 0)(1 × 1) surface (bottom trace in section 3.3) shows no feature in the energy region where peaks are observed for CoO monolayers.

The assignment of the 2.4 eV peak on the $(2 \times 2)$ surface to an adsorbate-induced surface state applies also to the peaks between 3 and 4 eV observed for higher oxygen coverages.
For the $c(8 \times 2)$ surface a splitting of the peaks is observed. The energy of the low-energy peak coincides with the one of the peak found for the $c(10 \times 2)$ surface. Some areas with $c(10 \times 2)$ reconstruction on the $c(8 \times 2)$ surface could explain this intensity. However, a double-peak structure similar to the one found for thicker CoO(1 1 1) layers cannot be excluded.

The spectra for the $(2 \times 2)$ and $(3 \times 3)$ reconstructions show peaks at the high-energy cutoff. Their energy cannot be determined reliably, because the peak is cut off by the Fermi function. For the $(2 \times 2)$ surface a lower bound for the energy would the peak position (4.5 eV) which is 4 eV above the low-energy cutoff corresponding to the vacuum energy. Using the photon energy of 4.65 eV a binding energy relative to $E_{\text{Vac}}$ of $<0.65$ eV is estimated. The binding energy of image-potential states on a metal surface is given by $E_b = 0.85 \, eV/(n + a)^2$. Therefore, we assign the observed peak to the first image-potential state. From the measured binding energy a quantum defect of $a > 0.14$ can be estimated in agreement with its position in the band gap of the project bulk band structure of Ir(1 0 0) [53]. The cobalt oxide monolayer might further influence the binding energy due to its dielectric behavior (see section 3.2) or quantum-well effects [54]. For higher oxygen contents the work function increases further and the image-potential states cannot be excited with a photon energy of 4.65 eV. Therefore these states are not observed for the $c(10 \times 2)$ and $c(8 \times 2)$ reconstructions.

For CoO on Pd(1 0 0) $c(4 \times 2)$ and $(9 \times 2)$ phases have been found [55] which are similar to the ones on Ir(1 0 0) of this study. Photoemission finds for these structures a strong peak near $E_F$ indicating a metallic surface in agreement with our results. The work function increases with oxygen concentration in accordance with our observations and theoretical calculations [56].

4. Conclusions

The energies extracted from the two-photon photoemission spectra shown in figures 2–5 are collected in table 1. Figure 6 shows the data as a function of layer thickness and oxygen concentration, respectively. The work function is plotted as filled squares. The main and minor peak positions are shown by filled and open circles, respectively. Additional data from scanning tunneling spectroscopy [57, 58] are marked by crosses.

The work function of the three data points for the lowest oxygen concentration show an almost linear behavior (see thin line in figure 6). Extrapolation to zero oxygen concentration yields a work function of $4.76 \pm 0.1$ eV. Another path to obtain a work function value for a full monolayer of Co without oxygen starts at the clean Ir(1 0 0) surface for which we measured a work function of 5.86 eV. A work function of 5.10 eV was determined for 0.8 ML of Co on Ir(1 0 0) (5 × 1)-H. Extrapolating to full monolayer coverage of Co we obtain a work function of 4.91 eV. Considering that the 0.8 ML surface consists of epitaxial four Co atom wide strips between Ir chains on Ir(1 0 0) [59, 60], the extrapolated work function value agrees reasonably well with the value of 4.76 eV extrapolated to zero oxygen coverage. The latter value is also in good agreement with the work function of 4.66 eV for 1 ML of Co on Cu(1 0 0) [61]. The slightly lower value can be attributed to the lower work function of the Cu(1 0 0) substrate (4.63 eV [53]) compared to the Ir(1 0 0) substrate (5.86 eV).

The work function of metal films reaches the asymptotic value for two or more layers [61, 62], so for one monolayer the substrate work function is still noticeable.

The clear identification of the conduction band minimum in two-photon photo-emission from CoO(1 0 0) indicates the absence of excitonic effects in the first step of the process.
The electron and hole are decoupled after excitation by the photon. This may be understood from the fact that the used excitation energy of 4.65 eV is larger than the band gap of ∼3 eV (see figure 1). The electron might be excited into higher conduction band states and relaxes down to the conduction band minimum. Similarly, a deeper-lying hole might relax into the valence band maximum. The relaxation processes break up the binding between electron and hole and at the end only the electrons from the conduction band minimum are excited by the second photon. Since the excess energy of ∼1.65 eV from the excitation process is smaller than the band gap, the decay via Auger-like processes and the creation of further electron pairs can be excluded. For Si(1 0 0) the relaxation into the conduction band minimum proceeds via phonons [24]. This might also be a plausible relaxation mechanism for cobalt oxide which has pronounced optical phonons as an ionic crystal [63]. Time-resolved measurements for CoO(1 0 0) would be needed to confirm the relaxation process via phonons according to their picosecond time scale.

The conduction band minimum is not observed in two-photon photoemission spectra from CoO monolayers and CoO(1 1 1) films up to 4 BL. We attribute this to the metallic character of these surfaces indicating that an insulating oxide has not developed on the metallic Ir(1 0 0) substrate. Most optical phonons as an ionic crystal [63]. Time-resolved measurements for CoO(1 0 0) would be needed to confirm the relaxation process via phonons according to their picosecond time scale.

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### 5. Summary

Two-photon photoelectron spectroscopy was used to study the unoccupied electronic states of cobalt oxide layers on Ir(1 0 0). For thicker layers of (1 0 0) orientation the conduction band minimum is found 2 eV above the Fermi level. Time-resolved measurements would be desirable in order to understand the relaxation processes from the initial excitation of the electron to the conduction band minimum. Layers with (1 1 1) orientation and thickness ≤4 bilayers show no evidence for the conduction band minimum. This is attributed to the metallic character of these layers. Theoretical calculations are needed to clarify the character of the surface state found around 3.4 eV for these surfaces.

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