SEMIEMPIRICAL THEORY FOR SURFACE CORE-LEVEL SHIFTS

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Abstract:

Numerical results are given for the surface core-level shifts at clean single crystal surfaces, stepped and reconstructed surfaces and surfaces with chemisorbed atoms. These results demonstrate that surface core-level shifts can be used as a diagnostic tool to study various surface effects.

Recently, several experiments have been performed to study surface core-level shifts[1,2,3]. The surface core-level shift arises from the change in electrostatic potential as one goes from the bulk to the surface of a solid[4] and has been measured for low-index single crystal transition metal surfaces[1,2,5], for reconstructed surfaces Ir(100)[3] and W(100)[6], for the stepped surface Ir(332)[7] and for the hydrogen covered Ta(111) and W(111) surfaces[5]. Although calculations using the tight binding technique have been able to closely reproduce experimental data obtained for low index surfaces[4,7,8], its extension to more complex systems, (reconstructed and stepped surfaces, etc.) is not straightforward. In this paper we propose a simple bond-breaking model for the core-level shift which may be applied to various surface structures like clean single crystal, stepped and reconstructed surfaces and surfaces with chemisorbed atoms. Thus we are able to demonstrate that studies of the surface core-level

shifts can be used as a diagnostic tool to investigate various interesting surface effects including chemisorption and surface segregation.

Following Johansson and Mårtensson[9], the surface core-level shift in a solid with atomic number Z can be written as

$$\Delta_c(Z) = (E_{coh}^{b}(Z^{*}) - E_{coh}^{s}(Z^{*}))$$
$$- (E_{coh}^{b}(Z) - E_{coh}^{s}(Z)) \qquad (1)$$
$$- (E_{imp}^{b}(Z^{*},Z) - E_{imp}^{s}(Z^{*},Z)) \, ,$$

where Z^{*} denotes a core-excited atom, $E_{coh}^{b(s)}(Z)$ is the cohesive energy of a Z-atom in bulk (surface) and $E_{imp}^{b(s)}(Z^{*},Z)$ is the heat of solution of species Z^{*} in bulk (surface) Z. Assuming a fully screened core hole and increasing the valence charge by one electron, the excited atom can be treated as a (Z+1) impurity in the host. In addition the contribution of the final term in Eq. (1) is expected to be small[4] (we estimate it to be of the order of 0.05 eV for the studied transition me-

tals[10]) and is therefore neglected in the present study. Consequently, Eq. (1) can be simplified to[4,9]

$$\Delta_c = (E_{coh}^b(Z+1) - E_{coh}^s(Z+1))$$
$$- (E_{coh}^b(Z) - E_{coh}^s(Z)) \qquad (2)$$
$$= E_s(Z+1) - E_s(Z),$$

which is simply the difference of two surface energies for neighbouring elements.

Since reliable values of $E_s(Z)$ for various solid surfaces are scarce, they have been calculated from bulk thermodynamic data using a bond-breaking model. In this approach, which has also been successfully applied to the study of surface segregation in alloys[11], the cohesion energy $E_{coh}^{b(s)}$ can be written as

$$E_{coh} = \frac{1}{2}(N_1 E_1 + N_2 E_2).$$

Here, N_1 and N_2 denote the number of nearest- and overnext-nearest-neighbours, respectively. Writing the overnext-nearest-neighbor bond energy E_2 as

$$E_2 = E_1 e^{-q(d_2 - d_1)},$$

where E_1 is the nearest-neighbor bond energy and d_1 and d_2 are the corresponding bond lenghts, then

$$E_{coh} = \frac{1}{2} N_{eff} E_1,$$

where

$$N_{eff} = N_1 + e^{-q(d_2 - d_1)} N_2.$$

N_{eff} is determined by using for $e^{-q(d_2-d_1)}$ the approximate value 0.3 in the case of fcc-crystals and 0.6 in the case of bcc-crystals. Note, the factor $e^{-q(d_2-d_1)}$ in the expression for N_{eff} results from Pauling's argument[12] concerning bond-strength or equivalently from the usual distance-dependence of the hopping integral[13]. Thus, the surface energy is given

by

$$E_s(Z) = \frac{N_{eff}^b(Z) - N_{eff}^s(Z)}{N_{eff}^b(Z)} \Delta H^{vap}(Z), \quad (3)$$

where s and b refer to surface and bulk respectively and where $E_1 = 2\Delta H^{vap}/N_{eff}^b$ has been used implying a structure independent bond-energy and that this energy is the same in the bulk and at the surface[14]. $\Delta H^{vap}(Z)$ is the heat of vaporization[15] of the elemental substance Z. Combining Eqs. (3) and (2) and assuming identical crystal structures[16] for species Z and (Z + 1), one obtains

$$\Delta_c(Z) = \frac{\Delta N_{eff}(Z)}{N_{eff}^b(Z)} (\Delta H^{vap}(Z+1) - \Delta H^{vap}(Z)), \quad (4)$$

with $\Delta N_{eff}(Z) = N_{eff}^b(Z) - N_{eff}^s(Z).$

The factor $\Delta N_{eff}/N_{eff}^b$ in Eq. (4) permits us now to perform calculations for various atomic structures like single crystal, reconstructed and stepped surfaces, etc., and also for core-level shifts from second surface layer atoms.

In order to test the usefulness of this approach, we present in Fig. 1 the core-level shifts for low-index faces of the 3d, 4d and 5d transition metals calculated with the help of Eq. 4. In the light of the simplicity of the model the agreement with the available experimental data and previous calculations by Johansson et al.[4,9] is most satisfactory. As already noted previously[4,9], the sign of the shift is positive at the beginning and negative towards the end of a series which is due to the dominatly parabolic shape of ΔH^{vap} as a function of Z. As would be expected, the closest packed surfaces give rise to the smallest observed shifts. The negative values for Δ_c obtained for V and Cr occur as a result of a dip in ΔH^{vap} in the middle of the 3d series.

the core-level shift from the top layer
will be larger by approximately a factor
of 2. Comparison with experimental data
from W(111) and Ta(111) are presented in
table 1 and show a good overall agree-
ment.

Calculation:
○ fcc(111) hcp(0001) △ bcc(110)
◇ fcc(100)   ⅄ bcc(100)
△ ☐ fcc(110)   ▽ bcc(111)
●▼▲ Experimental values

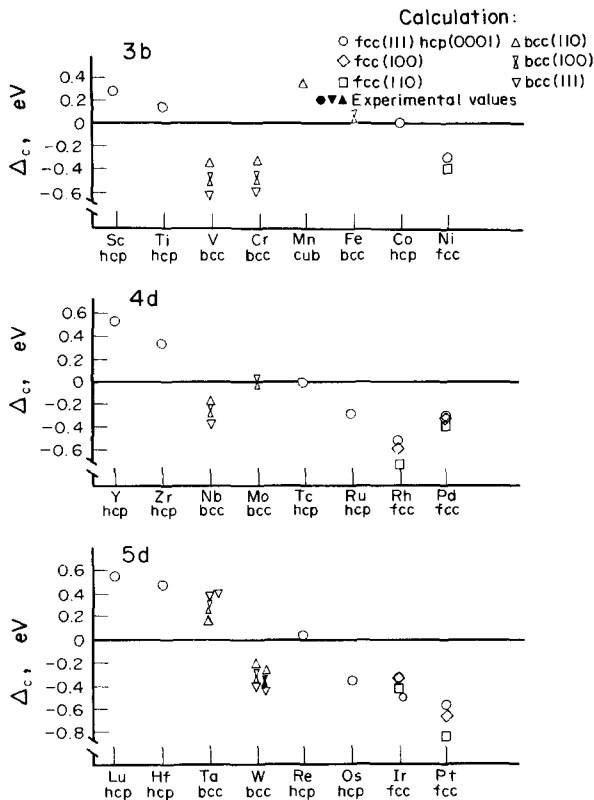Fig. 1   Calculated and experimental
         surface core-level binding-
         energy shifts Δ_c for the 3d,
         4d and 5d transition metal se-
         ries. The zero of energy corres-
         ponds to the bulk value. The
         experimental data for Ta, W
         and Ir are taken from Ref. 5,
         2 and 3 respectively.

Table I   Surface core-level shifts
          for clean and hydrogen cove-
          red bcc (111) surfaces. Δ_c^1
          and Δ_c^2 refer to shifts for
          first and second layer metal
          atoms. Experimental values
          are taken from Ref. 5.

	CORE-LEVEL SHIFT (eV)			
	clean		H - covered	
	theory	expt.	theory	expt.
Ta (111)				
Δ_c^1	0.35	0.40	0.53	0.63
Δ_c^2	0.17	0.19	0.34	0.34
Δ_c^1/Δ_c^2	2.1	2.1		
W (111)				
Δ_c^1	-0.39	-0.43	-0.26	-0.28
Δ_c^2	-0.18	-0.10	-0.06	≈ 0
Δ_c^1/Δ_c^2	2.1	4.3		

In the following we use Eq. (4) to cal-
culate new results on surface core level
shifts. First, we calculate Δ_c for atoms
in the second surface layer. Since the
coordination in that layer deviates from
the bulk value, a core-level shift for
those atoms is also expected. This effect
is most pronounced for the more open sur-
faces such as fcc(110) and bcc(111). For
the latter case the effective number of
broken bonds ΔN_{eff} in the top layer is
5.8 whilst in the second layer it is 2.8.
Thus, from Eq. (4) it may be seen that

In the case of surface contraction which
is expected to be the largest for the
open surfaces mentioned above, the dis-
tance of the top layer atoms to their
nearest neighbors in the underlayer de-
creases. The bond energies are therefore
expected to increase, which results in a
decrease of Δ_c in magnitude. As a conse-
quence of this, the ratio of the top and
the underlayer core-level shifts may
change. As an illustrative example, the
discrepancy between the theoretical and
experimental values for Δ_c^1/Δ_c^2 on W(111)

(table I) can be attributed to this effect.

Secondly, we analyse Δ_c at stepped surfaces. Recent XPS measurements from a stepped Ir(332) surface[7] have shown for the core-level $4f_{7/2}$ a structure which has been interpreted as the superposition of 3 peaks. Here, the two surface peaks have been attributed to emission from terrace and step sites. In the bond-breaking picture the lower coordination of the step sites is manifested by the larger core-level shift which is experimentally observed. The (332) surface is composed of terraces with (111) orientation separated by $(11\bar{1})$ steps (Fig. 2) and as expected the core-level shifts of the terrace atoms mirror those

Table II   Surface core-level shifts for (111) and (332) surfaces of Ir. Δ_c^t and Δ_c^s refer to shifts for terrace and step atoms. Experimental values are taken from Ref. 7.

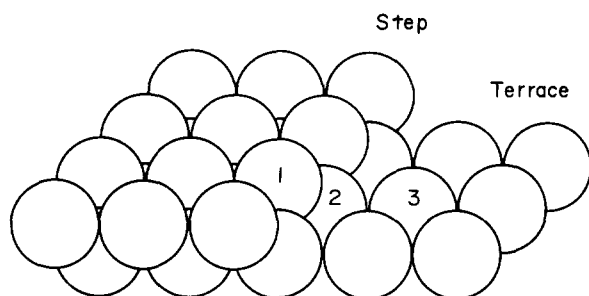|	CORE-LEVEL SHIFT (eV)	
	theory	expt.
Ir (111) Δ_c	-0.30	-0.50
Ir (332) Δ_c^t	-0.30	-0.48
Δ_c^s	-0.46	-0.75
Δ_c^s / Δ_c^t	1.51	1.56

Step

Terrace

Fig. 2   Hard-ball model of a Ir(332) stepped surface. The three inequivalent sites on this surface are denoted by 1, 2, 3.

of the low index (111) face. Results obtained by using Eq. (4) with ΔN_{eff} values 5.9 and 3.9 for the step and terrace site, respectively, are given in table II.

While our absolute values are somewhat smaller than experimentally observed, the ratio of step to terrace core-level shift agrees well with experiment. This suggests that the heat of vaporization does not represent the surface bonds properly for this system. Further it is to be noted

that in general the terrace atoms (marked 2 in the figure) adjacent to the step have a higher coordination (but less than bulk) as compared to other terrace atoms. This should be considered while deconvoluting the experimental core-level line shapes.

Another important application of core-level shift measurements is to systems with chemisorbed atoms. For the substrate atom an additional term needs to be included in Eq. (4) to account for adsorbate-substrate interactions. Then, the average core-level shift for a substrate atom can be given as

$$\Delta_c(Z) = \frac{\Delta N_{eff}(Z)}{N_{eff}^b(Z)}\left(\Delta H^{vap}(Z+1)-\Delta H^{vap}(Z)\right)-\Delta_c^a,$$
(5)

where

$$\Delta_c^a = \left(E_X^{ad}(Z+1) - E_X^{ad}(Z)\right)\cdot\theta$$
(6)

is the difference of adsorption energies for X on Z and (Z + 1) surfaces. The adsorbate coverage (ratio of adsorbate to

substrate atoms) is denoted by θ. Pub-
lished values[17] for $E_X^{ad}(Z)$ have been
used here to calculate the core-level
shift for hydrogen-covered ($\theta=1$) Ta(111)
and W(111) surfaces. The results, presen-
ted in table I, exhibit very good agree-
ment with experiment. On these open sur-
faces, due to its small size, hydrogen
can penetrate into the surface layer[18].
Consequently its interaction with first
and second layer atoms has been taken
in the first approximation equal when
evaluating Δ_c^2 in table I.

Regarding the variation of the core-
level shift with θ one expects it from
Eq. (6) to be linear. However, the ad-
sorption energy is coverage-dependent.
At higher coverages adatom-adatom inter-
actions come into play and lead to qua-
dratic and higher order terms in Δ_c^a
thereby making $\Delta_c(Z)$ to depend non-li-
nearly on coverage. This non-linear be-
haviour has been recently observed[19]
for H/W(111).

Further in the case of island formations
(low coverage) one expects at least two
surface core-level shifts. One arising
from atoms covered with adsorbate and the
other from the clean portion of the sur-
face. Since the surface core-level shifts
are significantly effected by adsorbates,
such measurements may suppliment the low
energy electron diffraction (LEED) ana-
lysis of the adlayer structure.

We have also studied Δ_c at the recon-
structed surfaces Ir(100)-(1 X 5) and
W(100)-($\sqrt{2}$ X $\sqrt{2}$)R45°. Fig. 3 shows the
geometries of these two systems which
have been proposed on the basis of LEED
results[20,21]. The reconstructed Ir(100)-
(1 X 5) surface looks similar to the un-
reconstructed Ir(111) surface and thus in
this model the core-level shift is ex-
pected to be the same for these two sur-
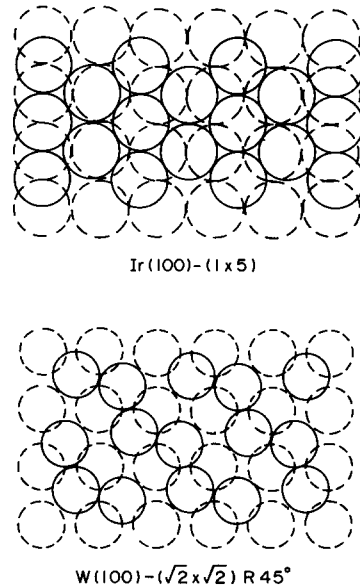faces as is confirmed by the experiment[3].

Ir(100)-(1x5)

W(100)-($\sqrt{2}$x$\sqrt{2}$)R45°

Fig. 3   Proposed geometries for the
reconstructed Ir(100)-(1 X 5)
and W(100)-($\sqrt{2}$ X $\sqrt{2}$)R45° sur-
faces[16].

For W(100) clean and hydrogen-covered
surfaces surface core-level shift measu-
rements have been performed recently[6].
For the clean surface two surface core-
level shifts have been observed which
have been attributed to the coexistence
of reconstructed and unreconstructed
domains. In the following we discuss
how the observed spectra may also be
interpreted in terms of shifts associ-
ated with first and second layer atoms
in these two domains.

For the clean, unreconstructed surface
ΔN_{eff} for the first and second layer
atoms is 4.6 and 0.6 respectively. For
the case of homogeneous reconstruction,
these values change to $\approx$4.2 and $\approx$4.0. The
resulting core-level shifts for the two
cases are shown in table III. Our value
for $\Delta_c^{1,0}$ is in good agreement with the
measured value[6] of -0.35eV. However our
value of $\Delta_c^{1,r}$ is larger than the ob-
served shift[6] of -0.13eV. Generally,

Table III Calculated surface core-
         level shifts for W(100).
         $\Delta_c^{1,0}(r)$ and $\Delta_c^{2,0}(r)$ are the
         core-level shifts for the
         first and second layer atoms
         of the unreconstructed (re-
         constructed) surface.

W (100)	CORE-LEVEL SHIFT (eV) theory
$\Delta_c^{1,0}$	-0.30eV
$\Delta_c^{2,0}$	-0.04eV
$\Delta_c^{1,r}$	-0.28eV
$\Delta_c^{2,r}$	-0.07eV

the effects of hydrogen chemisorption on W(100) will be the same as previously discussed on W(111). It should be noted that for low hydrogen coverages the analysis of van der Veen et al.[6]

predicts that the core-levels from the reconstructed and unreconstructed domains move in opposite directions.

Several effects may cause these discrepancies. In the analysis of the experimental data, effects arising from the second layer have been completely neglected. In addition, it is known[21] that hydrogen chemisorption can significantly change the electronic structure

of the substrate, thereby modifying the bond energies.

It has been shown above that surface reconstruction, stepped surfaces and chemisorption give rise to appreciable surface core-level shifts. It would be most interesting to further investigate the variation of these shifts as a function of temperature and coverage in those systems which undergo a structural phase transition. In addition, changes in position and intensity as a function of coverage in an adsorption experiment could perhaps provide valuable information on the adsorption site[3] and superstructures. So far experimental attention has been focused solely on the surfaces of metals. Note, measuring surface core-level shifts in alloys yields also information on surface segregation. This has been discussed theoretically in detail elsewhere[22,23]. For mixed-valent systems[24] the surface core-level shift gives valuable information about the surface valence.

In conclusion, the simple model presented here has proven successful in reproducing experimental data for a variety of surface-related problems. It further gives promise to be able to interpret data from more complex systems, where use of more sophisticated models would be difficult. It is hoped that this paper will stimulate further experimental work in this field.

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