Final state screening in core level photoemission of dilute-electron metals – an ongoing problem after 40+ years of debate

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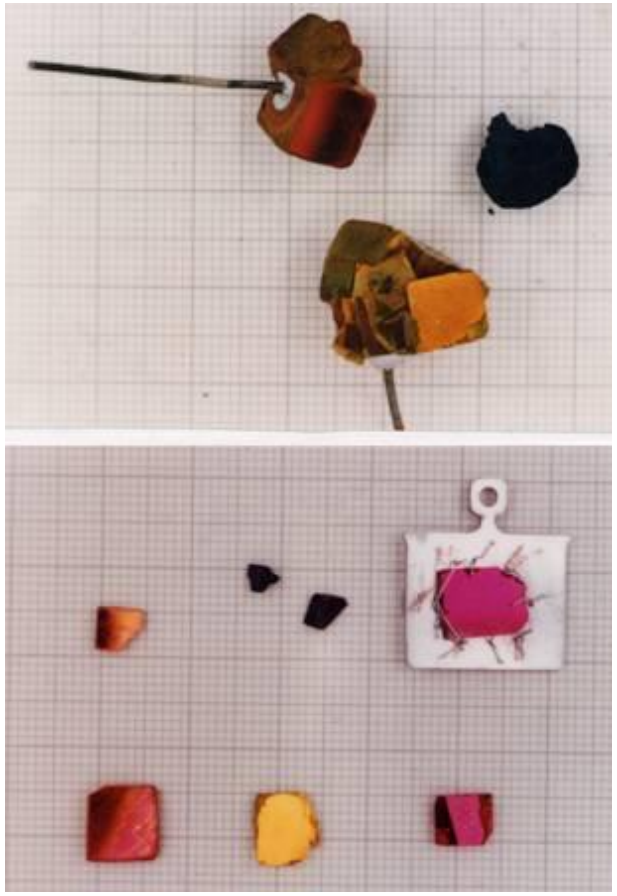


The experiments -

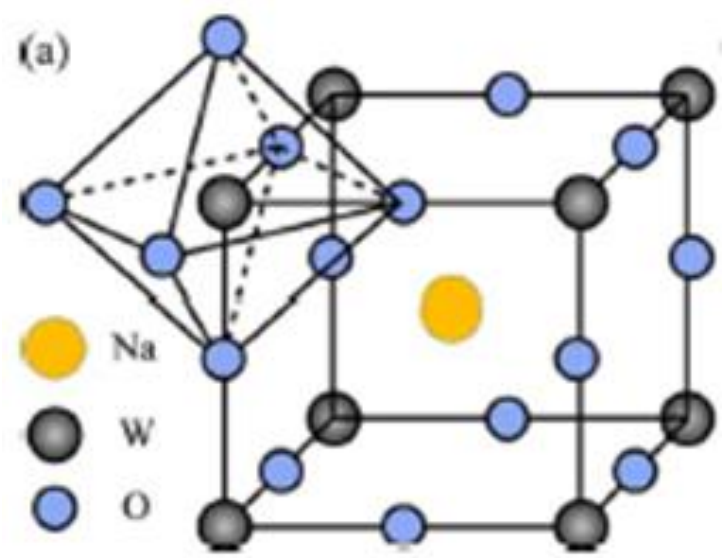
core lineshapes in photoemission spectra of:

* Metallic tungsten bronzes Na_xWO_3
* Metallic rutile-type dioxides MO_2
* Degenerately doped post transition metal oxides:
  Sn-doped In_2O_3 and Sb-doped SnO_2

The models:

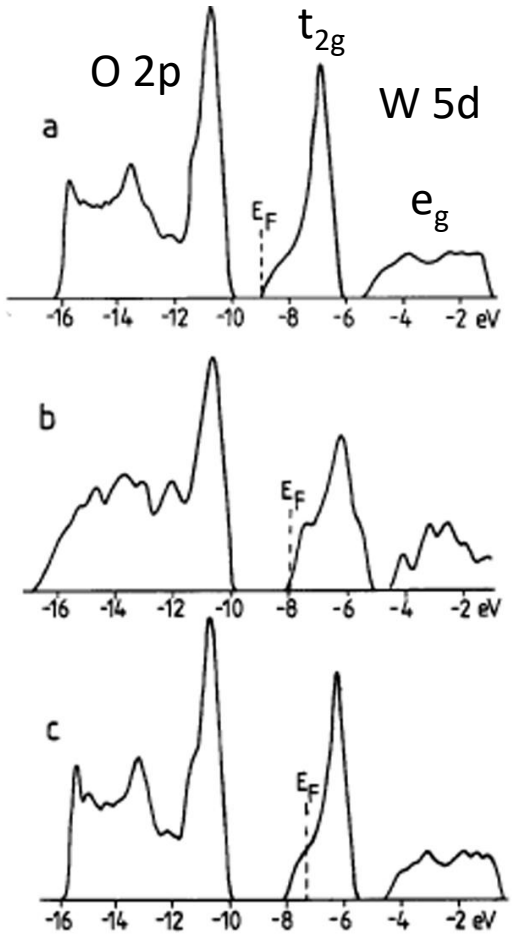
* The Kotani model with split-off screening state
* Intrinsic plasmon excitation: the Langreth weak coupling model
* GW + cumulant expansion (GW + C) method: an *ab initio* approach to many body excitations in response to creation of a hole.

The cubic metallic sodium tungsten bronzes Na_xWO_3 (0.0<x<1.0)



Colour due to conduction electron plasmon in visible region:

x<0.4	blue
x=0.50-0.60	purple
x=0.65-0.80	red
x>0.85	bronzy yellow



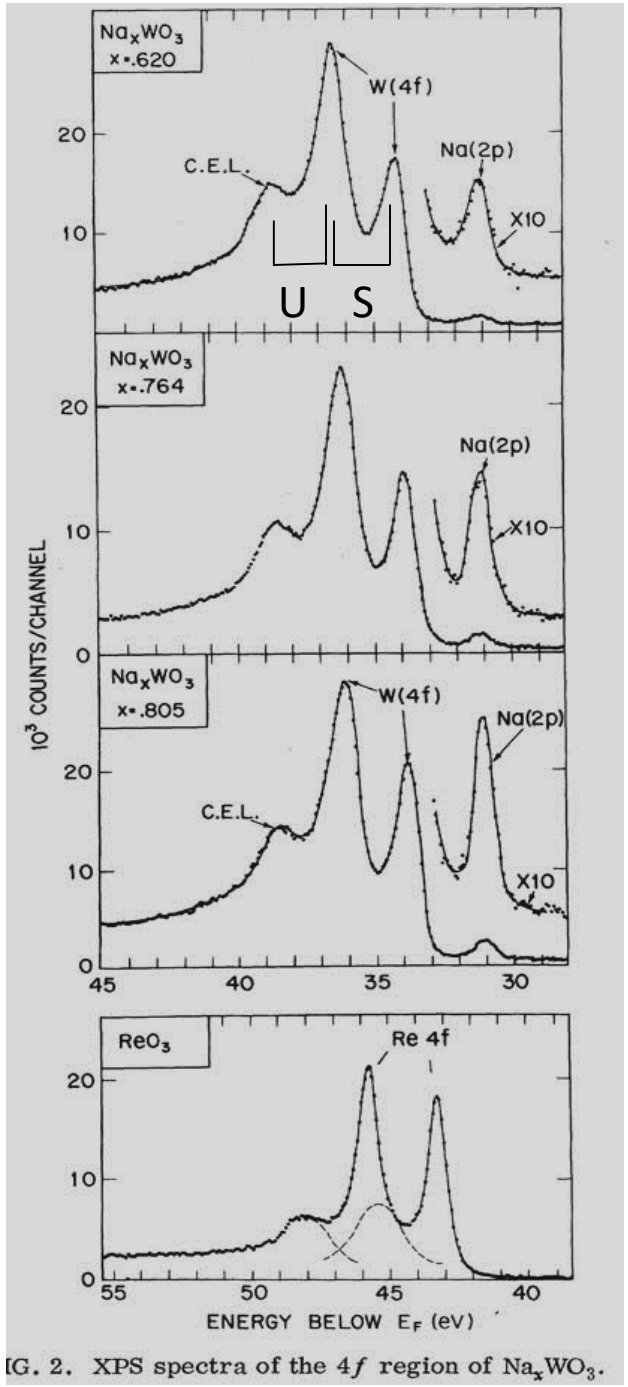
Density of states for (a) cubic WO_3 (b) monoclinic WO_3 (c) cubic $NaWO_3$
Solid State Communications 1983 **46** 575

x=0.0
WO_3 is a $5d^0$ W(VI) compound

x=1.0
$NaWO_3$ is a $5d^1$ W(V) compound

For intermediate x values the tungsten bronzes are formally mixed valent with W(VI)+W(V) But they are metallic, the 5d electrons are delocalised and all the W ions are equivalent.

Can XPS take a snapshot of valence fluctuation? A number of papers published in the early 1970s made this claim.



IG. 2. XPS spectra of the 4*f* region of Na_xWO_3.

VOLUME 34, NUMBER 12 PHYSICAL REVIEW LETTERS 24 MARCH 1975

Local Character of Many-Body Effects in X-Ray Photoemission from Transition-Metal Compounds: $Na_x WO_3$

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Bell Laboratories, Murray Hill, New Jersey 07974

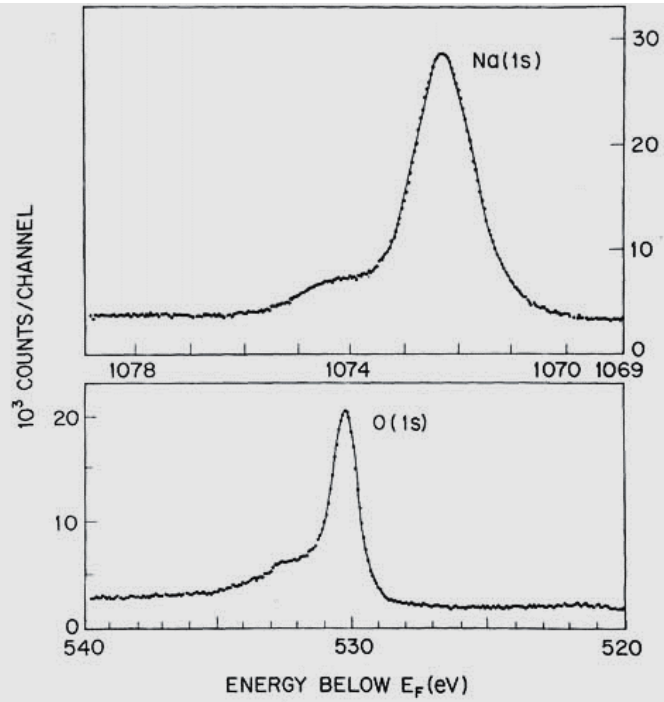


FIG. 3. XPS spectra of the Na and O 1*s* lines of $Na_{0.764} WO_3$.

Satellites are seen for both Na 1s and O 1s core lines.

Mixed valence W(V) + W(VI) can't be the whole story, especially as double peak structure is also seen in ReO_3 where all the Re ions are $5d^1$ Re(VI).

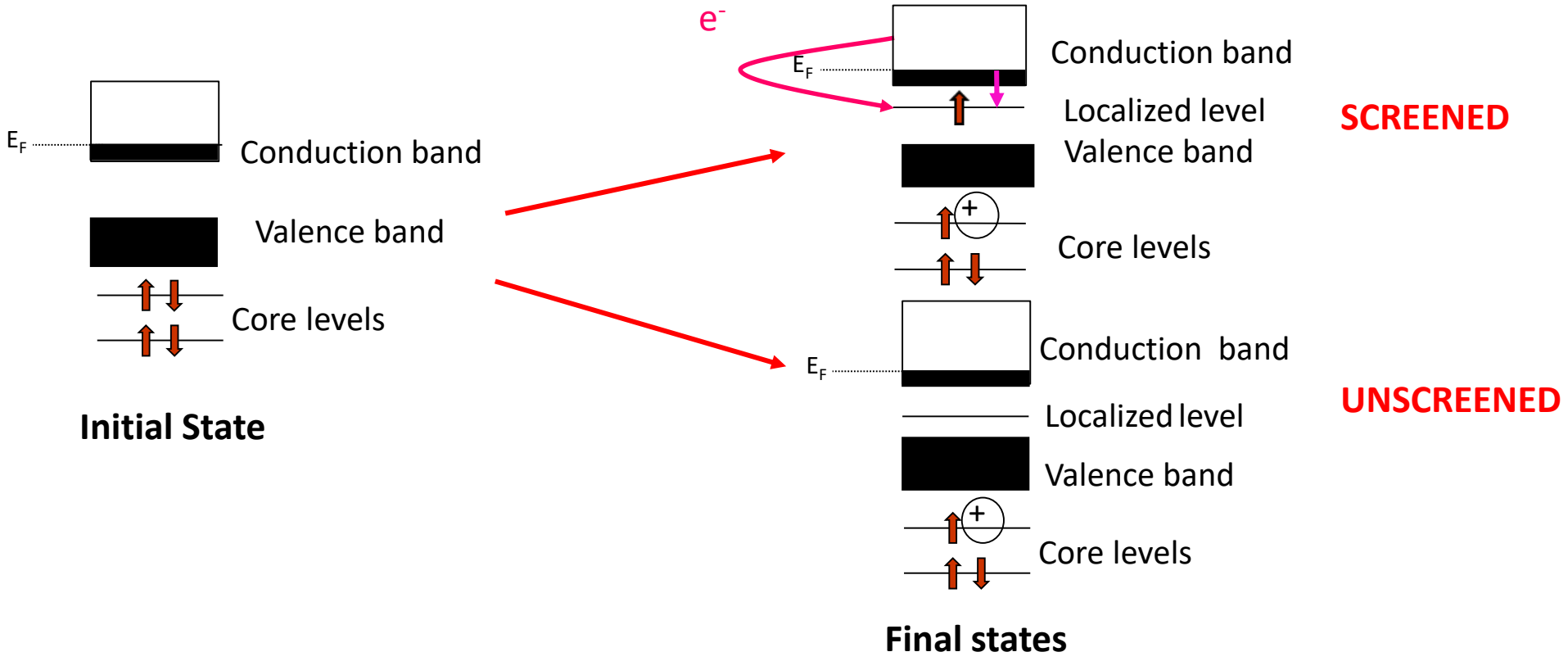
This led Wertheim to introduce two final state models – the Kotani (Friedel exciton) model and intrinsic plasmon excitation.

The Kotani model deals with a situation where the Coulomb interaction between a core hole and an orbital contributing to the conduction band in the initial state exceeds the conduction electron bandwidth.

Core level structure in narrow band metals due to final state screening

In the model proposed by Kotani (and Friedel) the core hole creates a localized state by “pulling” a state out of the conduction band: on the core-ionised atom the localised level no longer contributes to the conduction band. Two final states are possible.

- High binding energy peak corresponds to an ‘**unscreened**’ final state in which the localised state remains empty.
- Low binding energy peak corresponds to a ‘**screened**’ final state in which a conduction electron falls into the localised state.



Plasmons

Drude model

Collective longitudinal oscillation of the conduction electrons. Plasmon frequency ω_p depends on the density of conduction electrons n and increases as $n^{1/2}$

RPA Lindhart Model

Contribution to the $\varepsilon(q,\omega)$ dielectric function due to intra-band electron-hole pair excitations across the Fermi surface in the limit $q \to 0$. Plasmon energy depends on area of the Fermi surface.

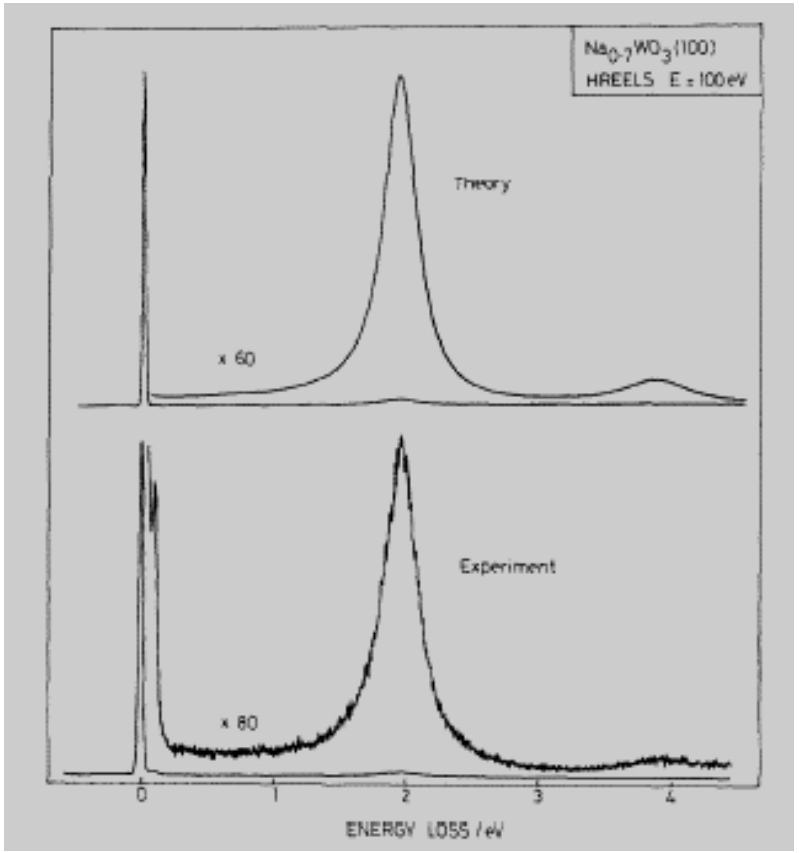
For a single isotropic band both models give:

$$\omega_p^2 = \frac{ne^2}{\epsilon(\infty)m^*}$$

Where the effective mass m^* is given by:

$$\frac{1}{m^*} = \frac{1}{\hbar^2 k_F}\left|\frac{dE}{dk}\right|_{k\,=\,k_f}$$

Plasmon energy associated with drop in reflectivity in optical spectra and loss features in electron energy loss spectroscopy.



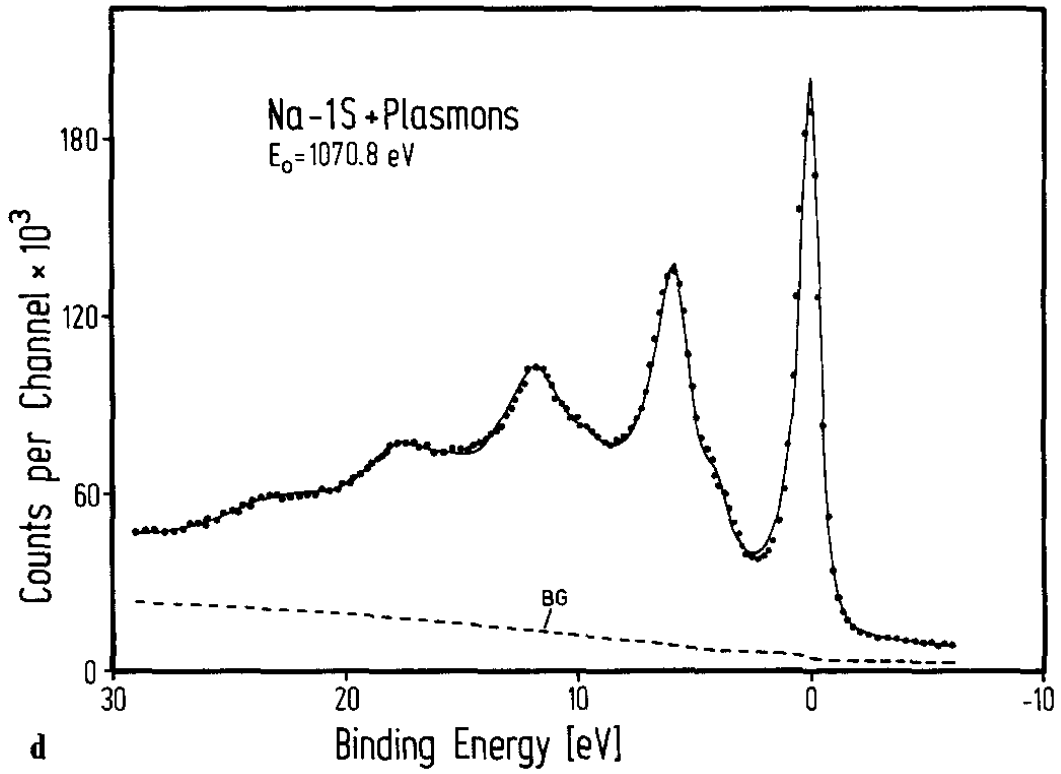
Cox, Hill, Egdell
Surface Science
1984 **141** 13

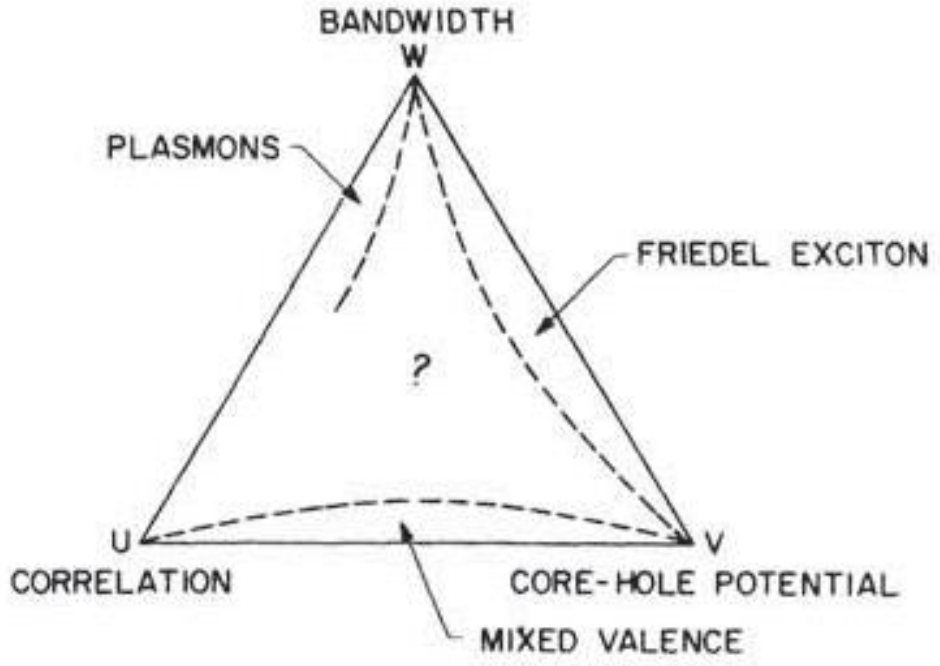
Carrier density in Na metal is 2.5 x 10^{22} cm^{-3} carrier density in $Na_{0.7}WO_3$ is 1.2 x 10^{22} cm^{-3} - but background dielectric constant $\epsilon(\infty)$ is about 5 so plasmon energy is about 2.0 eV as compared to 5.7 eV in sodium metal.

Problems with the plasmon model

*In the weak-coupling model developed by Langreth the intensity of the intrinsic plasmon satellite should increase as the electron gas gets more dilute with a $n^{-1/3}$ power law dependence. In dilute electron metals we are far from the weak coupling limit so does the model remain applicable?

* If intrinsic excitation of a single plasmon becomes strong we expect to see plasmon overtones, as in simple metals such as Na. For the sodium tungsten bronzes there is no hint of multiple losses – taking us back to the Kotani (Friedel exciton) model?? But why do we get an Na satellite when Na 3s states make little contribution to the conduction band.





Chalzalviel, Campagna and Wertheim, PRB 1977 **16** 697

The Electronic Structure of $Bi_{2-x}Gd_xRu_2O_7$ and RuO_2: A Study by Electron Spectroscopy

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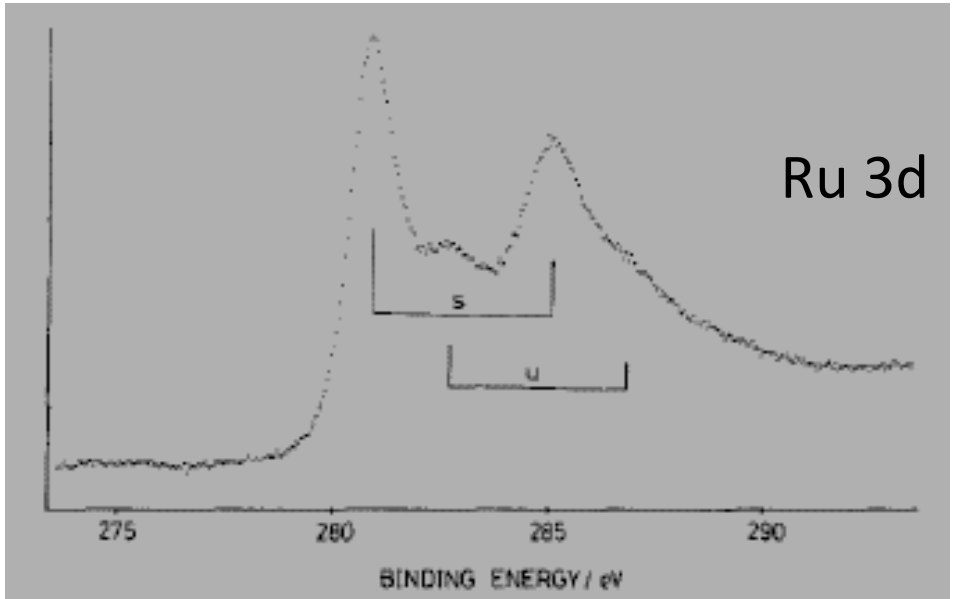

FIG. 10. Mg$K\alpha$ X-ray photoelectron spectrum of RuO_2 following removal of structure due to satellite radiation. The bars indicate the positions of overlapping spin–orbit doublets due to screened and unscreened final states.

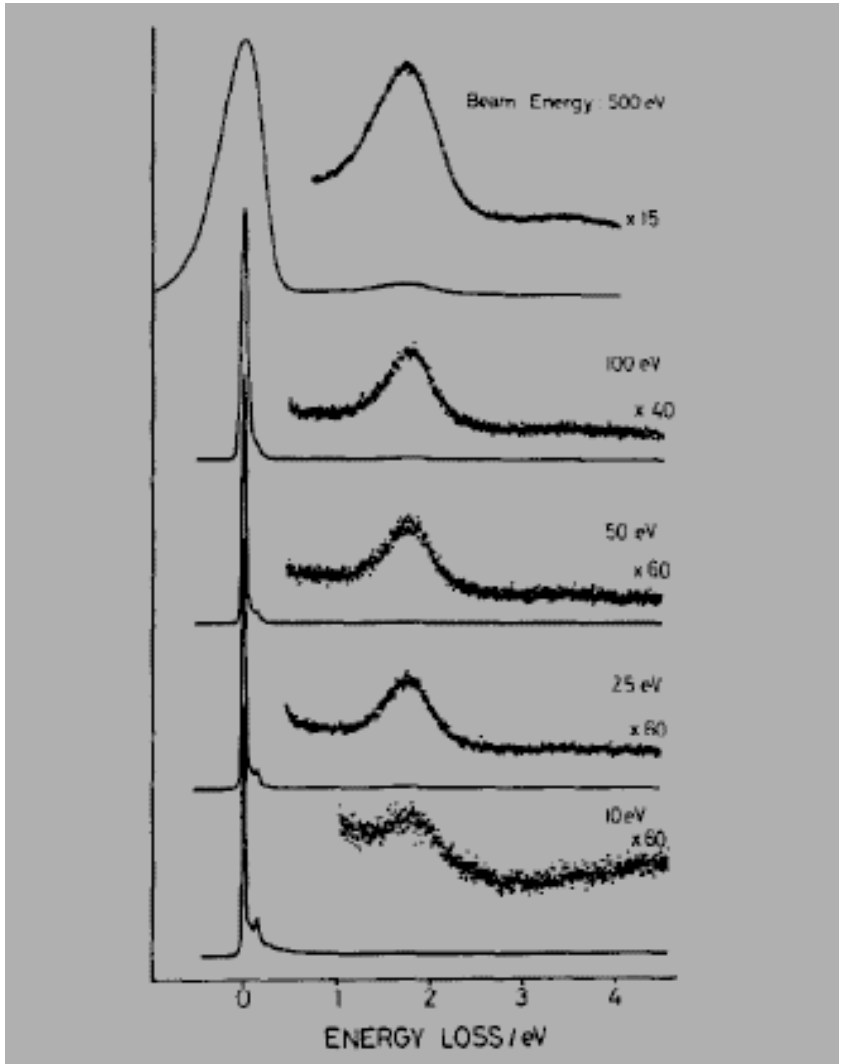

FIG. 9. Electron-energy-loss spectra of RuO_2 excited at differing electron beam energies between 10 and 500 eV. The 500-eV spectrum was excited with the unmonochromated electron source of the ESCALAB LEED gun. Other spectra were excited with a monochromated electron source.

The RuO_2 surface had been rigorously cleaned and the satellites were intrinsic.

Elsewhere in the literature the high binding energy unscreened doublet were assigned to a mysterious 'oxidised RuO_3 surface phase' even though RuO_3 is not known as a bulk phase.

Oxidation would decrease the carrier density in the oxidised layer, but no evidence from EELS that carrier density is lower close to the surface.

J. Solid State Chemistry 1986 **62** 36

Core-level X-ray photoelectron spectra and X-ray photoelectron diffraction of $RuO_2(110)$ grown by molecular beam epitaxy on $TiO_2(110)$

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Received 17 December 1996; accepted 29 May 1997

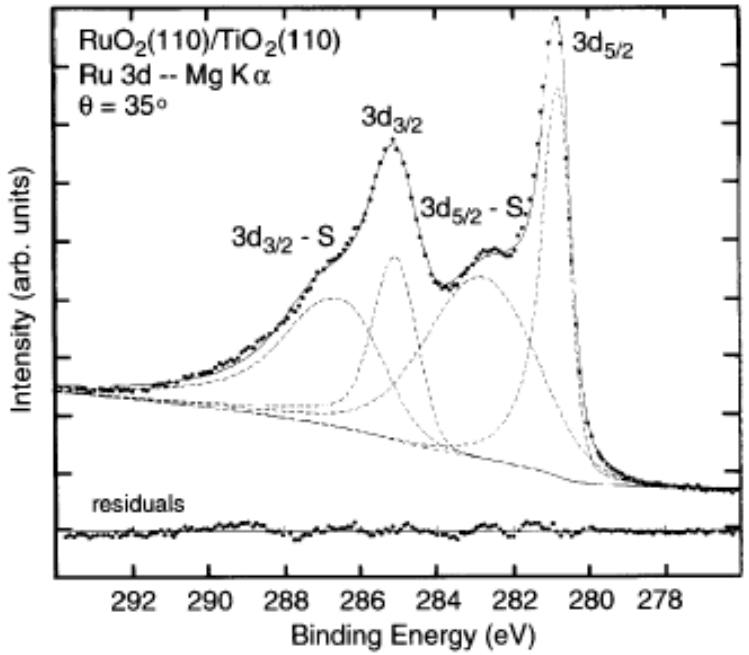


Fig. 4. High-energy resolution, Mg Kα X-ray excited Ru 3d XPS spectrum (pass energy (E_p) = 6 eV) for $RuO_2(110)/TiO_2(110)$ measured at $\theta = 35°$ showing the primary spin–orbit components, and the additional peaks, referred to as satellites in the text. A curve-fitting model in which the primary spin–orbit components are taken to be of similar shape as those in clean Ru(0001) metal was used.

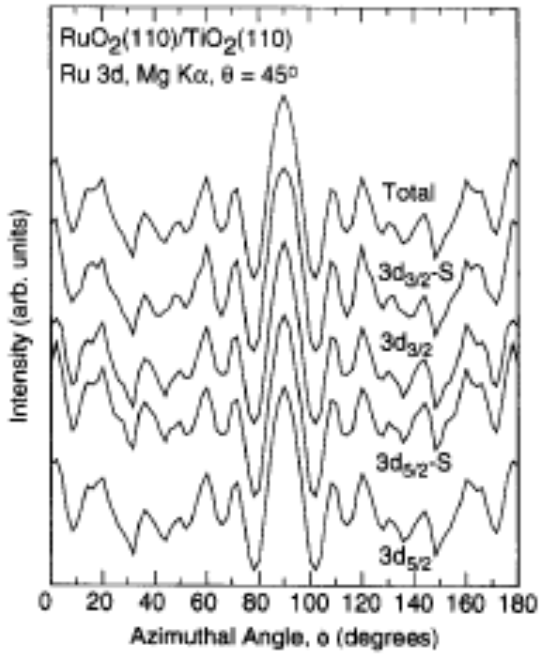
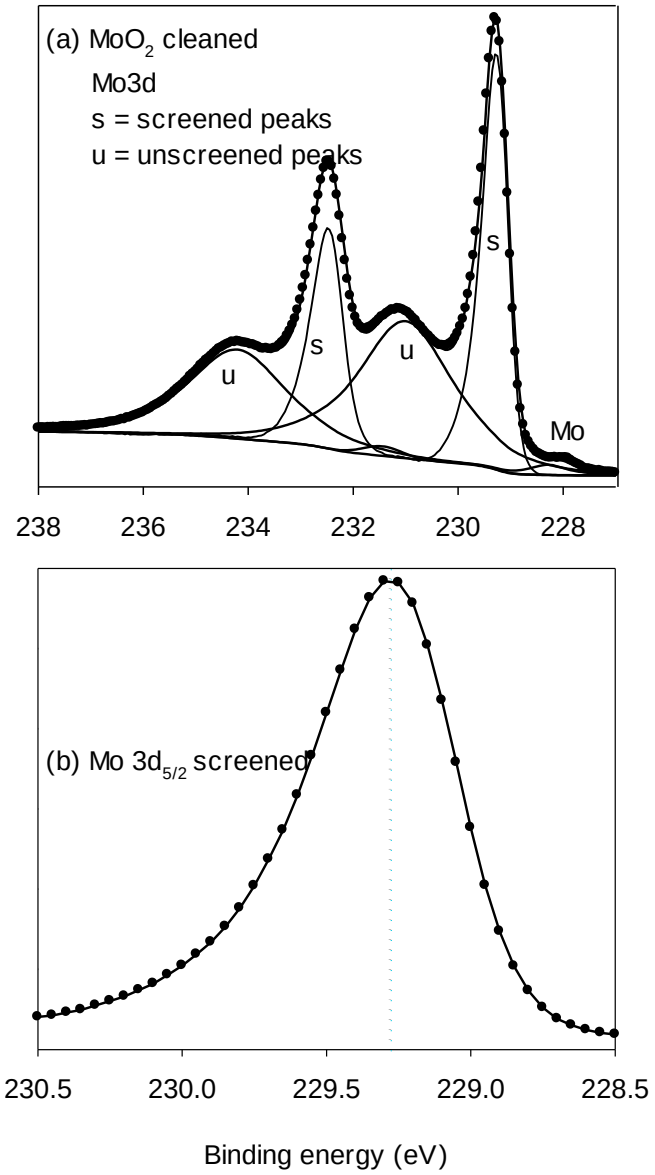


Fig. 7. State-specific, Mg Kα-excited XPD azimuthal scans for $RuO_2(110)/TiO_2(110)$ at $\theta = 45°$ for the total Ru 3d peak manifold, and each of the four components seen in Fig. 4.

X-ray photoelectron diffraction seems to prove beyond reasonable doubt that the “main peaks” and the “satellite peaks” (S) in XPS of metallic RuO_2 correspond to atoms in identical sites

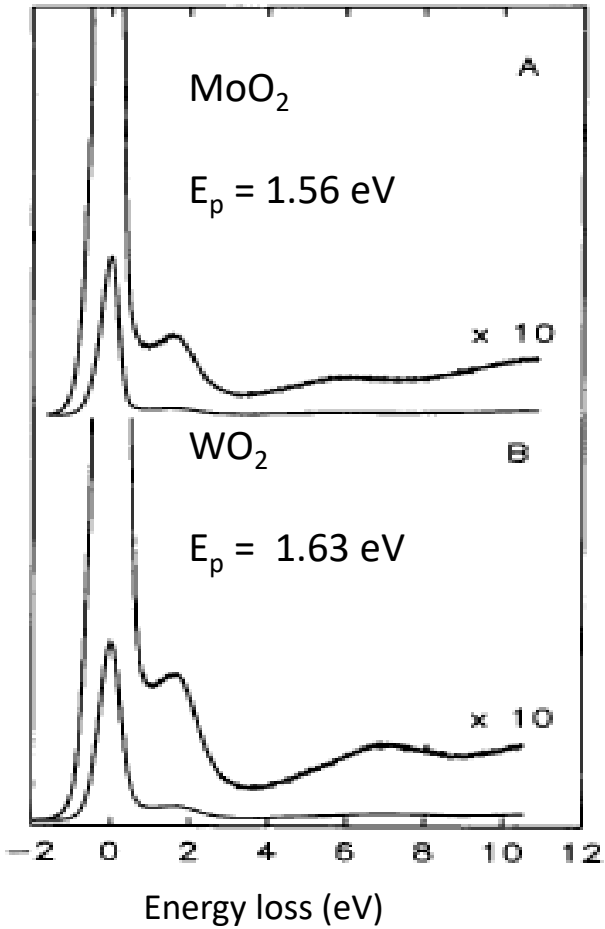
Core XPS of MoO_2



Screened to unscreened separation for Mo 3d core line is 1.73 eV.

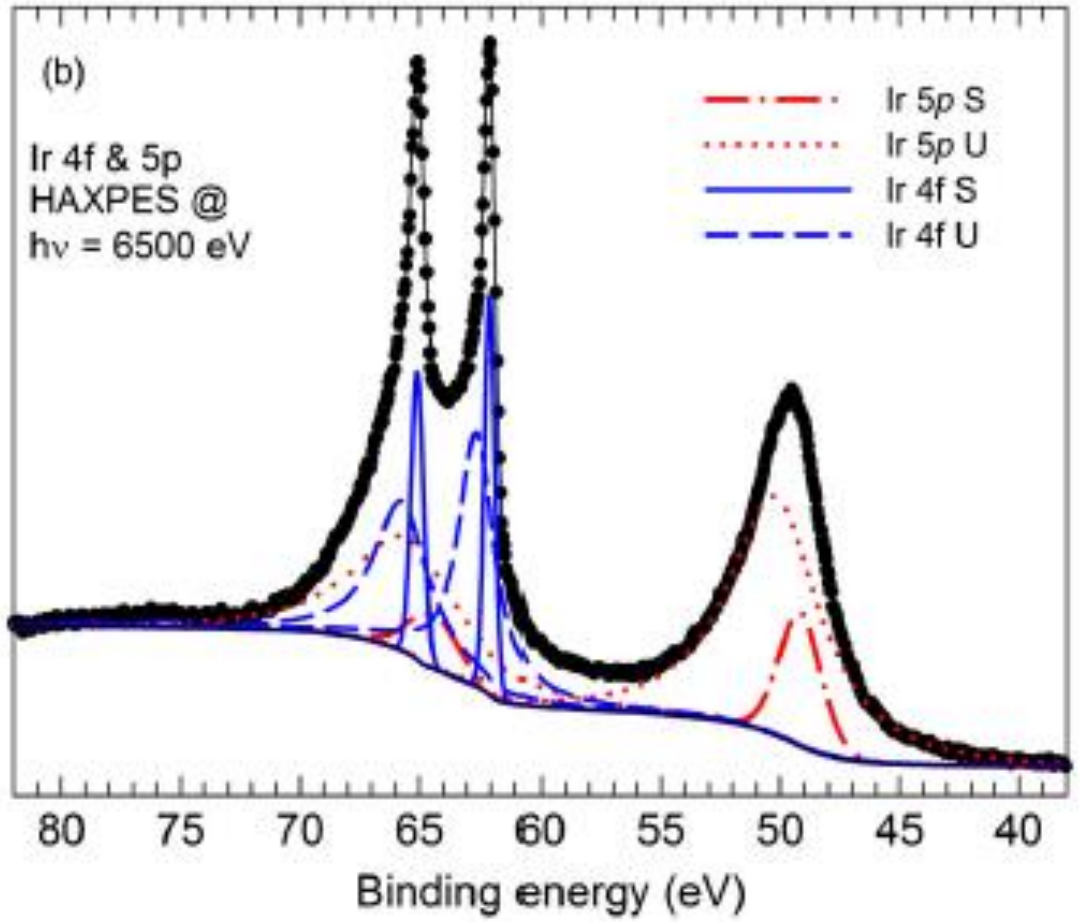
Plasmon energy measured in EELS is 1.56 eV

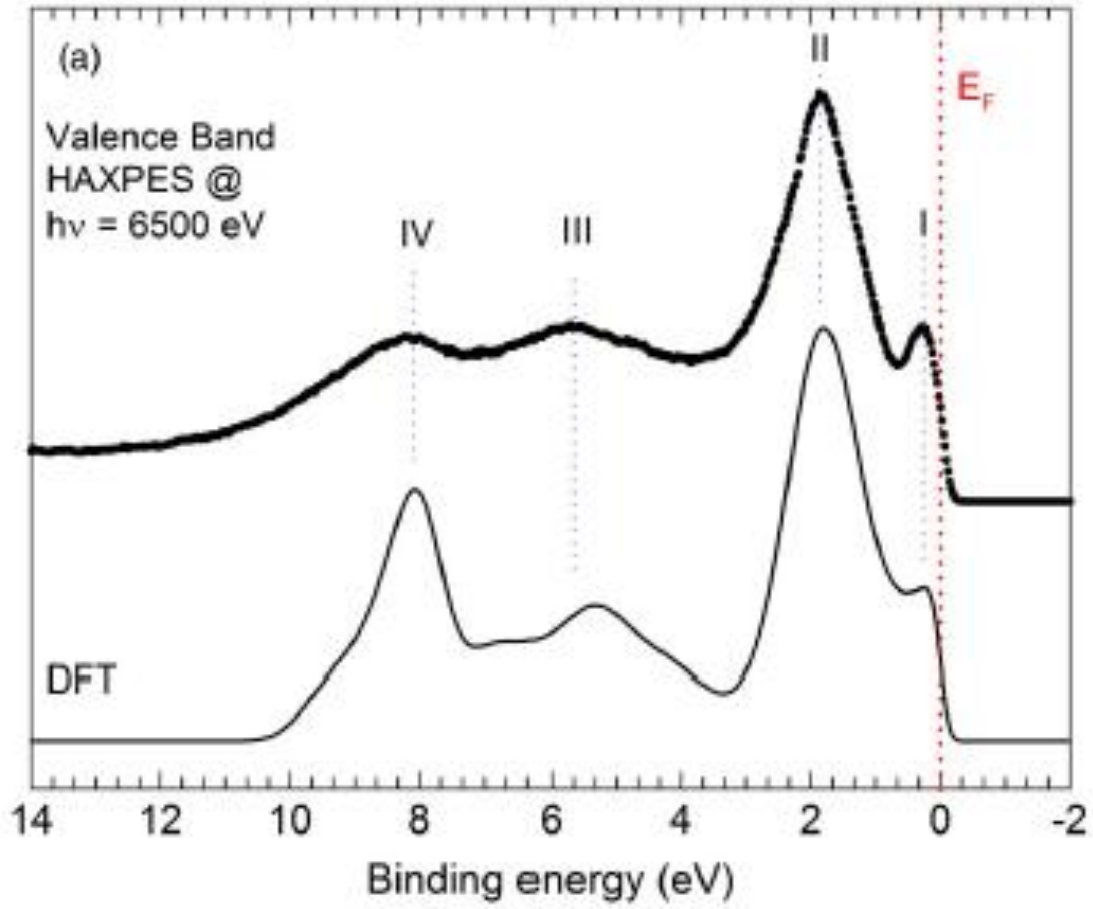
The catalytic literature abounds with papers that interpret complex peak shapes for Mo oxides purely in terms of different oxidation states for Mo



J. Phys. Chem. C 2010 **114** 4636
J C S Faraday 1996 **92** 2137

Excluding the idea of ‘surface phases’ – use HAXPES to increase probing depth





Typical satellites are found in Ir 4f HAXPES of metallic IrO_2 – although the proximity of Ir 5p is problematic.

Kahk, Oropeza, Borgatti, Panaccione, Payne, Egdell, Regoutz and others.
Physical Review Letters 2014 **112** 117601/1-6

PHYSICAL REVIEW MATERIALS 3, 025001 (2019)

Insights into the electronic structure of OsO_2 using soft and hard x-ray photoelectron spectroscopy in combination with density functional theory

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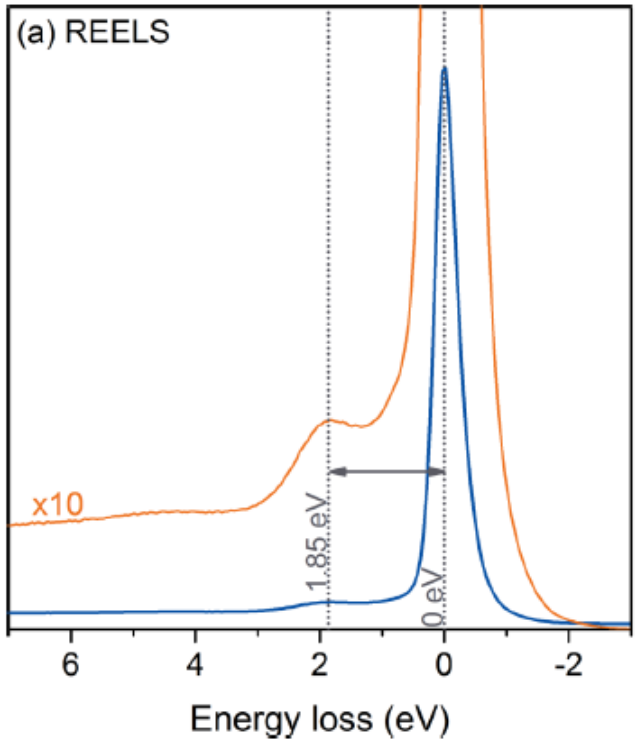
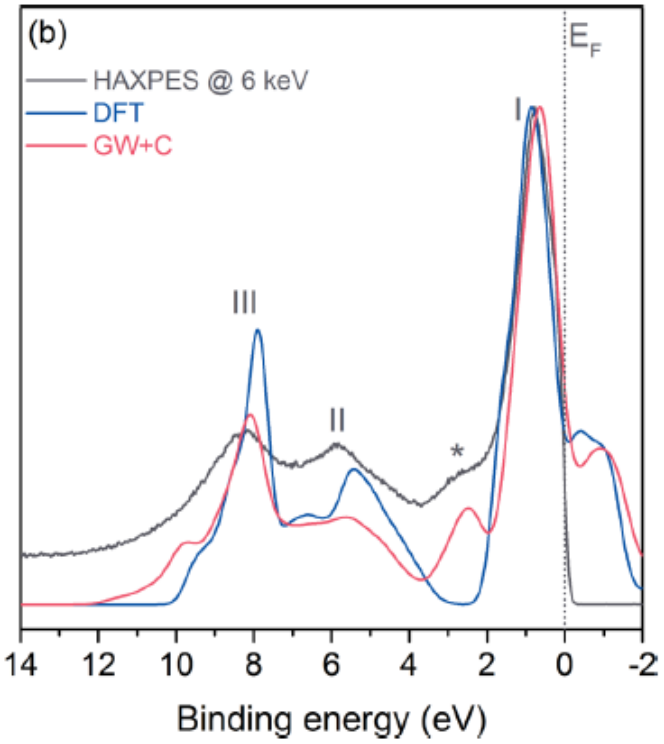
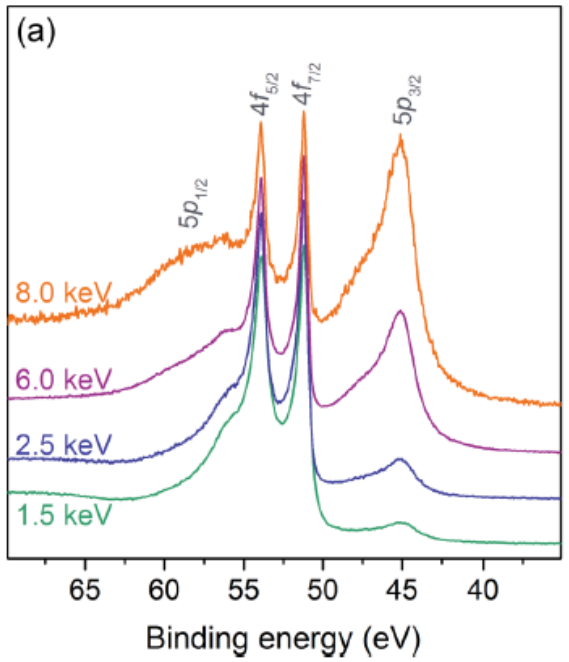
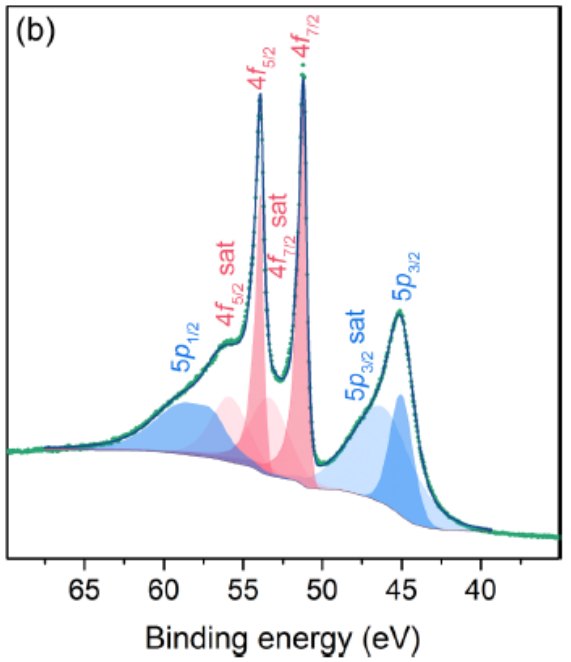








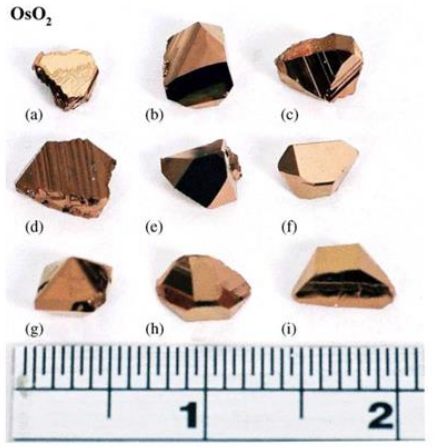


Fig. 2. Some representative crystals of OsO_2 grown in our laboratory.

At the time of this publication the GW + C method in Johannes Lischner's hands was unable to deal with core levels, but a plasmon satellite associated with the conduction band emerged from GW + C.

Core lineshapes in transparent conducting oxides (TCOs)

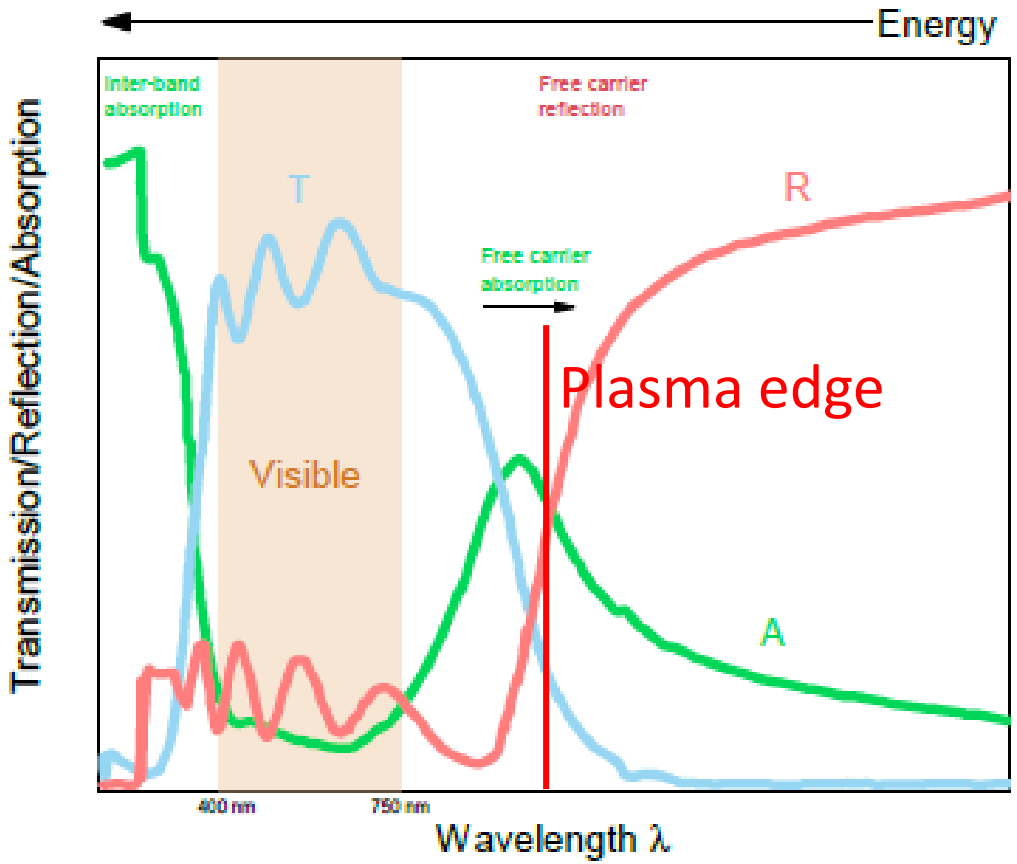
TCOs are degenerately-doped wide-gap post transition metal oxides with a window of transparency between strong absorption due to interband excitation and strong reflectivity at the plasma edge in the near infrared. e.g. Sn-doped In_2O_3, Sb-doped SnO_2.

In the ionic limit the valence band is composed of O 2p states and conduction band of metal 5s states – but there is very pronounced covalency which mixes O 2p and metal ns states.

Carrier concentration typically in the range up to 10^{21} cm^{-3}

Low effective mass ratios – typically 0.2-0.4

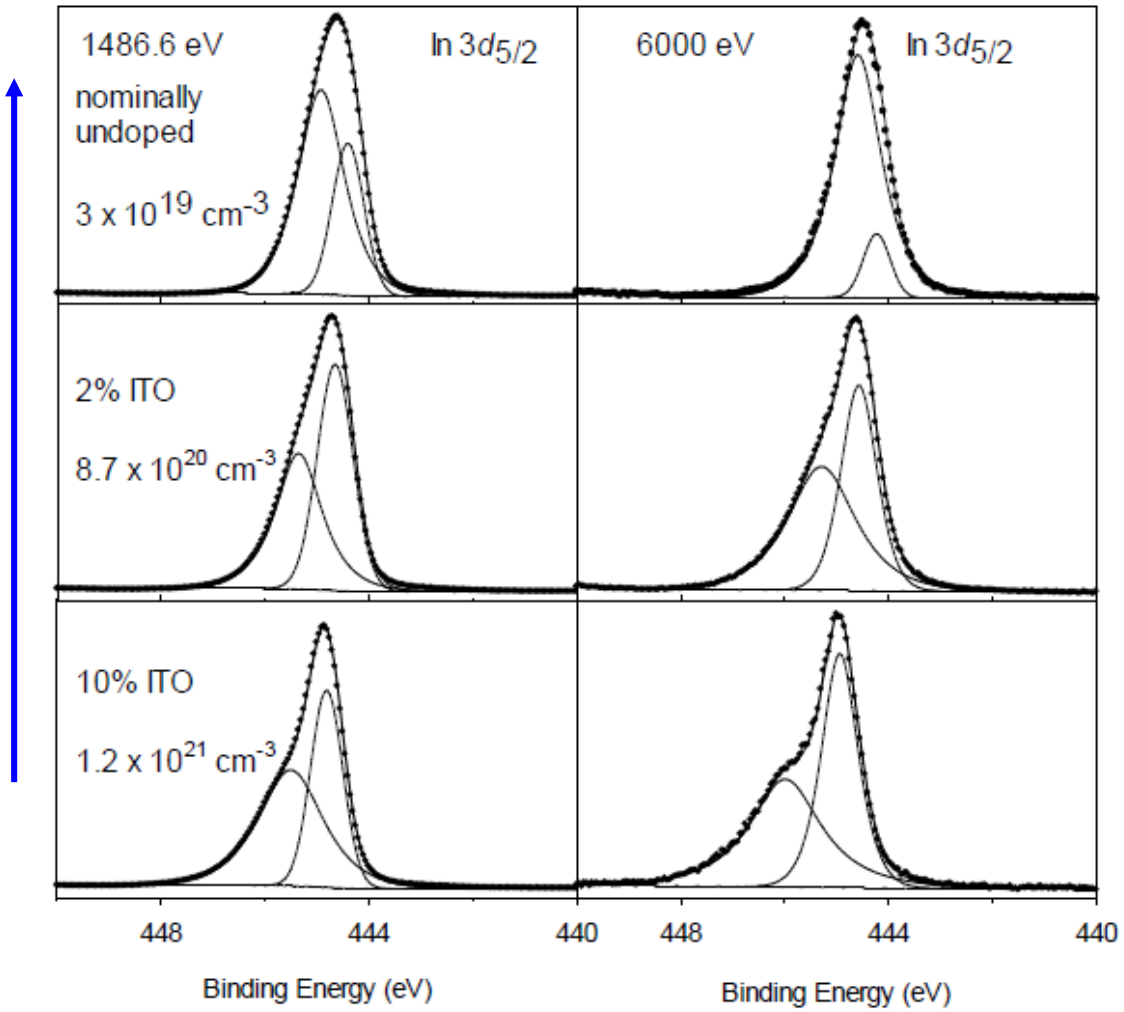
Occupied conduction bandwidths and plasmon energies are typically up to about 1 eV at a maximum.



Satellites in core XPS of degenerately doped indium oxide

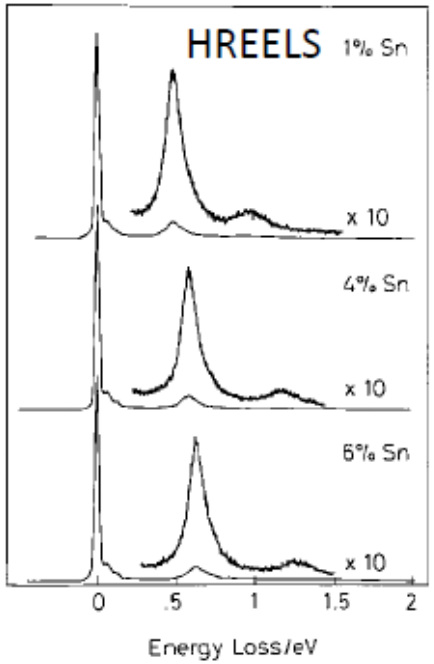
High binding energy component gets stronger as carrier density goes down as expected for a plasmon satellite.
But in the Kotani model we expect final state screened peak to get weaker as carrier density goes down i.e high binding energy feature to get stronger.

So both models qualitatively in agreement with experiments on Sn-doped In_2O_3.



PRB 2010 **81** 165207

Final state screening or plasmon satellite in narrow band free electron metal?

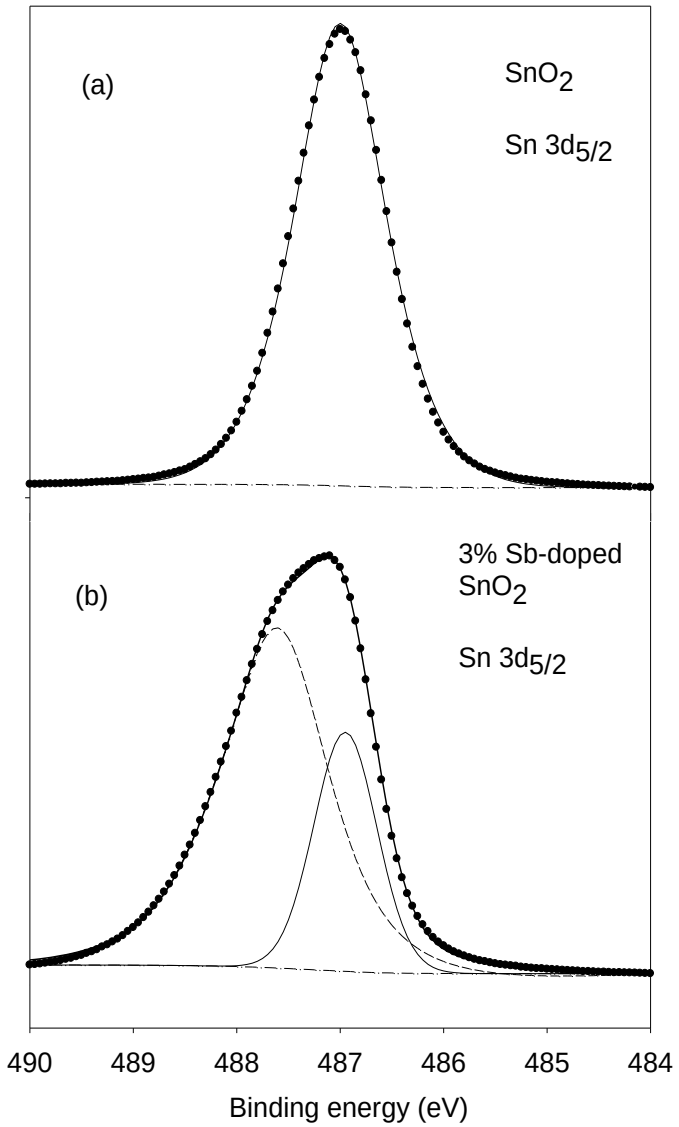


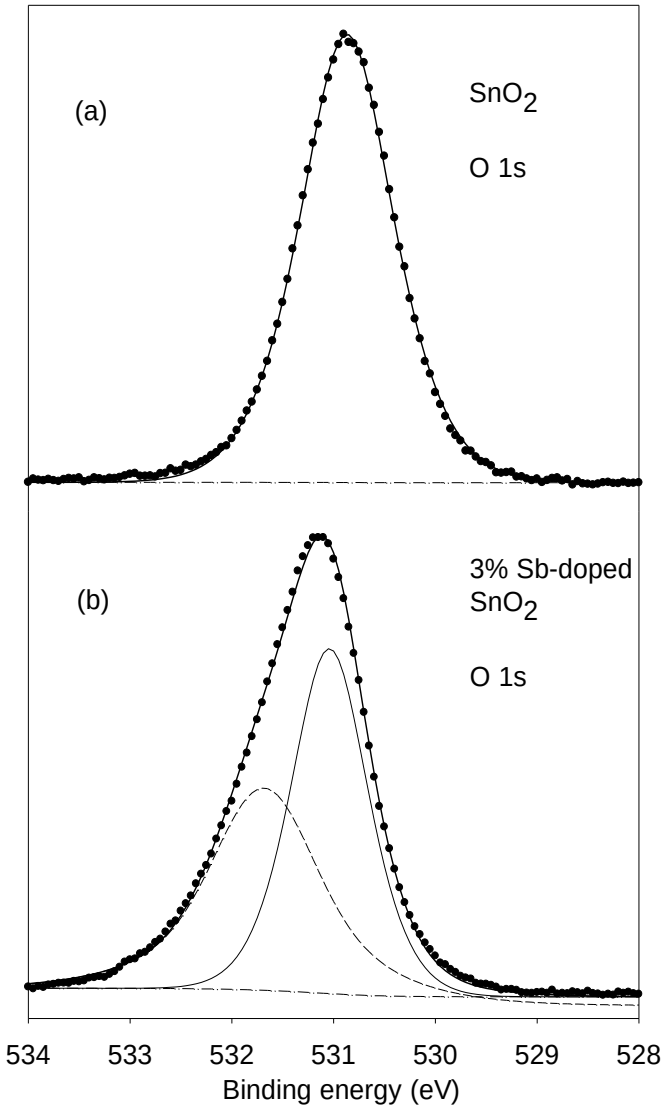
P A Cox, W R Flavell and R G Egdell
Journal of Solid State Chemistry 1987 **68** 340

Plasmon satellites in XPS of degenerately Sb-doped SnO_2

Note:

* The Lorentzian line shape for the high binding energy component of the doped sample.
* That the FWHM of the screened final state peak in the doped sample is less than for the undoped sample. This is because coupling to phonons is screened by the conduction electrons.



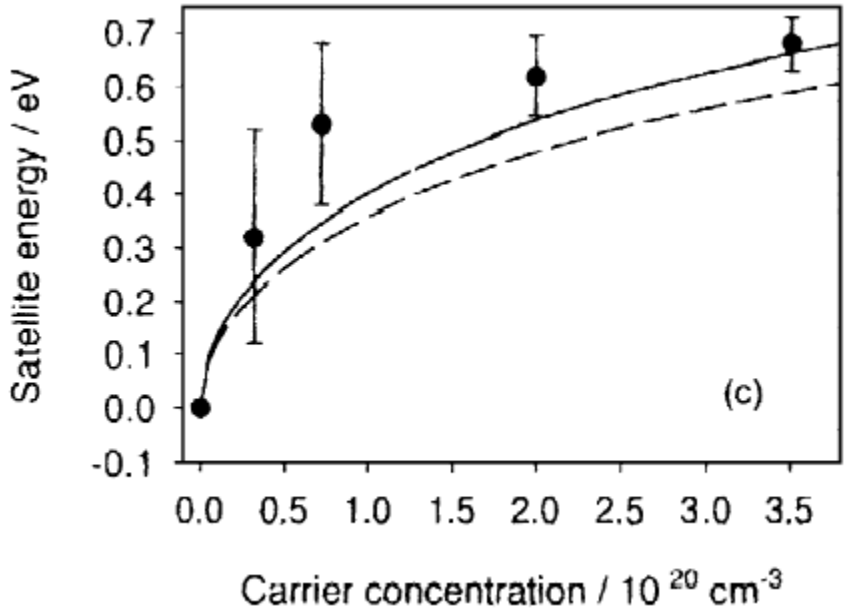


Peak separations for different core lines: Sn $3d_{5/2}$ 0.65 eV; Sn $4d_{5/2}$ 0.63 eV; O 1s 0.61 eV.

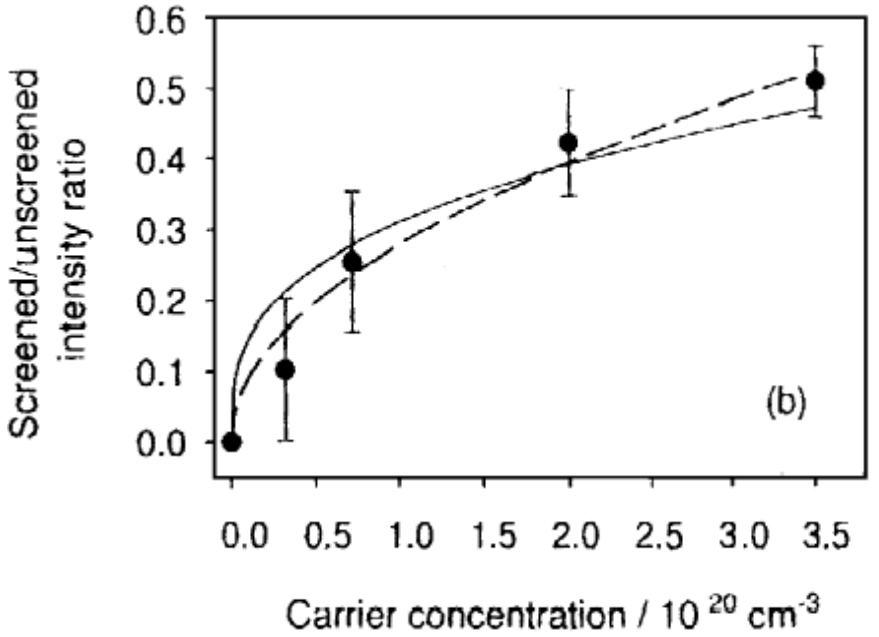
The differences seem barely significant. The plasmon energy is 0.66 eV as determined by HREELS.

Physical Review B 1999 **59** 1792-1799; Journal of Electron Spectroscopy and Related Phenomena 2003 **128** 59-66

Plasmon satellites in XPS of degenerately Sb-doped SnO_2

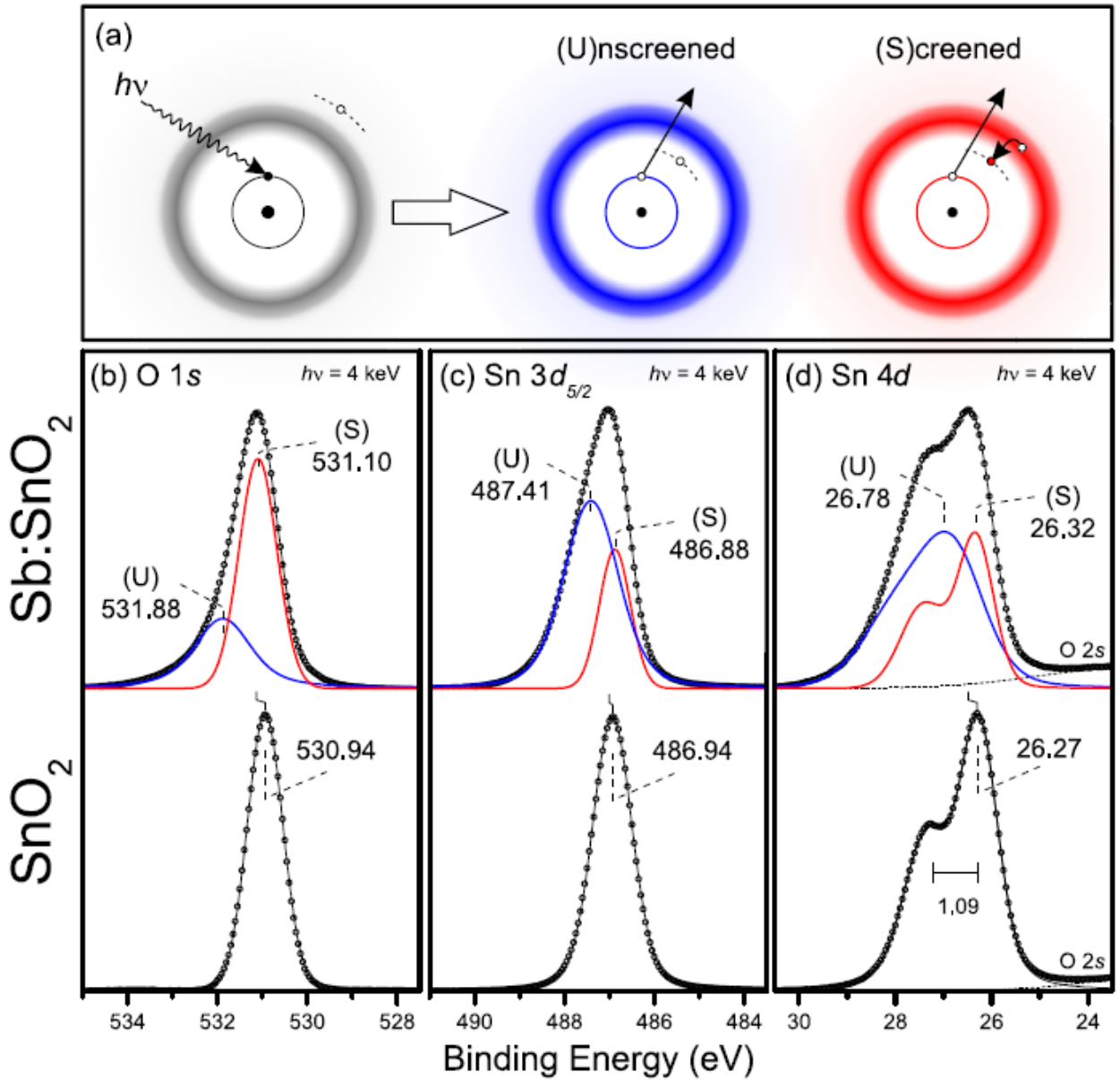


Screened-unscreened $3d_{5/2}$ peak separation as a function of carrier density.
Dashed curve shows surface plasmon energy measured by HREELS.
Solid curve shows estimated bulk plasmon energy.



Screened to unscreened peak intensity ratio for Sn $3d_{5/2}$ core line.
The Langreth weak coupling model predicts a $n^{1/3}$ variation shown by solid line (i.e. plasmon loss or unscreened feature gets stronger the lower the carrier concn.).
Dashed line shows a $n^{1/2}$ variation.

Sb-doped SnO_2 revisited with GW+C courtesy of Matteo Gatti and Francesco Borgatti



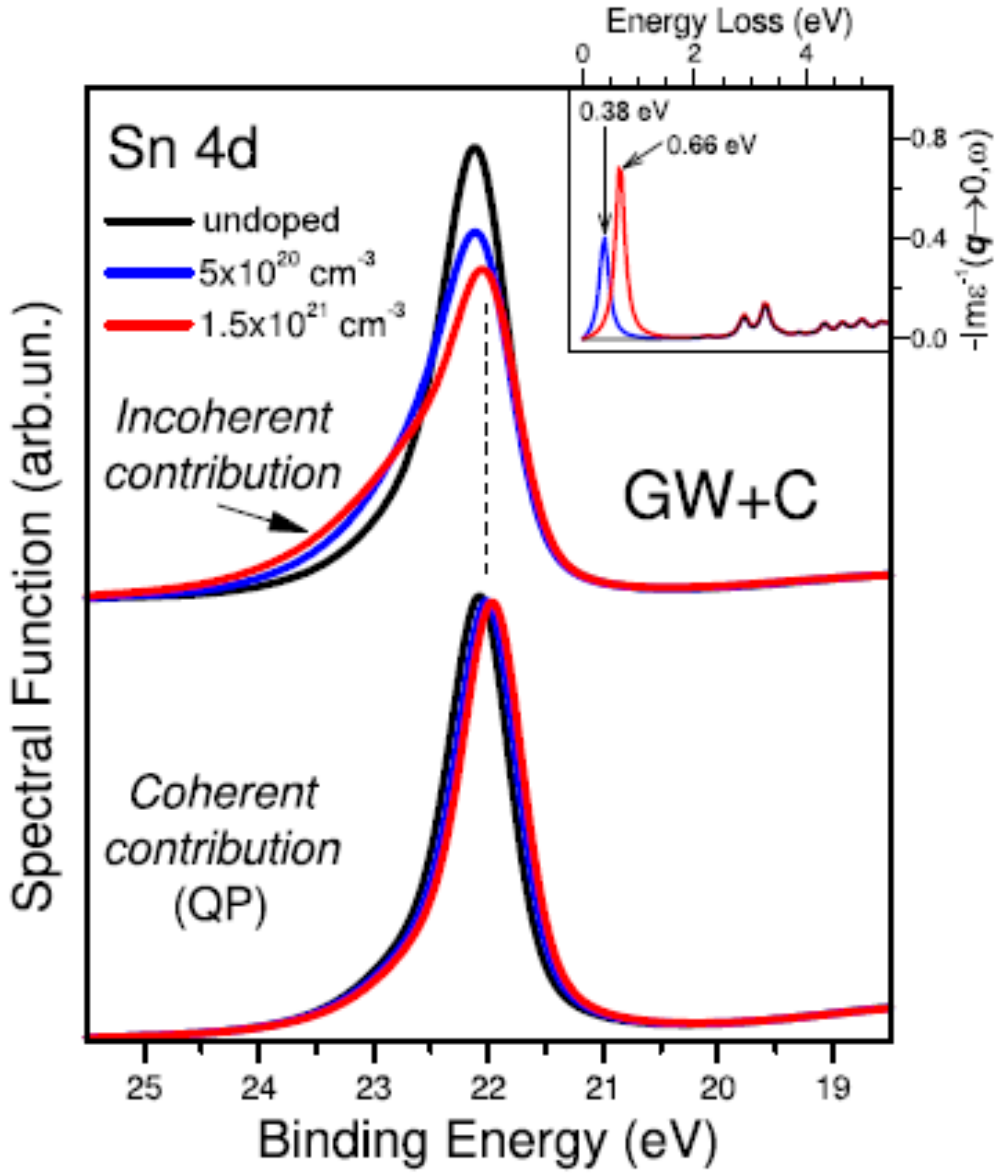
At the time the calculations were carried out Matteo could not deal with deep core levels using GW+C.

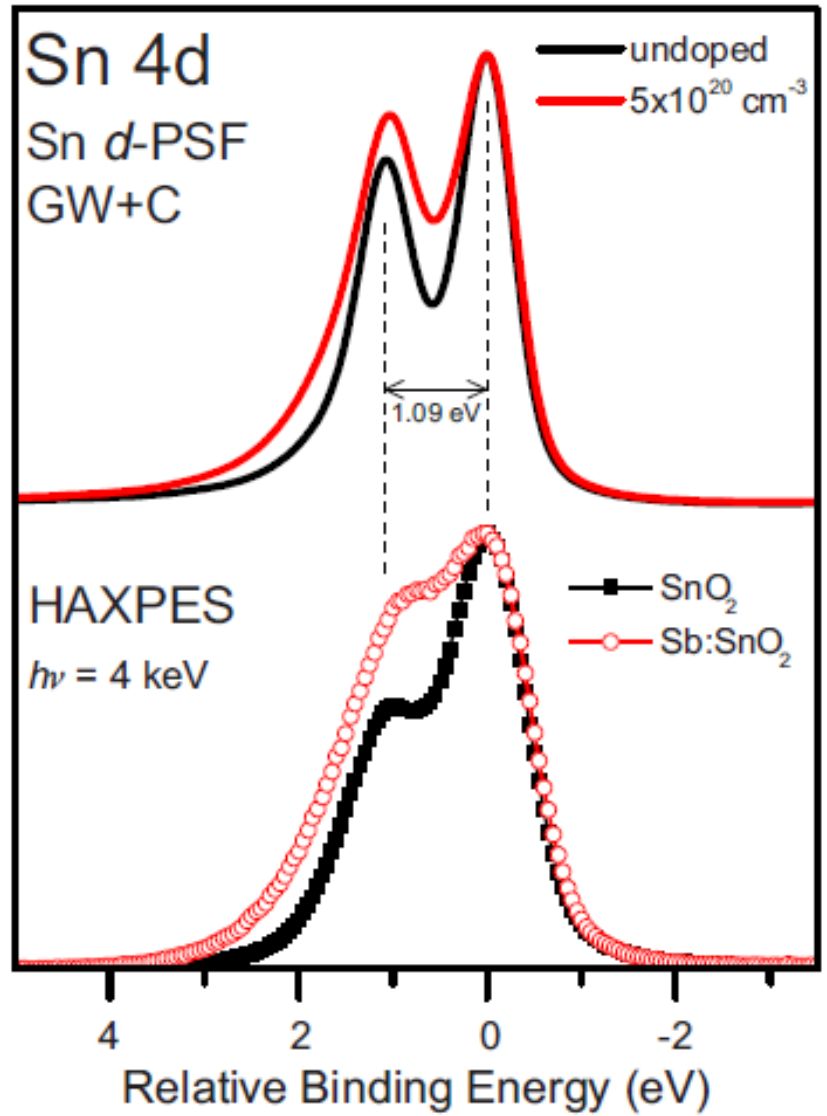
However it was possible to include the In 4d level in the valence electron calculations. This level is deep enough not to hybridise extensively with O 2p states, although mixing with O 2s and the ordering of O 2s and In 4d states in the starting GGA calculations caused many headaches.

Also the conduction electrons were introduced as an arbitrary homogenous electron gas rather than by introducing Sb as a dopant in a supercell calculations.

This seems to preclude a local trap orbital screening mechanism at the outset.

PHYSICAL REVIEW B **97**, 155102 (2018)


Energy Loss (eV)
0
2
4
0.38 eV
0.66 eV
0.8
0.4
0.0
-|mε⁻¹(q→0,ω)
Sn 4d
undoped
5x10^20 cm^-3
1.5x10^21 cm^-3
Incoherent contribution
GW+C
Coherent contribution (QP)
Spectral Function (arb.un.)
25
24
23
22
21
20
19
Binding Energy (eV)


Sn 4d
Sn d-PSF
GW+C
undoped
5x10^20 cm^-3
1.09 eV
HAXPES
hν = 4 keV
SnO2
Sb:SnO2
4
2
0
-2
Relative Binding Energy (eV)

How does the line shape vary with carrier density *n* in degenerately doped TCOs?

Model	Peak separation	Screened/unscreened intensity ratio	Lineshapes
Plasmon weak coupling model (Langreth)	Increases with increasing plasmon energy. For parabolic bands varies as $n^{1/2}$	Intensity of high binding energy plasmon satellite increases as carrier density goes down with $n^{-1/3}$ variation	High binding energy plasmon satellite has Lorentzian lineshape broadened by conduction electron scattering rate. Multiple plasmon overtones expected.
Local screening state model	Increases as Fermi levels moves up in conduction band. Power law dependence is $n^{2/3}$?	Probability of final state screening increases with increasing *n*. Power law dependence?	High binding energy unscreened final state Lorentzian broadened by lifetime of unscreened state. No muliples of loss structure.
GW + C (Matteo Gatti and colleagues)	Increases with increasing carrier density – non parabolic bands could be treated within model.	In calculations with two carrier densities, the plasmon satellite (unscreened peak) is weaker for the lower carrier density. This is at odds with the experiments!!	Lorentzian broadening due to imaginary part of the self energy. No plasmon overtones. In agreement with experiments.

Ir 4f XPS of IrO_2 (on Sb-doped SnO_2) interpreted in terms of a surface contaminant with Ir in a higher (or lower) oxidation state.

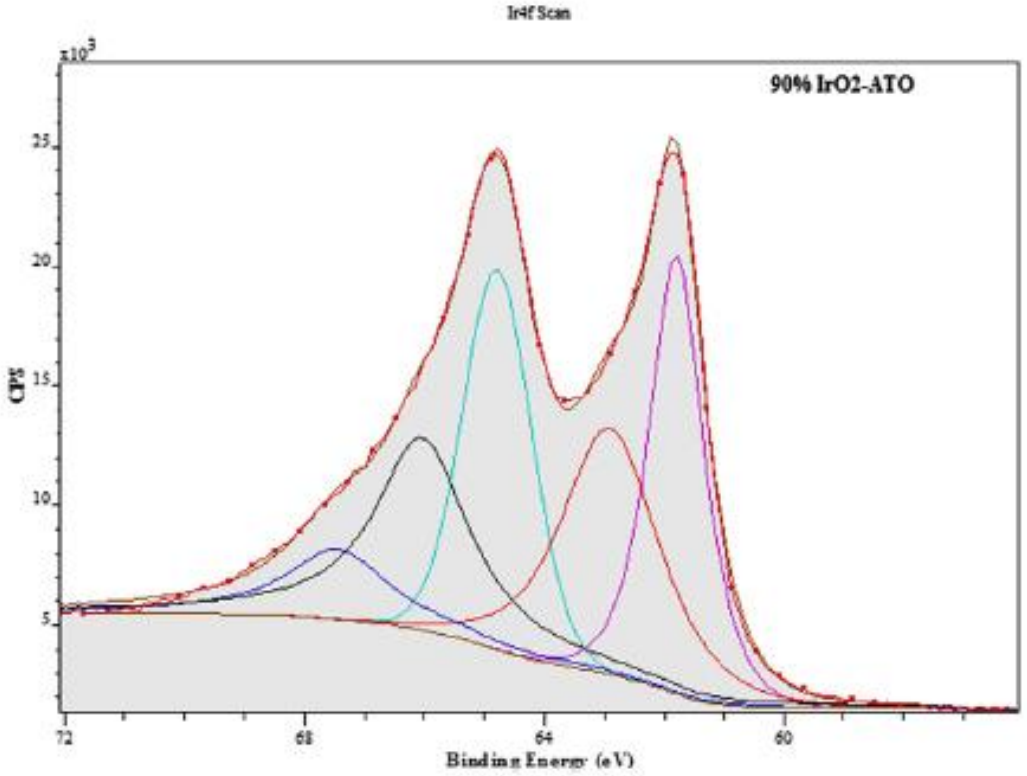


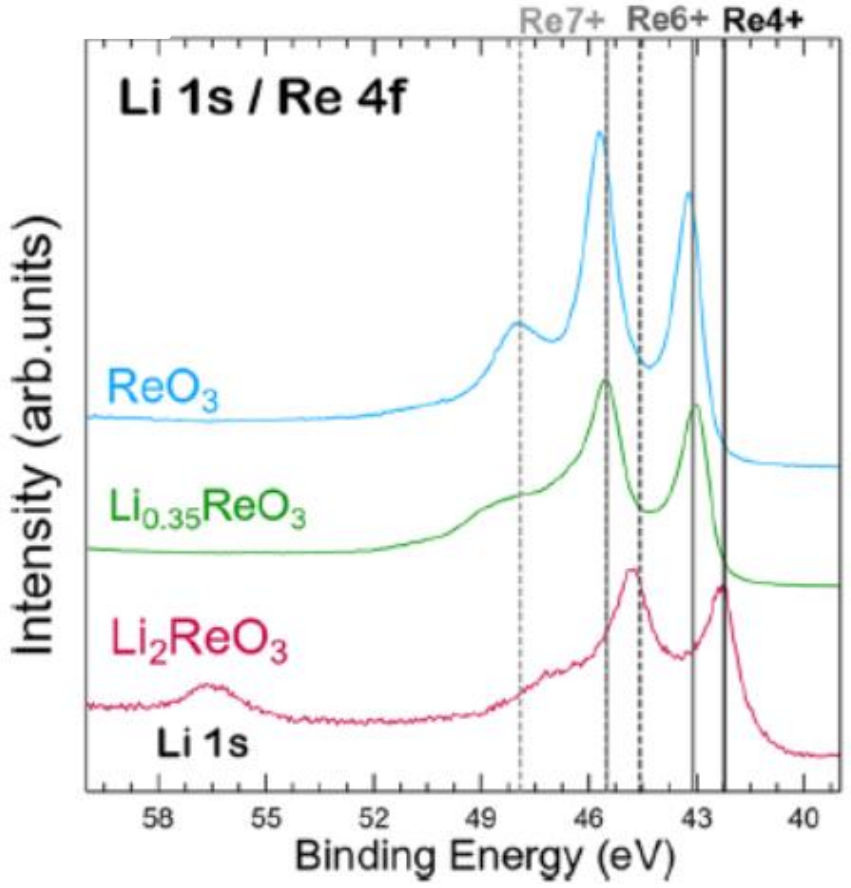
Fig. 9. Typical Ir 4f scans of IrO_2-ATO catalysts.

Journal of Power Sources 2014 **269** 451

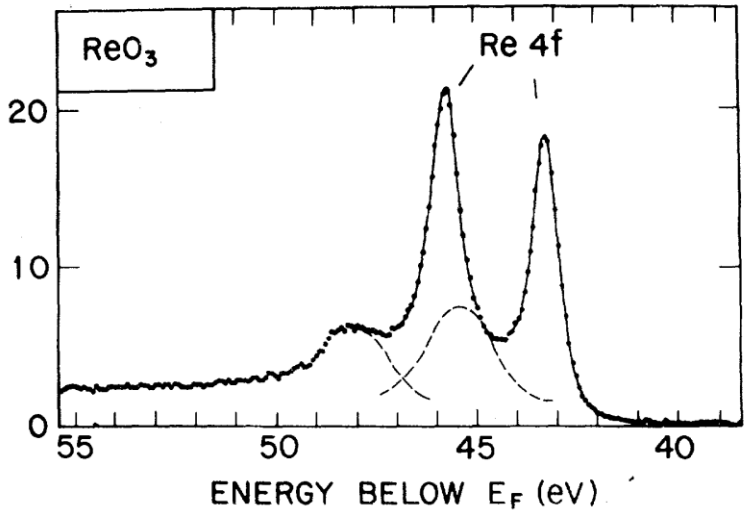
Despite 45 years of work on intrinsic satellite structure in core XPS of dilute-electron metals, about 80% of the papers that get through to publication in the contemporary literature attempt to interpret the spectra in terms of different oxidation states associated with surface phases or different chemical environments associated with for example cations adjacent to oxygen vacancies.

and Ir $4f_{7/2}$ (61.9 eV) were higher than for the metallic Ir (60.9 eV for $4f_{7/2}$ and 63.8 eV for $4f_{5/2}$) and was assigned to Ir^{4+} chemical state in the literature [8,43–46]. The pair of peaks at ~63 eV and ~66.2 eV have higher BE than Ir^{4+} and may be attributed an existence of higher oxidation state of IrO_2 [44]. Slavcheva [45] assigned the lower BE peak pair (61.9 eV) to Ir^{3+} and the higher BE peak pair (~62.9 eV) to Ir^{4+}. Due to the considerable disagreement in the literature [42], it is not possible to conclude exactly which Ir species is present. However it is certain that all the Ir species were present as oxides and no metallic Ir was detected. The Sn $3d_{5/2}$ peak at BE of

ACS Energy Lett. 2018, 3, 2513

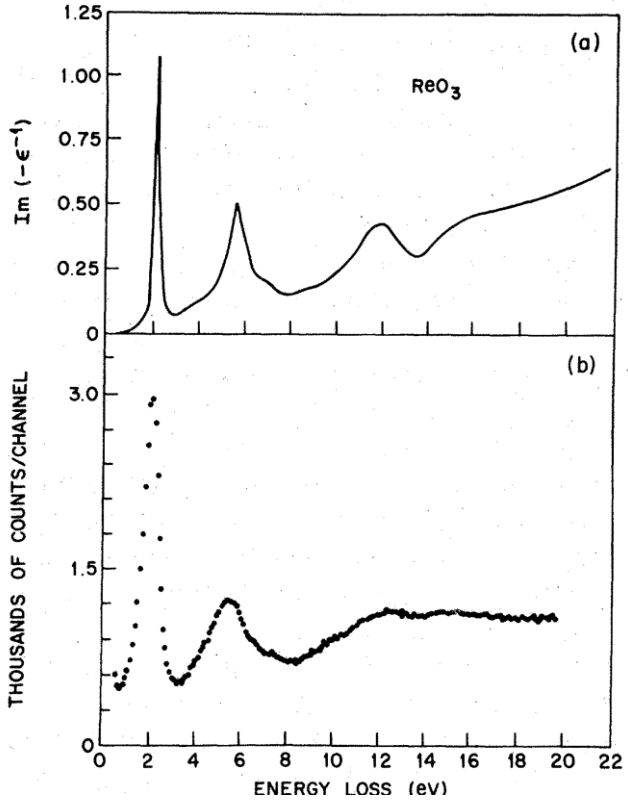


The high binding energy shoulder was attributed to Re_2O_7 surface contamination – despite the overall peak shape being a simple superposition of intrinsic screened and unscreened final states for ReO_3 as seen in 1975.



Wertheim's XPS of vacuum cleaved ReO_3 published in 1975.

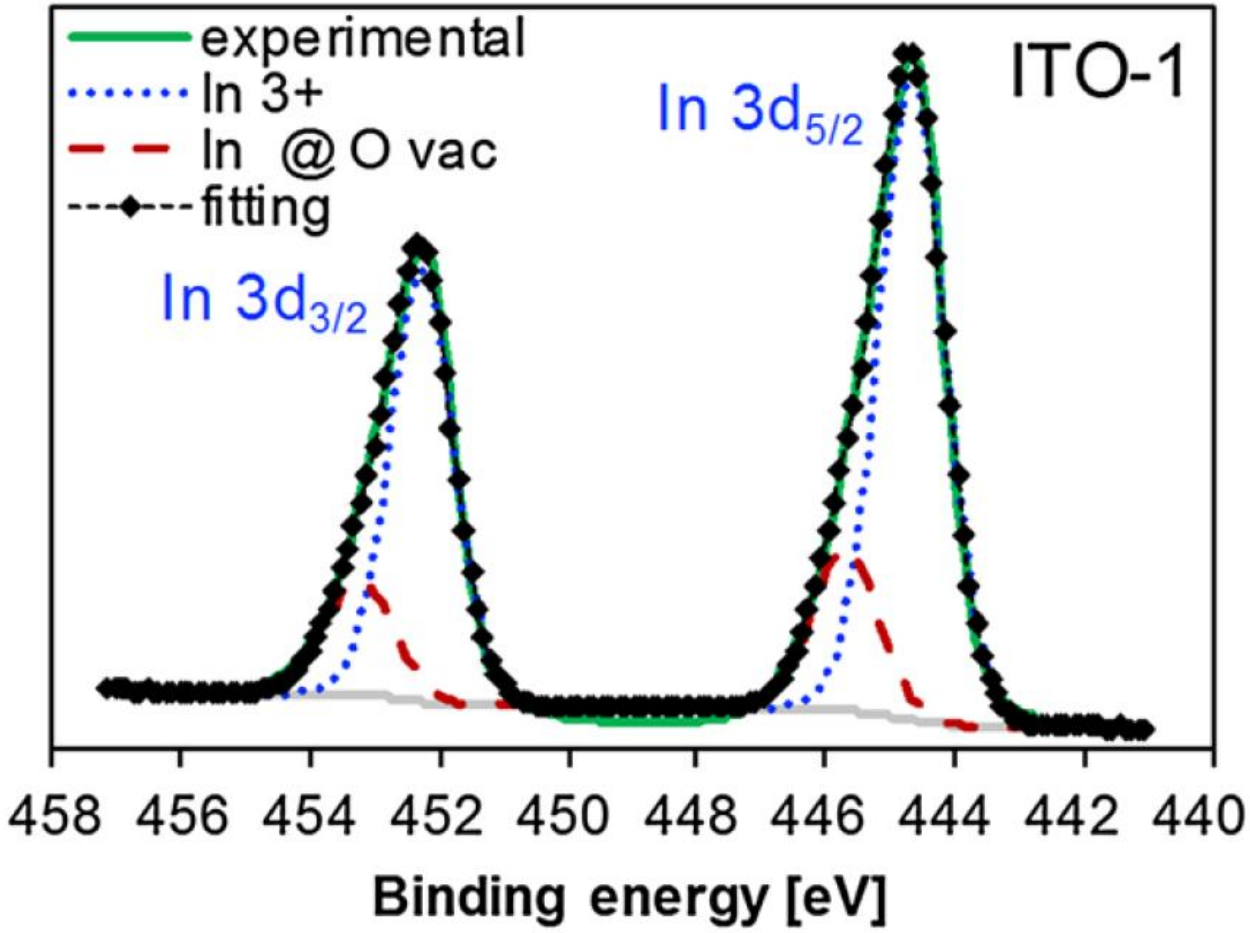
Phys. Rev. Lett. 1975 **34** 738



Electron energy loss spectrum of ReO_3 showing plasmon loss feature close to 2 eV, corresponding to the separation between screened and unscreened peaks in core photoemission.

Phys. Rev. B 1978 **17** 3790

High binding energy peak in In 3d core XPS of Sn-doped In_2O_3 assigned to In adjacent to an O vacancy



Journal of Electronic Materials 2017 **46** 1405

Cited in a very annoying paper submitted to Appl. Phys. Lett. I got to referee last week

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Wendy Flavell
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Graeme Beamson and Danny Law
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Pierro Torelli
Franceso Borgatti
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Chris McConville
Phil King and **James Mudd**
Tim Veal
Tien-Lin Lee
Matteo Gatti
Johannes Lischner