Covalency in oxygen chemisorption as probed by x-ray absorption

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X-ray absorption spectra at the O $1s$ edge are presented for $O(2\times2)/Ni(111)$, $O(2\times1)/Cu(110)$, and $O/Si(111)$-(7×7). The spectra yield information on the distribution of O $2p$ and np state character in the unoccupied states. The data are compared with that for oxides. We conclude that there is considerable covalency in the chemisorptive bond and that, even for transition metals, this arises mainly from interaction between the O $2p$ levels and the substrate sp bands.

I. INTRODUCTION

The purpose of this paper is to draw attention to the way x-ray absorption spectroscopy (XAS) of light chemisorbed atoms can be related to the concept of covalency of the chemisorptive bond.

Dipole selection rules and the local character of XAS dictate that the O $1s$ XAS spectrum is dominated by transitions in which an O $1s$ electron is excited to states with some O np character (see, e.g., Ref. 1). In this paper we will argue that the region up to ~ 15 eV above threshold is dominated by O $2p$ weight rather than O $3p$, $4p$, etc. We thus treat the spectral weight near threshold as if it is directly proportional to the O $2p$ weight.[2,3] This is a reasonable starting point because the variation of the transition matrix element due to solid-state bonding effects, which change the relative weights of the $2p$ wave function in the core and outer regions of the atom, is a secondary effect. (Such effects contribute $\sim 40\%$ to the matrix elements[4] and should not be neglected in the long run, but for a first ansatz we will not consider them.) We

will then show that O $2p$ mixing with substrate sp states over a large energy range is central to the covalency of the chemisorptive bond of oxygen on Cu, Ni, and Si.

We note that an O^{2-} ion has no unoccupied $2p$ states and the $1s \rightarrow 2p$ contribution to the spectrum would be missing for purely ionic oxides. The strength of the $1s \rightarrow 2p$ channel thus increases with increasing covalency of oxygen compounds and should be a sensitive probe of such covalency. Determination of a number expressing the % covalency is not possible, partly because we do not measure absolute intensities. Nevertheless, we contend here that observed spectra do give unusual insight into the nature of the surface chemical bond because we can visualize how covalency arises.

II. EXPERIMENT

The spectra of adsorbates were recorded in a partial (O on Ni) or an Auger (O on Cu, Si) electron yield mode using x rays from the BESSY (Berliner Elektronenspeicherring–Gesellschaft für Synchrotronstrahlung) electron storage ring. For the oxides, a total electron

yield mode was used. The SX-700 grating monochroma-
tor[5] and the high-energy toroidal-grating monochroma-
tor of the Fritz-Haber-Institut[6] were used to achieve en-
ergy tuning of the x rays with a resolution of 0.6 and 1–2
eV, respectively. Spectra were taken with incident light
perpendicular to the sample (electric vector of the light
parallel to the surface) to increase the contribution of
empty states in the surface plane and at 10° or 20° to the
surface to maximize orbitals directed perpendicular to
the surface. Single-crystal samples were cleaned in ul-
trahigh vacuum (below 10^{-10} Torr) and covered with
well-defined quantities of oxygen, using conditions and
dosages as published elsewhere.[7–10]

III. RESULTS AND INTERPRETATION

In Fig. 1 we compare the O 1s XAS spectra from NiO
and from O(2×2)/Ni(111) taken under two angles of in-
cidence. Figure 2 gives similar data from
O(2×1)/Cu(110) and Cu oxides and Fig. 3 for O on
Si(111)-(7×7) and SiO$_2$. The arrows mark the O 1s bind-
ing energies as determined by x-ray photoemission spec-
troscopy[10,11] (XPS) and are close to the XAS thresholds
for the chemisorbed layers.

The spectra of O on Cu and Ni show less structure
than those for NiO and CuO. In general, metals have
weaker XAS structure than chemical compounds, and
the observation of weak structure for the chemisorbed
species implies metallic bonding characteristics. After
the sharp peaks at threshold, the spectra of O on Cu and
Ni also show increased intensity over a large energy

FIG. 2. Same as Fig. 1, but comparison for O(2×1)/Cu(110)
and Cu oxides.

range which can only be attributed to O np character in
the broad Ni or Cu sp bands.

For CuO a detailed band-structure calculation with an
extended basis set has been made and analysis of the wave
functions has shown that the O p character up to at least
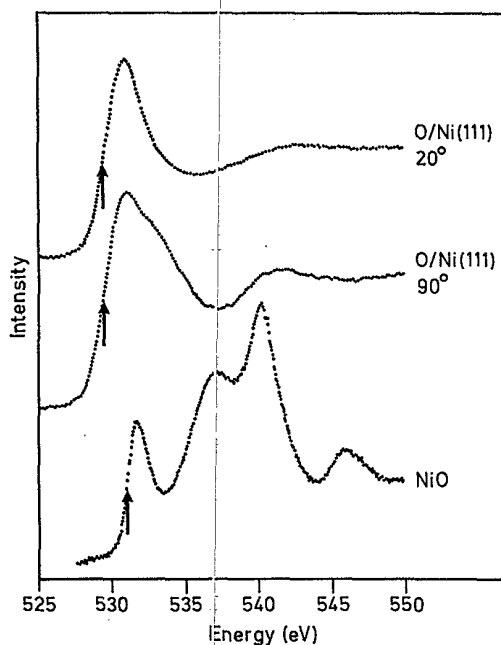~15 eV above threshold is dominated by 2p character.[2]

FIG. 1. Comparison of the O 1s XAS spectra from NiO and
from O(2×2)/Ni(111) taken under two angles of incidence.
The arrows mark the O 1s binding energies as determined by
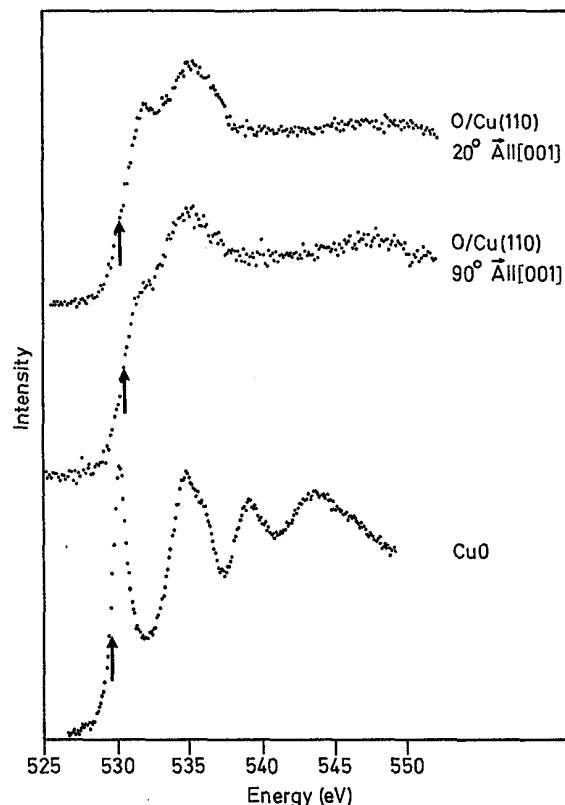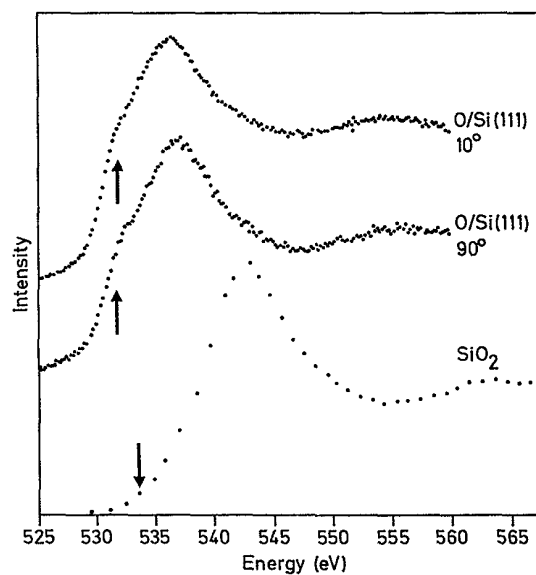the x-ray photoemission spectroscopy (Refs. 10 and 11).

FIG. 3. Same as Fig. 1, but comparison for O on Si(111)-
(7×7) and SiO$_2$.

We use the same value as a guide for chemisorbed O. We thus attribute most of the intensity and structure up to at least 10 eV (and probably ~15 eV) above the thresholds in Figs. 1 and 2 to O $2p$ character.

The spectra of the oxides and the O on Ni also exhibit sharp peaks at or near threshold. As for the transition-metal oxides,[12] we assign at least part of the threshold peak intensity to transitions to states of predominantly metal $3d$ character with some O $2p$ contribution. However, we note that the unoccupied Ni metal $3d$ band is only ~0.4 eV wide,[13] so that states with mostly Ni $3d$ weight should be close to E_F.

We cannot unambiguously separate spectral weight due to O $2p$ mixed in with Ni $3d$ and Ni $4sp$ bands. Our different curve resolutions only give the "$3d$" peak between 15% and 40% of all the intensity up to ~15 eV, whereby we give more credence to the lower values. Similarly for NiO and CuO, respectively, the threshold peaks due to O $2p$ character in "$3d$" bands have only ~(14±5)% and (12±5)% of the intensity integrated up to 15 eV above threshold. In the context of the assumption of constant O $1s \rightarrow 2p$ matrix elements, it is significant that the threshold peak intensities (areas) are so much lower than that due to O $2p$ weight in the metal $4sp$ states in the whole region up to ~15 eV above threshold. The implication is that for O on Ni the O $2p$ mixing with the $4sp$ states is more important for the covalency of the bonds than that with the metal $3d$ states. Likewise, for O on Cu(110) the implication of the wide spread of XAS intensity is that the empty O $2p$ character is mixed with the Cu sp bands over a wide energy range.

The anisotropy in the spectra of the chemisorbed materials reflects the directional character of the bonding. It is seen what while there is anisotropy in the energy distribution of the unoccupied states, the relative influence of s and d states in the chemisorptive bond between Ni(111) and oxygen is not strongly anisotropic. For Cu, the broad spread of the O $2p$ character is independent of polarization.

SiO_2 is generally considered to be about 60% ionic.[14,15] Still there is empty O $2p$ character spread over a wide energy range in the conduction bands above the band gap, which calculations show to have mainly Si sp character.[15] Also, for O on Si(111) Ciraci et al.[14] calculate ~1.4 electrons transferred to each O atom. Still, the covalent contribution is sufficient to give the O $1s$ XAS spectra shown in Fig. 3. For O/Si the weakness of the polarization dependence is not surprising since the axes of local C_{2v} point-group symmetry of the Si—O—Si bonds are tilted ~30° from the surface normal and are nearly randomly distributed in the azimuthal direction.[16,17]

The precise relation of XPS binding energies and XAS thresholds for insulators is not clear, but the large band gap of SiO_2 is reflected in observation that the broad peak of the SiO_2 O $1s$ XAS spectrum (Fig. 3 and Ref. 16) is well above the O $1s$ XPS binding energy. For O chemisorbed on Si(111), the absorption extends all the way down to the XPS threshold, reflecting the fact that the band gap of Si is much smaller than that of SiO_2, and that the O $2p$ character is mixed in with Si states over a wide energy range.

IV. DISCUSSION

In this paper we discuss the O $1s$ XAS spectra within the framework of covalency in the surface chemical bond of adsorbed oxygen and the role of substrate sp states spread over a large energy range. This framework is not standard, but is attractive for discussion of chemisorption. There is a large body of evidence to show that the chemical bonds in transition-metal oxides have a large covalent component[18] and the Madelung term in chemisorbed oxygen is even less conducive to ionic bonding. Van Hove deduced from analysis of low-energy electron diffraction (LEED) structure and work-function data that the surface chemical bond to oxygen could not be highly polar.[19] Also, the O $1s$ core-level shifts in photoemission are not consistent with purely O^{2-} ions on surfaces and cluster calculations of both oxides and adsorbate systems indicate charge transfers typically less than one electron per O atom.[20] Finally, Godby et al. have calculated only small charge transfer for O on Ni(001).[21]

There is less evidence on the spread of O $2p$ weight over a large energy range, because until very recently few theoreticians have had good reason to consider such high-energy unoccupied states. However, in addition to the arguments presented for CuO above, cluster calculations do indicate that the O $2p$ weight is spread into very-high-energy states. Also, the landmark paper of Liebsch on the electronic structure of O on Ni(001) (Ref. 22) showed that the O $2p$ character was mixed into many different unoccupied states. Thus, the large spread of O $2p$ weight in XAS is not totally unexpected. Further, we believe that it is not in contradiction to inverse photoemission results.[23]

Our observation of O $2p$ character in the unoccupied $4sp$ states implies that the hybridization potential mixing the O $2p$ and metal $4sp$ states is large. Thus, there must be considerable $4sp$ character associated with occupied (bonding) states of predominantly O $2p$ character. This is in accord with deductions of Liebsch[22] and Godby et al.[21] on the electronic structure of O on Ni(001) and is probably true for O on many transition-metal surfaces.

V. CONCLUDING REMARKS

The concepts of ionic and covalent character in bonds are themselves crude and do not give a full picture of the charge distribution in a bond. Nevertheless, it must be admitted that the concepts have a long tradition and have been tremendously successful in rationalizing a large amount of solid-state chemistry and physics[18,24] and give a natural framework for discussion of O $1s$ XAS spectra from adsorbates and the chemisorptive bond. The new aspect of this paper is the emphasis we place on trying to trace covalence in XAS spectra. In this respect, the site and symmetry selectivity of XAS confer on it advantages not possessed by other techniques. We have seen that there is clearly a strong covalent contribution to the chemical bonding of chemisorbed oxygen on Ni, Cu, and Si surfaces, in accordance with published ideas. We have also been able to deduce that although the three surfaces are very different, in each case the hybridization of the O $2p$ states with unoccupied sp bands dominates the distri-

bution of unoccupied O $2p$ character. The contribution of the metal $3d$ orbitals to this covalency is rather small, even for Ni surfaces.

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[3]For atoms it is sensible to define atomic states up to the Rydberg limit. In solids the higher-energy wave functions extend increasingly to adjacent sites, so that definition in terms of atomic states becomes of questionable utility. However, our experience with analysis of wave functions in CuO suggested that the atomic description was sensible for O $2p$ states.

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[23]There is some inverse photoemission (IP) data in which peaks have been associated with empty "O_{xy}" and "O_z" bands. Some comparison of XAS and IP data is clearly necessary, although we cannot give an exhaustive discussion here and restrict ourselves to discussion of the Ni—O bonding. NiO XAS shows major peaks 5.3 and 8.5 eV above the threshold peak. This is in good agreement with the observation of peaks at $\sim$5.5 and 9.5 eV above the threshold peak ($\sim$9.5 and 13.5 eV above E_F) in IP [G. A. Sawatzky and J. W. Allen, Phys. Rev. Lett. **53**, 2339 (1984); S. Hüfner, J. Osterwalder, T. Riesterer, and F. Hulliger, Solid State Commun. **52**, 793 (1984)]. The small discrepancies can be associated with experimental errors or the core-hole potential in XAS. The metal $4sp$ peaks in IP of NiO have low relative intensity because of their low IP cross section relative to that of the $3d$ states. The same peaks give strong intensity in O $1s$ XAS only because they have a higher O $2p$ weight. We must expect similar difficulties in detecting all the high-energy states with empty O $2p$ character in IP of chemisorbed oxygen, because of their low cross sections. For O(2×2)/Ni(111) Altmann *et al.* (Ref. 9) have identified a band with O p_z character between 1.1 and 2.8 eV above E_F in IP. Our results are not inconsistent with such assignments, but because of our poorer resolution we cannot identify their state.

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