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Comparative Study of Adsorbate Systems and Corresponding Compounds Using X-Ray and UV-Photoemission

I. Hexagonal(0001)Co/CO, O₂ versus Oxides and Carbonyls

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Adsorption / Katalyse / Komplexverbindungen / Oberflächenerscheinungen / Photoemission

Photoemission studies using XPS and UPS (HeI, HeII) on clean and gas-covered hexagonal (0001)-Cobalt-single-crystal surfaces are reported (300 K). To interpret the results on the adsorbates namely Co/CO and Co/O₂, compound systems, such as CoO, Co₃O₄ and Co₂(CO)₈ are studied parallel and comparison is made. It is shown that the emission from Co/O₂ is similar to that from CoO and not to that from Co₃O₄ and that the Co/CO-systems resembles the Co₂(CO)₈-photoemission characteristics. Assignment of CO-peaks as far as the sequence of the 4σ, 1π and 5σ is concerned is shown to be the same as in free CO. The C1s spectrum of the carbonyl is analysed using theoretical predictions of atomic populations, which show the bridging ligands to carry more electron density than terminal ones. From comparison with adsorbate systems it follows that the differences in the adsorbate system are not as pronounced as in the case of the carbonyls.

Es wird über XPS- und UPS-(HeI, HeII)-Messungen an einer reinen und gasbelegten (Sauerstoff, Kohlenmonoxid) (0001)-Fläche von Kobalteinkristallen bei Raumtemperatur berichtet. Zur Interpretation werden parallel Verbindungssysteme wie CoO, Co₃O₄ und Co₂(CO)₈ untersucht, die aus den gleichen Elementen wie die Adsorbatphase bestehen. Es zeigt sich, daß die Emissionscharakteristika des Sauerstoffadsorbats im Valenz- und „core-electron“-Bereich denen von CoO und nicht von Co₃O₄ ähneln. Ebenso läßt sich Co₂(CO)₈ mit dem Kohlenmonoxidadsorbat korrelieren. Über die Analyse der Energieabhängigkeit kann die Reihenfolge der dem adsorbierten CO zuzuordnenden Banden ermittelt werden. Die Sequenz des adsorbierten CO's entspricht der des freien Moleküls. Das C1s-Spektrum des Carbonyls kann über theoretisch vorhergesagte Elektronendichten gedeutet werden. Die terminalen Liganden tragen demnach eine geringere Elektronendichte als die Brückenliganden. Über den Vergleich der C1s-Spektren des Carbonyls mit dem des Adsorbats zeigt sich, daß die Elektronendichteunterschiede auf verschiedenen koordinierten Liganden im Adsorbat nicht so ausgeprägt sind wie in der Carbonylverbindung.

Introduction

One of the most active fields in surface physics during recent years has been and still is the study of chemisorption processes. A reason probably is that no final conclusion has been reached yet about the nature of a chemisorptive bond between a particular metal and foreign atoms or molecules as to whether this interaction has to be described by a localized or a delocalized theoretical model. Considering the similarities of intermetallic bond energy, molecular dissociation energy and chemisorption bond energy it seems to be difficult to decide whether to treat the surface interaction as a perturbation of the crystal by a foreign atom or to think of a "surface compound" which is perturbed by the rest of the crystal.

A priori it seems reasonable that examples of both types of systems should exist. The widely investigated Ni/CO-system is claimed to be one of the classical cases in which a localized description is adequate while this description fails in connection with hydrogen adsorption. These statements are confirmed by theoretical arguments as well as by certain experimental results such as changes in electrical resistance or work function measurements [1].

Another experimental and theoretical approach to shed some light on these central problems of chemisorption, which has until now found rather little attention, is to compare adsorbate systems with corresponding compounds. In such an approach chemically and physically well characterized materials, containing the same elements as the adsorbate systems

are studied as references for the adsorbate system. If there is experimental evidence for similarities the essentials of a theoretical model consistent with the experimental results for the reference system can then be used to describe the surface system. Occurring dissimilarities offer the possibility to correct the model description.

To follow these lines of thought one is forced to look for systems which are as well open to chemisorptive as to compound studies in the above described sense. These are systems where a variety of stable compounds is accessible. Thinking of oxygen and carbonmonoxide adsorption, nickel is not very suitable. Although there are oxides and Ni/O-adsorbates for instance, there is only one counterpart to the interesting Ni/CO-adsorbate system, namely Ni(CO)₄. In contrast to this there exist several oxides and a family of stable carbonyls from the neighboring elements and iron. Some of these carbonyls are of special interest in containing more than one metal atom and thus form ligand-stabilized metal clusters. This means, they can be taken as "adsorption models realized in nature". Examples are:

Iron	FeO	Fe ₂ O ₃	Fe ₃ O ₄
	Fe(CO) ₅	Fe ₂ (CO) ₉	Fe ₃ (CO) ₁₂
Cobalt	CoO	Co ₃ O ₄	
	Co(CO) ₈	Co ₂ (CO) ₈	Co ₄ (CO) ₁₂ Co ₆ (CO) ₁₈

Due to the fact that in cobaltcarbonyls the ligand to metal ratio is more similar to the situation present in adsorbates

we report on cobalt-oxygen and cobalt-carbonmonoxide-systems in this paper.

Since the first paper by Eastman and Cashion [2] photoemission turned out to be one of the most powerful tools in the study of surface phenomena. As photoemission can be correlated with one-electron theory via Koopmans' Theorem it is well suited to test localized versus nonlocalized theories although it is known that many-electron effects influence the photoemission process [3]. We therefore have investigated the above mentioned systems using HeI and HeII excitation for the UPS- and MgK_α -radiation for the XPS-regime.

Experimental Setup

The spectrometer system (Leybold-Heraeus, Cologne), — see Fig. 1 — consists of an analysing and a preparation chamber. The latter is equipped with an argon ion gun and a gas inlet system. The sample mounted on a turnable sample-holder can be transported from the preparation to the analysing position. UPS- and XPS-spectra are recorded using a 180° spherical analyser with pre-retardation (Leybold-Heraeus, Cologne) [4]. According to Fig. 1 the system is pumped by two turbo pumps and a titanium-sublimator which allow to work at basis pressures below $1 \cdot 10^{-10}$ Torr, measured in the analysing chamber. The moveable sample rod can be heated up to 600°C and cooled down to -170°C .

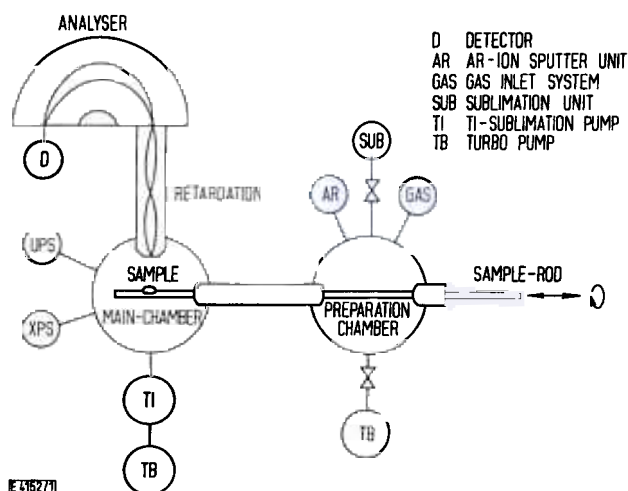


Fig. 1
Spectrometer system with 180° spherical analyser

The Clean Single-Crystal-Surface

Because of the good cleaning conditions tungsten and nickel surfaces in different orientations are frequently used substrates. In connection with cobalt there arise difficulties from the hcp-fcc transition between 380°C and 431°C [5].

Nevertheless recently reported [6] LEED studies show a well ordered surface structure after sputter-anneal-cycles of the polished single crystal-(0001)-surface.

By making use of similar preparation conditions as in the LEED study, the spark-mashed crystal (Material Research, England) with purity 99.999% was oriented on a goniometer-head and was chemically polished without pressure using a modified Honeywell-receipt [7]. Correct orientation was controlled during the process by Laue-diffraction. In the preparation chamber the crystal was cleaned by several sputter (250 V–400 V)-anneal (80° – 200°)-cycles until no oxygen and carbon could be detected.

In this connection it is remarkable that although in the XPS-excited valence band spectrum no oxygen was detectable the UPS

spectrum resolved a well defined oxygen peak (see Fig. 5). This is simultaneously due to escape depth effects, as to final state effects, which we think to be the dominating feature in this respect. The peak inserted in Fig. 5 shows the approximate intensity of the oxygen peak if the reduction of intensity should be attributable to escape depth changes only. A similar situation was met by Plummer et al. [10] in the study of oxygen on tungsten.

To reduce the very rest of oxygen on the surface the crystal was annealed in a hydrogen atmosphere. Fig. 2 shows spectra of the clean (0001)-surface as measured by HeI [24] and MgK_α . The energy scaling is done relative to the Fermi-edge which is defined by threshold extrapolation as indicated in Fig. 2. The spectra are not comparable straightforward since different resolution for XPS and UPS have to be taken into account. From metals with high density of states at the Fermi-edge, Pd for example, the resolution of the instrument is known to be 220 meV for HeI-radiation [8]. The XPS resolution at the same analyser conditions can be determined from a core-level state and is found to be 0.5 eV for Ag $3d_{5/2}$ (1/2 line width) [8]. Thus, one expects to have a steeper valence band edge for HeI than for XPS. The XPS valence band reaches half of maximum height for Co about 1 eV below the intensity onset, which is more than can be explained by altered resolution. One reason could be that parts of the high intensity peak at lowest binding energy in the HeI spectrum is strongly energy dependent, contributing to the XPS spectrum only in broadening the Fermi-edge, because its intensity is reduced.

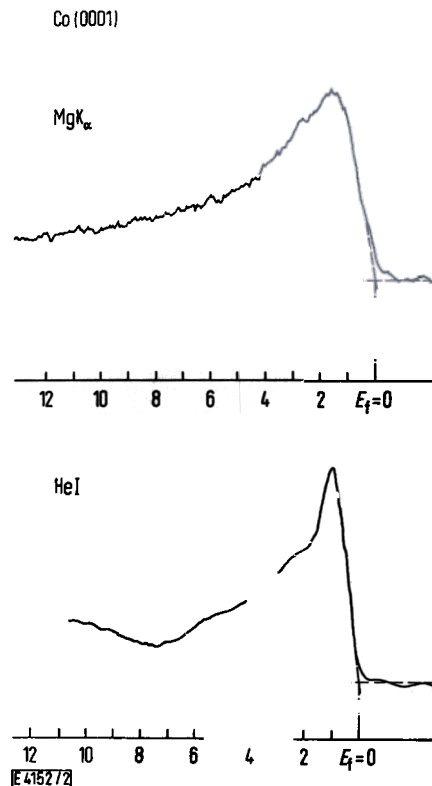


Fig. 2
Photoemission spectra of the clean single crystal surface

The overall shape of XPS and UPS spectra is similar to the results of Eastman [9] (UPS) and Baer et al. [10] (XPS) obtained from polycrystalline samples, but is completely different from those of Spicer et al. [11] reported earlier, particularly in the absence of a peak near -5 eV. As Eastman [9] found — with $h\nu = 10.6$ eV — for a mostly (70%) hexagonal sample — we observe a narrow peak at -0.9 eV (corresponding to 0.3 eV in Eastman's energy scaling) and one broader shoulder at -2.4 eV below the Fermi-edge, dropping to intensity zero till 6–7 eV. All other structures seem to

be due to inelastically scattered electrons. A similar situation is observed in the XPS-spectrum with a peak at -1.7 eV and a weak shoulder at -2.8 eV indicating unresolved structure. Having characterized the clean surface we turn over to coverage experiments.

The System Cobalt/Oxygen

a) The Adsorbate

The clean single crystal surface was exposed to varying amounts of high purity grade oxygen, which causes considerable changes in the emission spectra (see Fig. 3):

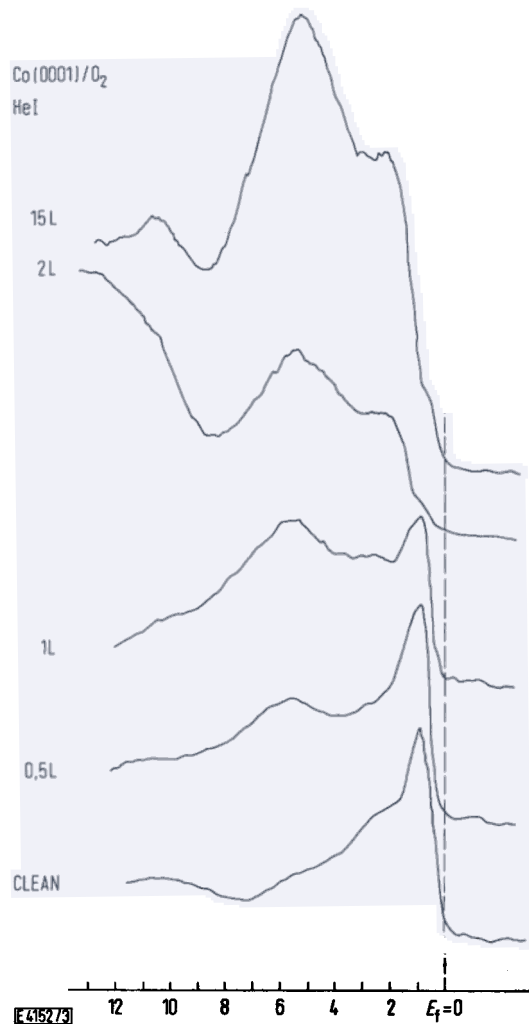


Fig. 3

Photoemission spectra of clean and oxygen covered (0001)-cobalt-surface with varying amounts of oxygen at 300 K

At very low exposure (<1 L) an additional peak evolves at -5 eV $- -6$ eV strongly growing with growing exposure. At the same time the peak near the Fermi-edge decreases in intensity, remaining as a small shoulder when the exposure exceeds 1 L. The peak at -2.4 eV keeps its intensity and at higher coverages these peaks dominate the high energy band edge. The peak position at -6 eV — due to oxygen 2p-emission — is independent of exposure. In addition to this peak, which is probably identical with Spicer's [11] -5 eV peak, arising from oxygen as surface contaminant on

the sample, a further peak at -10.5 eV grows up and becomes well resolved at exposures between 10 L and 20 L.

To demonstrate the qualitative effects of oxygen adsorption on the photoemission spectra a difference spectrum is shown, computed from clean and highly covered surface. To do this the secondary electrons distribution was estimated and

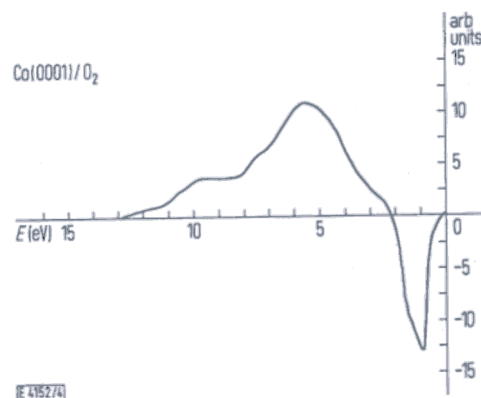


Fig. 4

Difference spectrum as calculated from oxygen covered and clean cobalt (0001)-surface

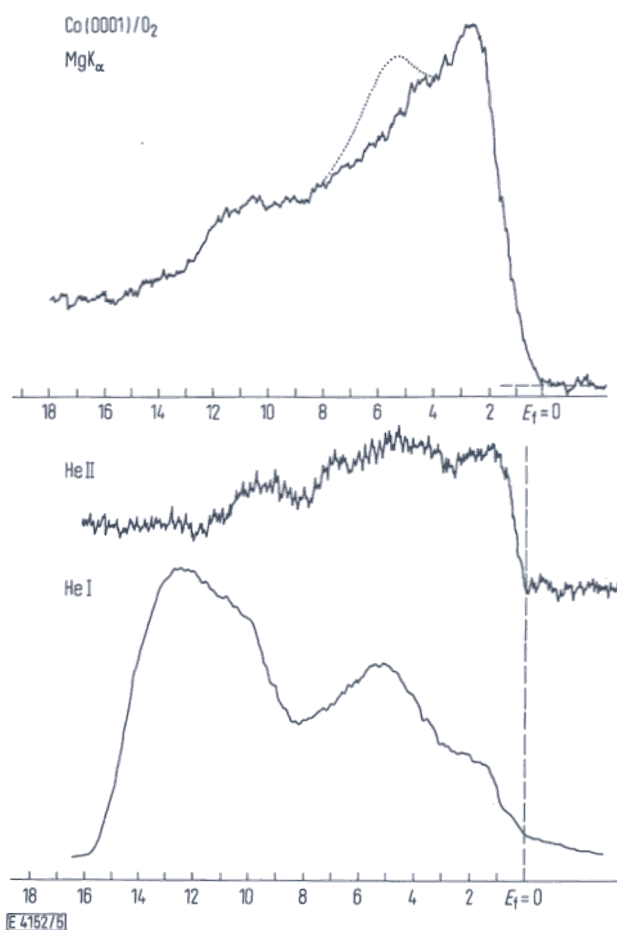


Fig. 5

Photoemission spectra of (0001)-cobalt surface measured with different excitation energies. The coverage is the same for all spectra. In the XPS-curve the dotted line indicates oxygen emission if the intensity were only reduced by escape depth changes

subtracted before the difference spectrum was evaluated (Fig. 4). The assigned spectral structures can all be met in the difference spectrum, too. Especially a strong "negative" peak is found in the region near the Fermi-edge indicating a region of states sensitive to adsorption. The fact, that the peak is negative is in agreement with earlier findings on other transition metals [16].

To gather additional information for the assignment the oxygen covered surface was excited by three different energies. The spectra are compiled in Fig. 5 together with a HeI spectrum taken from Fig. 3. The dominating d-emission in connection with the XPS-spectrum is remarkable and the HeII spectrum exhibits some extra structure in the O 2p-energy-region, which will be discussed in detail, when we compare the adsorbate emission to the compound spectra.

The consequence of oxygen chemisorption on inner shell spectra are shown in Fig. 6 where the Co 2P_{3/2}-lines are plotted with and without oxygen on the surface. The other spectrum shows the lines of lowest binding energy up to 80 eV for an oxygen covered surface. While the clean crystal exhibits only very weak satellite structure without pronounced maxima, which can be assigned to plasma losses [9], the oxygen covered surface shows very strong satellite lines at about 5 eV below the Co-peak which itself is shifted by 2 eV relative to the clean metal Co-peak. The width of the shifted lines is considerably broader than that of the clean metal lines. The same observation has been made with polycrystalline Co [8]. After annealing an oxygen covered sample for 1 hour the line

width shrunk by a factor 1.2 but it remains still broader than the metal signal.

b) The Compound System

Having presented the experimental observations for the covered surface this is the point to come back to lines of thought outlined in the introduction:

To interpret our observations we want to reference to compound systems. In this special case we are forced to compare to solid oxides. The two cobalt oxides which are well characterized namely CoO and Co₃O₄, have been subject to photoemission studies by Kim [12], Brundle [13], Eastman [14] and Wertheim [15]. While some experimental results for different excitation energies are available for CoO [14], only XPS measurements on Co₃O₄ have been reported [15].

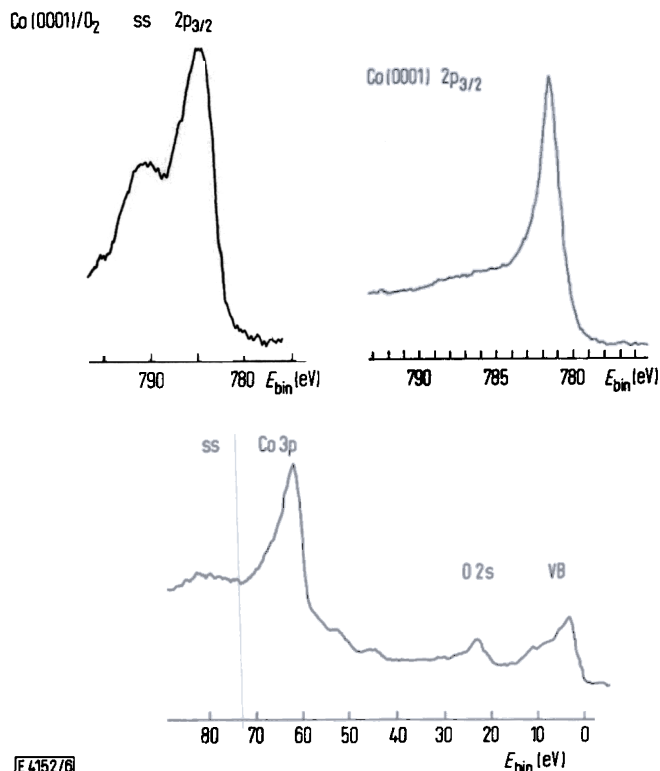


Fig. 6

XPS-photoemission from clean and oxygen covered (0001)-surface in the 2p and 3p/valence-band region (ss: shake up satellite)

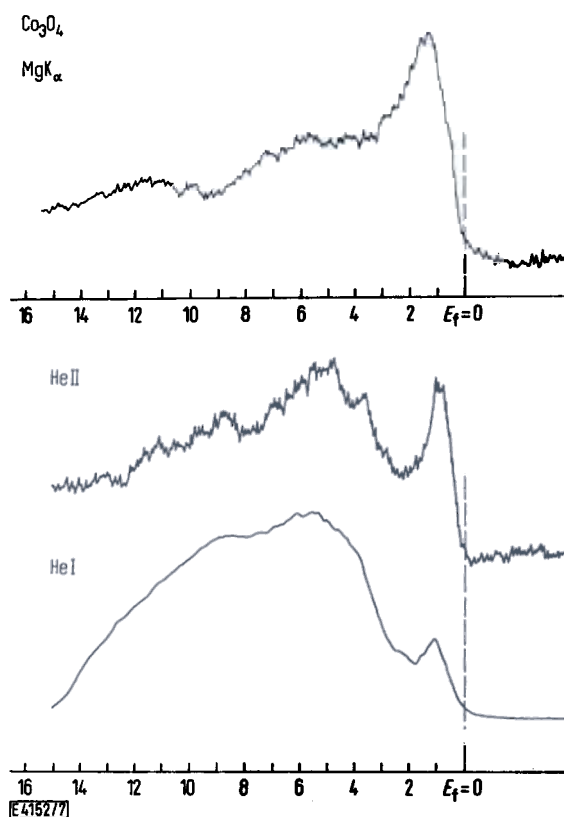


Fig. 7

Photoemission from Co₃O₄ powder sample excited by MgK_α, HeI and HeII

In Fig. 7 the results of our own measurements of the valence band of Co₃O₄ powder samples (Merck, Germany), using XPS, HeI and HeII are compared. The XPS-spectrum shows the same features as that obtained by Brundle et al. [13]. There is also a good correlation between UPS and MgK_α results. We find a single peak at low binding energies followed by a strong peak with highest maximum between -5 eV and -6 eV after a deep minimum in the current distribution. At -11 eV a small peak similar to the one at 10.5 eV for CoO is observed. This peak is assigned to a satellite structure arising from shake up excitation from occupied oxygen levels to vacant metal levels of correct symmetry. Support on this

interpretation is gained by comparison with the separation between shake up peak and main peak in inner shell spectra. Further information is given by the energy dependance. The shake up satellite decreases in intensity, a further peak grows up at -8.4 eV which is the location of a minimum in the XPS spectrum.

In the oxygen region of the Co_3O_4 spectrum a pronounced extra structure is again resolved in the HeI spectrum. Some explanation for this structure can be given if one thinks of the ionization of a closed shell O^{2-} -ion from the 2p-sub-shell. A spin-orbit splitting $2p_{1/2, 3/2}$ (0.6 eV) [17] is expected, which is too small, so that the splitting should be due to the ligandfield, introduced by surroundings. The additional sub-structure found for Co_3O_4 but not for CoO may be explained in terms of Tanabe-Sugano-estimations, taking into account the different ligand fields of the Co_3O_4 (spinell) and CoO (rock salt) structures.

We assign this emission to Co^{II} in tetrahedral surrounding which is not present in CoO. This statement is based on a discussion of all possible oxidation states and ligand fields (T_d, O_h) enlarging the preliminary calculations of Brundle et al. [13]. A detailed discussion of this aspect would lead away from the subject of this paper and will be published separately.

The inner shell spectra of Co_3O_4 especially the Co 2p-region, do not show as pronounced satellite peaks as CoO, although some structure is found, too. This again is in agreement with Brundle's results.

c) Comparison between Adsorbate and Compounds

If we now compare XPS and UPS photoemission of the cobalt oxides with cobalt-oxygen adsorbates striking similarities can be observed:

The emission from a highly oxygen covered (0001)-surface is nearly indiscernable from the emission of a CoO powder sample with rock-salt-structure. This coincidence is complete even as far as the detailed structure of the spectrum and the energy dependance is concerned. Taking into account all available informations we come to the following assignments for adsorbate and compound systems: (All energies in eV)

adsorbate	0.9	adsorption sensitive state
	1.5–3.8	d-band states
	4.5–6.7	oxygen peaks
	10.3	satellite structure
compounds (relative to energy zero)		
CoO [14]	–1.0 – –3.0	metal d-states
	–5.0 – –6.5	oxygen p-states
	–10.5	satellite structure
Co_3O_4	–1.1	metal d-state Co^{III}
	–3.7	metal d-states Co^{II}
	–5.2 – –6.6	oxygen p-states
	–8.4	? satellite structure
	–11.0	satellite structure

In the spectra the emission at lowest binding energy, except of course the adsorption sensitive resonance at 0.9 eV must be attributed to d-band emission. The structure between

-5 eV and -7 eV can be assigned to oxygen 2p emission because this structure is found in all cases in this and in other studies [16]. At higher binding energy a peak attributable to shake up emission is observed, which is supported by intensity reduction in going to lower excitation energies and by the excellent agreement of the energy separation of shake up in inner shell spectra and valence band spectra (ΔE (ss- $\text{O} 2p_{3/2}$)). The fact, that the shake up can be explained in terms of cluster approaches [8, 12] where the Co-atom is surrounded by O^{2-} -ions leads us to consider the adsorption of oxygen on cobalt under these experimental conditions to be dissociative and not molecular, although it is probable that in the initial state of the interaction process the oxygen contacts the surface as a molecule.

The Cobalt-Carbonmonoxide System

In contrary to the situation found for oxygen the interaction of CO with transition metal surfaces at comparable experimental conditions is claimed to be molecular also in the final adsorption state. To test this statement in the light of adsorbate compound comparison we studied the cobalt-carbonmonoxide system.

a) The Adsorbate

The cleaned crystal with (0001)-surface was exposed to varying amounts of high purity grade carbonmonoxide. Fig. 8 shows HeI-spectra obtained at different exposures. As in the cobalt/oxygen system the small peak at the Fermi-edge is

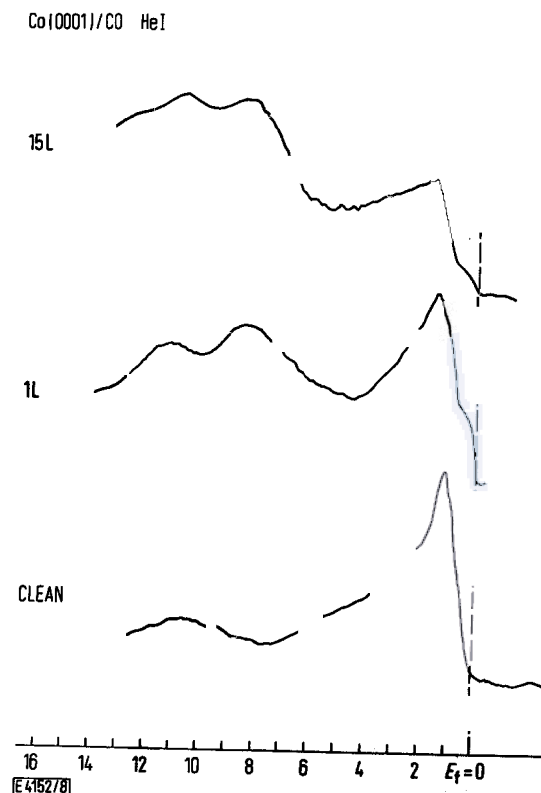


Fig. 8
Photoemission from clean and CO-covered cobalt (0001)-surface at 300 K

strongly reduced when exposure reaches 1 L. A peak at low binding energy is observed, followed by a minimum at 5 eV. Between -7 eV and -12 eV two maxima are resolved with highest intensity at 8 eV. This structure is maintained even at very high coverages where the relative intensities of the peaks alter. The difference spectrum (Fig. 9) underlines the mentioned features and again verifies the adsorption sensitive peak near the Fermi-edge in agreement with the results of oxygen on Co(0001). Difference spectra with comparable shape have been found for CO on Ni and on Fe [16b].

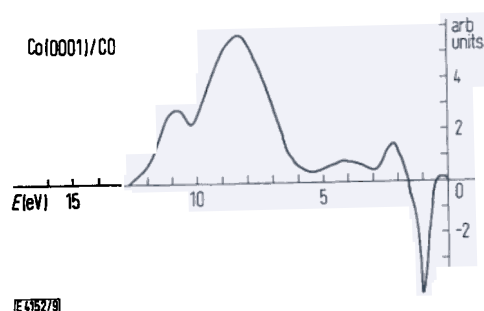


Fig. 9
Difference spectrum calculated from CO-covered and clean cobalt (0001) surface

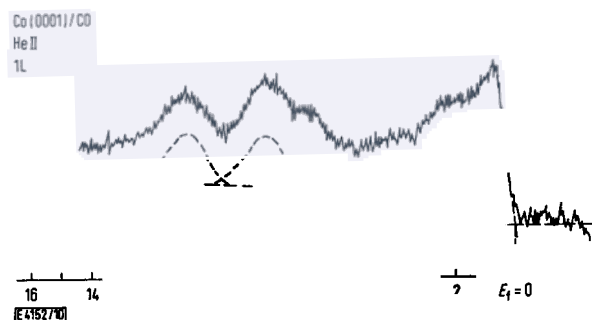


Fig. 10
HeII-spectrum from CO-covered (1L) Cobalt-(0001)-surface at 300 K

Since the measurement of the energy dependance turned out to be helpful in extracting additional information the HeII spectrum is shown in Fig. 10. The peak around -8 eV exhibits some substructure at the low binding energy side of the HeI maximum. The XPS-spectrum is relative structureless as it was in the case of the oxygen covered surface. Nevertheless, comparing the spectrum from clean and CO-covered surface, some intensity is found in the region between -7 eV and -12 eV, which is due to CO-adsorption. In comparing the Co/CO-UPS-spectra with those of Ni/CO [16b] and Fe/CO [16b] one has to correlate both maxima between -7 eV and -12 eV with emission from CO, namely 4σ , 1π , and 5σ and the peak near the energy zero to d-band emission which is also in agreement with result on Co/O₂. The splitting of the band at -8 eV observed in the HeII spectrum of Co/CO must be due to the different energy dependance of the ionization cross-sections of 4σ and 1π orbitals [16b]. Taking the relative intensities of the corresponding CO-gas spectrum into account, the ratio $5\sigma/1\pi$ always gets smaller

in going from HeI to HeII which is in agreement with the assignment [21] that the peak at lower binding energies is due to 5σ and not to 1π . The energy dependance of the emission spectra is similar to the Co/O₂-system in that the adsorbed gas is only seen in the XPS valence band as a small additional intensity broadening. No clearly separated satellite structure is resolved in the valence band spectrum.

The inner shell 2p-spectrum of cobalt shows similar small shake up structure as in Co₃O₄.

b) The Compound System

As mentioned at the beginning carbonyl compounds are well suited references. They are in contrast to the cobalt-oxides molecular compounds in the gas phase and retain their molecular character when condensed to solids.

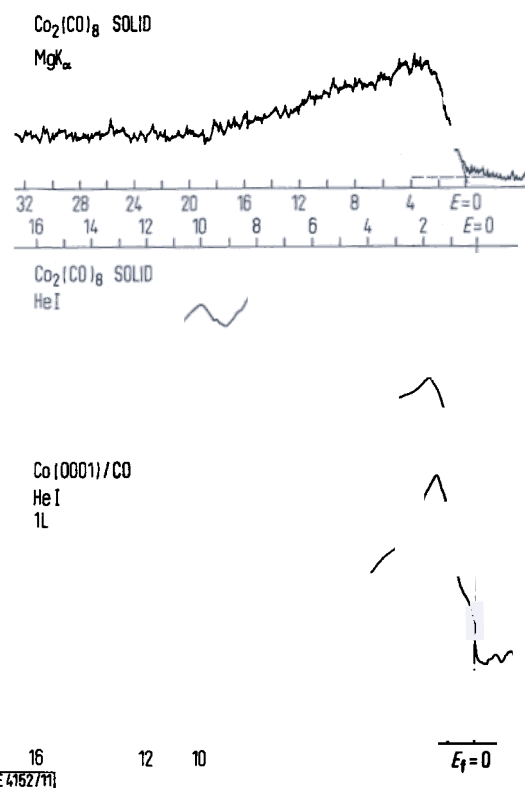


Fig. 11
XPS- and UPS-spectra from solid Co₂(CO)₈. The corresponding photoemission from CO-covered cobalt-(0001)-single-crystal surface is included for comparison

In Fig. 11 the HeI and XPS-spectra are shown for the simplest neutral carbonyl Co₂(CO)₈. The compound (Fluka AG, Germany) was cleaned by sublimation with P₄O₁₀ and measured as a thin film on a stainless steel sample holder at liquid nitrogen temperature. Care had to be taken in connection with the material of the sample holder since on gold and copper the compound decomposed under vacuum conditions. No charging was detectable as well by standard techniques [18,19] as by rotational dependance of line position [20]. The X-ray and UV-fluxes were kept rather small to avoid damaging of the sample. Spectra which are discussed in the following have been obtained by accumulation

of spectra, each taken in 2 minutes from three different samples. After five minutes the sample started to decompose, which was indicated by a peak at higher binding energies in the C1s-spectrum (Fig. 13).

In the HeI spectrum of a well prepared $\text{Co}_2(\text{CO})_8$ -sample peaks are shown near the energy zero and in the region between -7 eV and -12 eV , where a double maximum is resolved. This double maximum disappears when the sample decomposes. In the HeII spectrum the effect on the -7 eV peak is not as pronounced as in the surface system, so that no final assignment can be made as far as the sequence of 1π and 5σ orbitals in this region is concerned if one is at all able to separate σ and π .

Comparison with theory via Koopmans' Theorem should yield additional information. Fig. 12 summarizes results obtained by the authors using an extension of the CNDO-formalism [21]. A reasonable linear correlation can be made plotting experimentally available spectra versus theoretical densities of states. The theoretical results predict a separated region of d-states at lowest binding energies and a region of the spectrum at higher binding energies which can be assigned to the CO molecule and to CO-metal interaction. This is in good agreement with the experimental results.

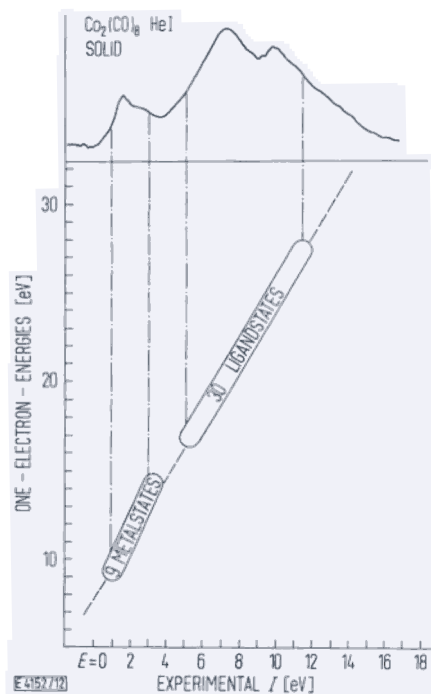


Fig. 12

Correlation of experimental spectra from $\text{Co}_2(\text{CO})_8$ (solid) with one-electron-energies calculated by an extended CNDO-method

Because of the low symmetry of the compound (C_{2v}) the CO orbitals split, so that no statement from a theoretical point of view can be made concerning the assignment of 5σ , 1π and 4σ , although a theoretical distribution with two maxima is found. The experimental fact, that the minimum separating the two maxima is not as pronounced as in the adsorbate system supports this result. The valence band

calculated for a tetranuclear cluster contains essentially the same characteristics. The similarity to the dinuclear cluster is complete, with the exception of a more pronounced minimum separating the peaks in the CO-region and a slightly altered "d-band"-shape. Experimental results seem to agree with these theoretical findings not only for cobalt carbonyls but also for other transition metal carbonyls such as iron-carbonyls [8].

c) Comparison between Adsorbate and Compound

The spectra taken from compound and adsorbate systems show striking similarities and it is evident to make the following assignment as far as the valence band spectra are concerned: (All energies in eV)

adsorbate

- 0.9 adsorption sensitive state
- 1.5 - -4.0 d-band emission
- 6.9 - -8.1 CO 5σ and 1π emission
- 11.1 CO 4σ emission
- 13.2 ? satellite structure

$\text{Co}_2(\text{CO})_8$ (relative to energy zero)

- 1.8 maximum of d-metal orbitals
- 6.5 - -10.0 CO-region

Emission from metal d-states at the energy zero and CO emission at higher binding energy is observed, resolving double maximum structure in both cases.

The inner shell spectra of the adsorbate and the compound remain to be discussed. The question in mind in this respect is whether it is possible to experimentally differentiate between different adsorption sites, because the resulting different "chemical surroundings" should induce chemical shifts in C1s and O1s spectra.

In our C1s and O1s, 2s spectra no clear splitting of peaks but just a broadened structure can be resolved, which shows, that the effect is not too large relative to the line width of the inner shell line at least in our instrument, which is run without monochromator. The C1s spectra are reproduced in Fig. 13. Since the compound sample is found to be not charged we think, that differential charging is not responsible for the observed line broadening. The C1s-line can be decomposed into three components with intensity ratio 1:2:1 which may be assigned to bridging ligands and two different terminal ligand types, although it cannot be excluded, that the third peak and part of the second peak is due to shake-up-transitions. The O1s line is more symmetric than the C1s line so that a substructure is not distinctly recognizable from the spectrum.

Again comparison is made to theoretical calculations. Atomic populations have been shown [22] to correlate with chemical shifts from XPS measurements. The above mentioned calculations [23] predict the bridging carbon atoms to have higher populations than the terminal ones while on the oxygen atoms the differences are considerably smaller. Thus the broadening can be explained by different charges on different ligand types. The asymmetry of the C1s line is in agreement with the predicted distributions.

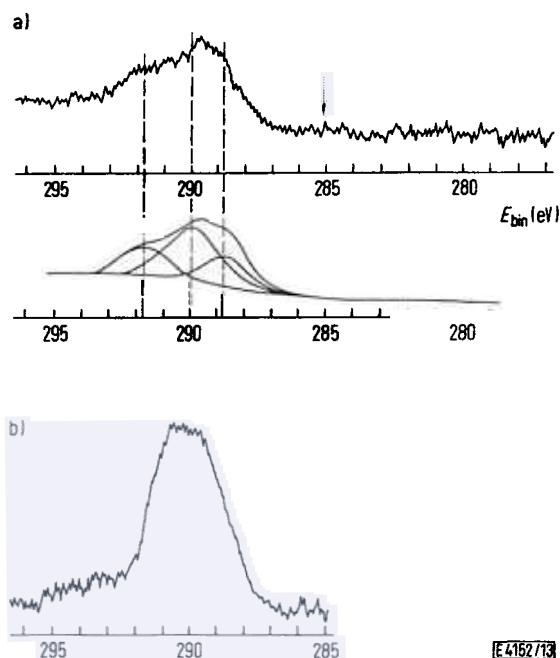


Fig. 13

- a) C1s-XPS-spectrum from solid $\text{Co}_2(\text{CO})_8$. The position of the surface contaminating carbon is indicated by an arrow. The additional peak, evolving when the sample decomposes is situated at 293.2 eV.
- b) C1s-XPS-spectrum of the CO-covered (0001)-surface (1L) at 300 K

In going from the dinuclear to the tetranuclear cluster theory demonstrates that carbons and oxygens become similar in populations. Extrapolation of these findings leads to the assumption that the differences in a surface system, also if terminal and bridged adsorption occurs, are rather small which is indicated in the spectra by a narrower C1s-line.

Conclusions

From the results of this study some general information may be drawn:

It is instructive to compare adsorbate systems and compound systems containing the same elements. There are distinct similarities and dissimilarities which strongly depend on the actual composition of the sample.

1. Adsorption of oxygen on Co(0001)-single crystal surface at 300 K leads to photoemission similar to that of CoO and not Co_3O_4 as far as valence band- and inner shell emission is concerned. Rather intense shake up satellites are found attributable to ligand-metal excitation.

A possible explanation for this similarity can be given in terms of dissociative adsorption on the surface with infusion of oxygen into the first monolayers establishing a quasi-octahedral ligand field. The structure of the cobalt-oxygen interface seems to be not as well defined as the corresponding oxide since the signal from the surface has considerably larger line width than that of the defined oxide.

2. Adsorption of CO on Co(0001)-single crystal surface at 300 K is comparable to adsorption of CO on other transition elements and leads to a typical CO emission with double maximum in the range of -7 eV to -12 eV. The high density of states at the Fermi-edge of the clean metal is drastically reduced on adsorption indicated by a well resolved "negative" peak in the difference spectrum. The relative ordering of levels in the CO-region is evolved by energy dependant UPS and is shown to be the same as in free CO-molecules.

Comparison with photoemission characteristics of $\text{Co}_2(\text{CO})_8$ which is a molecular crystal, exhibits striking similarities, with the exception of the adsorption sensitive state at the Fermi-edge. The d-orbital emission is nearly at the same position as the d-band emission of the adsorbate relative to the CO 5σ , 1π and 4σ ionizations and has even similar shape. This similarity can be interpreted in terms of molecular, nondissociative adsorption with the carbon of carbonmonoxide attached to the surface.

The inner shell C1s spectrum of $\text{Co}_2(\text{CO})_8$ can be interpreted in terms of three components attributable to three different ligand types in $\text{Co}_2(\text{CO})_8$ where the relative shifts are in the region of about 1 eV–1.5 eV. The sequence of component peaks parallel theoretical studies on $\text{Co}_2(\text{CO})_8$ leading to the conclusion that bridging CO-groups carry more negative charge than terminal ones.

3. By comparison of theoretical studies on transition metal cluster compounds with varying number of transition metal atoms especially atomic populations with shifts and shape of inner shell spectra of CO covered surface- and cluster spectra one finds the theoretical prediction verified that large shift differences for surface sites with different geometries are not to be expected.

From a general point of view the above shown comparisons give some evidence for a localized description of adsorption for these gases under these given experimental conditions. This is as well true for oxygen adsorption which can be interpreted in terms of ligand field estimations as for CO-adsorption where all essential features of the spectrum are shown by surface systems and by the studied compounds, containing two transition metal atoms and a lot of CO ligands. On the first view this is puzzling since the ratio: number of ligands/number of metal atoms in the compound is greater than one while for the surface system this ratio is frequently smaller than one at low coverages, but if one thinks of the high symmetry of those compounds, the number of different ligands is reduced, so that comparison even makes sense in this respect.

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During the publication of this paper we received a manuscript by E. W. Plummer and co-workers on photo-electron spectroscopic measurements of a large variety of carbonyl compounds. In this paper the similarities between carbonyl compounds and CO-adsorbate systems have also been recognised.

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