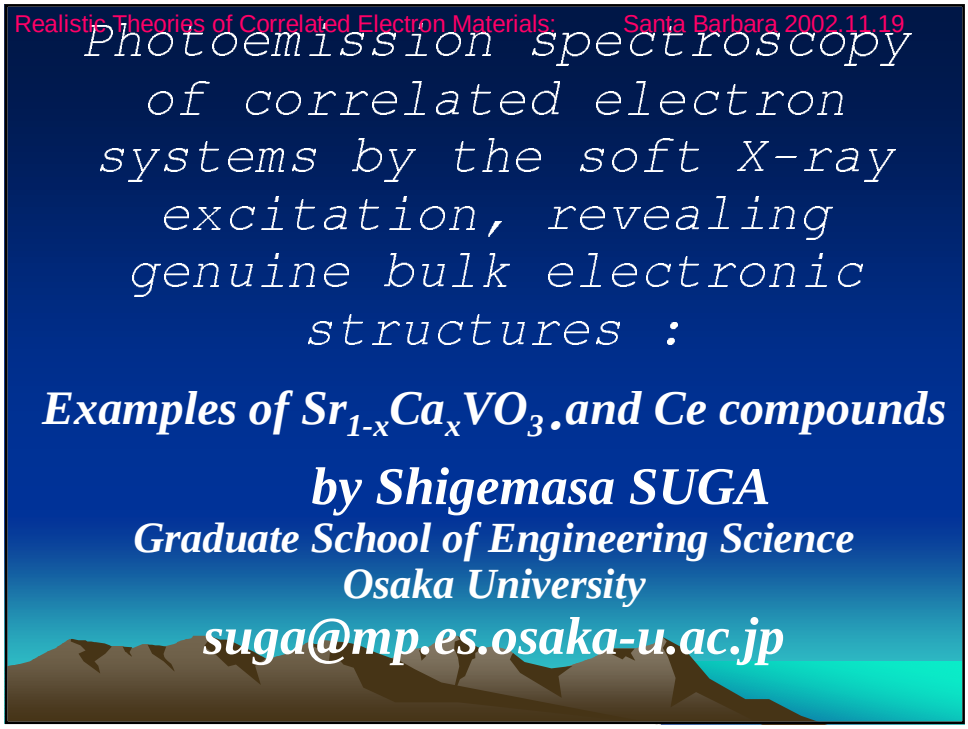
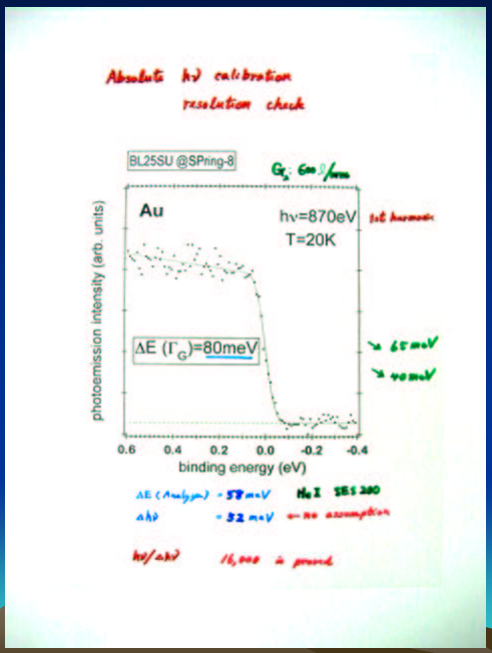
Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on



Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on

Role of High Resolution Photoemission Spectroscopy (PES) in the soft X-ray region

- In many materials with strong electron correlation, bulk and surface electronic structures are different
- For theoretical analyses are required reliable knowledge on genuine bulk and surface electronic structures
- High resolution spectra on high quality samples are required
- By use of the state-of-the-art soft X-ray PES technique, such studies are now feasible



an example at BL25SU of SPring-8, Japan

hν/ Δhν> 20,000 near 870eV with use of 1,000/mm grating

total resolution with

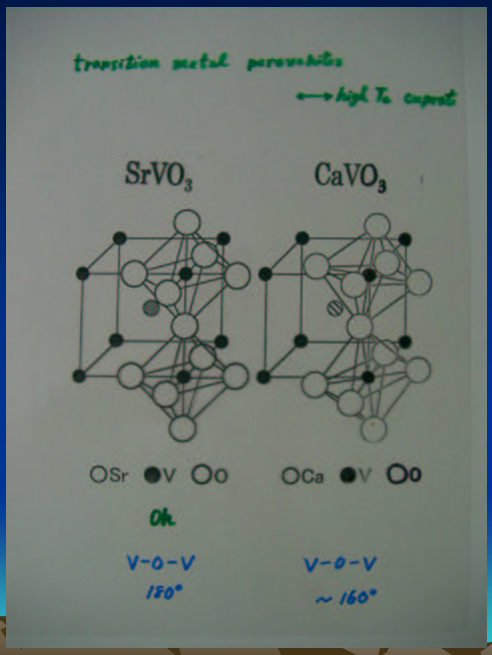
ΔE_K< 80~100 meV is conventionally achieved near 1 keV

On high quality sample surfaces, much more bulk sensitive results can be obtained

Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on

$Sr_{1-x}Ca_xVO_3$

- $3d^1$ metallic system
- remains paramagnetic down to 50mK
- Fermi liquid behavior
- simplest strongly correlated TM oxides
- band width W may change through this system by V-O-V bond angle change
- 180°in $SrVO_3$ and 160°in $CaVO_3$
- ideal system for PES study
- effective mass shows a moderate increase
- electron specific heat γ 6.4 & 7.3mJ/K^2mol



HPES studies of perovskites are very important

3d electronic states are thought to be more itinerant in $SrVO_3$ than $CaVO_3$ due to the bond angle effect (or buckling effect)

Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on

VOLUME 74, NUMBER 13 PHYSICAL REVIEW LETTERS 27 MARCH 1995

Systematic Development of the Spectral Function in the $3d^1$ Mott-Hubbard System $Ca_{1-x}Sr_xVO_3$

I. H. Inoue,[1,*] I. Hase,[1] Y. Aiura,[1] A. Fujimori,[2] Y. Haruyama,[1,†] T. Maruyama,[1,‡] and Y. Nishihara[1]
[1]*Electrotechnical Laboratory, Umezono, Tsukuba 305, Japan*
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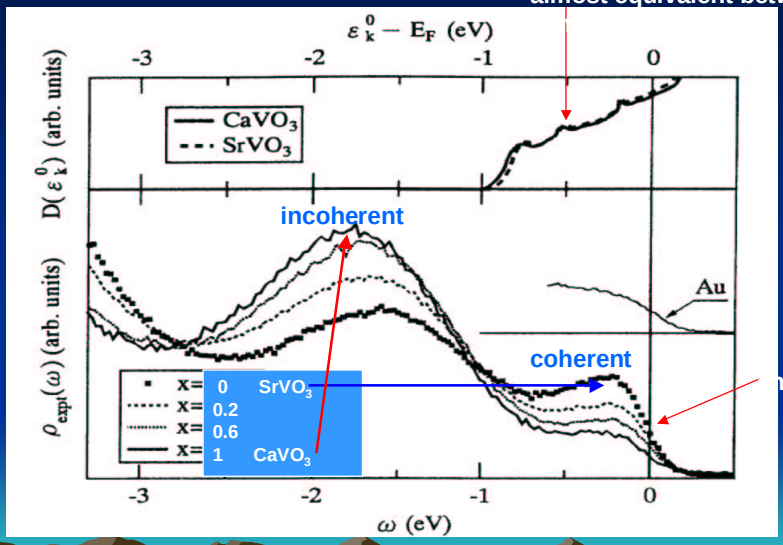
(Received 15 August 1994)

We present an experimental manifestation of how the single-particle density of states around the Fermi level (E_F) changes near a Mott transition. In a metallic perovskite-type $3d^1$ Mott-Hubbard system $Ca_{1-x}Sr_xVO_3$, as one decreases x the spectral weight of the coherent band near E_F is gradually transferred to that of the precursor of the lower Hubbard band ~2 eV below E_F. The momentum dependence of the quasiparticle self-energy and hence the long-range exchange or correlation is shown to become progressively important as one approaches the Mott transition from the metallic side.

I.H.Inoue et al. Phys.Rev.Lett.74,2539(1995)

$Sr_{1-x}Ca_xVO_3$ polycrystals: scraped

APW band cal. DOS are almost equivalent between



hanges

strong x dependence of the spectra is observed

incoherent peak is too strong! Why? ← surface effect

Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on

EUROPHYSICS LETTERS 15 July 2001

Europhys. Lett., **55** (2), pp. 246–252 (2001)

Electronic structure of $Ca_{1-x}Sr_xVO_3$: A tale of two energy scales

K. MAITI[1](*), D. D. SARMA[1](**), M. J. ROZENBERG[2], I. H. INOUE[3](***), H. MAKINO[4], O. GOTO[5], M. PEDIO[6] and R. CIMINO[7]

Abstract. – We investigate the electronic structure of $Ca_{1-x}Sr_xVO_3$ using photoemission spectroscopy. Core level spectra establish an electronic phase separation at the surface, leading to a distinctly different surface electronic structure compared to the bulk. Analysis of the photoemission spectra of this system allowed us to separate the surface and bulk contributions. These results help us to understand properties related to two vastly differing energy scales, namely the low-energy scale of thermal excitations ($\sim k_BT$) and the high-energy scale related to Coulomb and other electronic interactions.

monochromatized Al Kα **ΔE~0.45eV : not enough for accurate discussion**

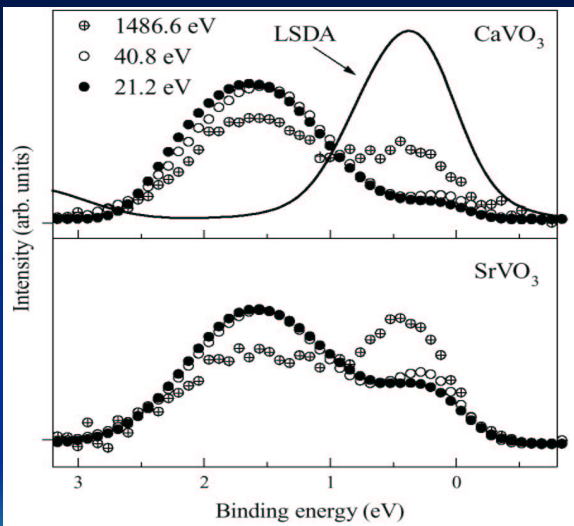


Fig. 2

single crystal

surface cleaning by repeated scraping

Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on

bulk & surface deconvoluted

bulk spectra are in agreement with DMFT cal by Hubbard Hamiltonian

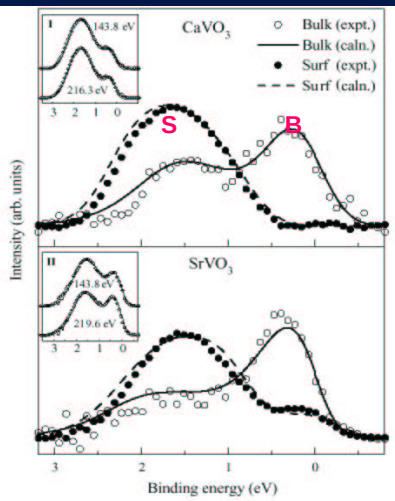
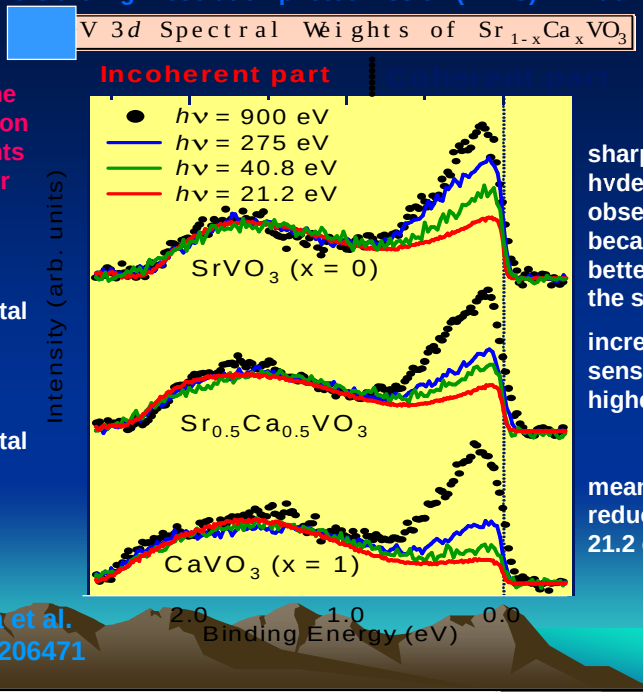


Fig. 3 – Extracted $\rho^b(\omega)$ (open circles) and $\rho^s(\omega)$ (solid circles) obtained from the spectra shown in fig. 2. The solid and dashed lines superimposed on the spectra are the results of DMFT calculations. Insets I and II show the comparison of experimental valence band photoemission results (open circles) of $CaVO_3$ and $SrVO_3$, respectively, for different photon energies along with the synthesized spectra (solid lines) obtained from $\rho^b(\omega)$ and $\rho^s(\omega)$.

How important is the high resolution photoemission (HPES) in wide hν region!!



We have done high resolution measurements on cleaved or fractured surfaces

single crystal

single crystal

polycrystal

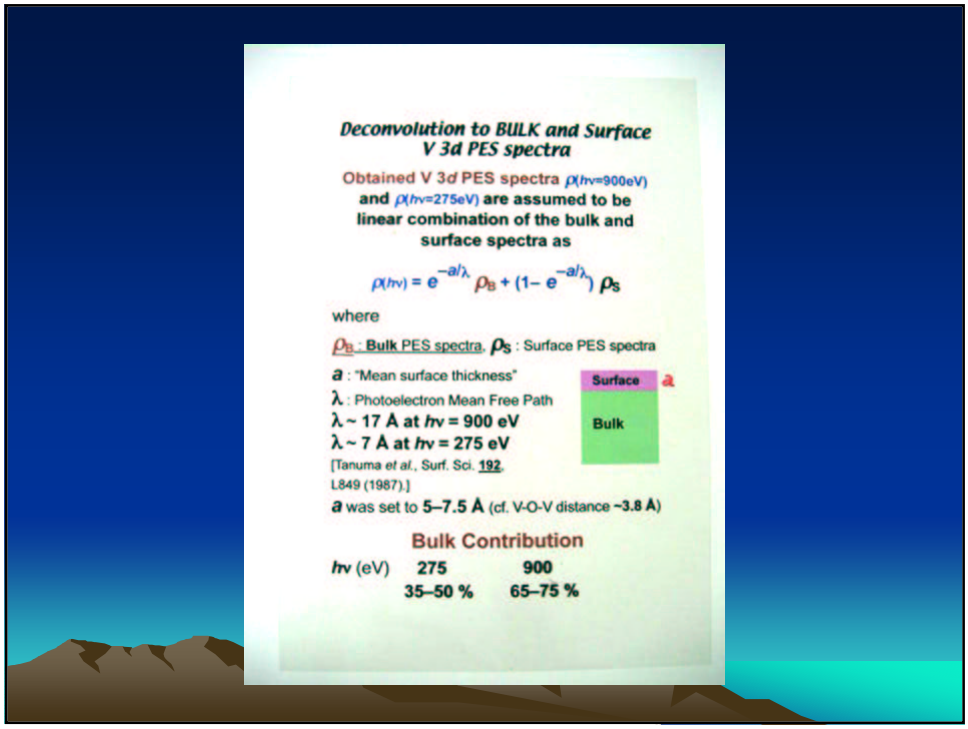
sharper hvdependence is observed because of the better quality of the surface

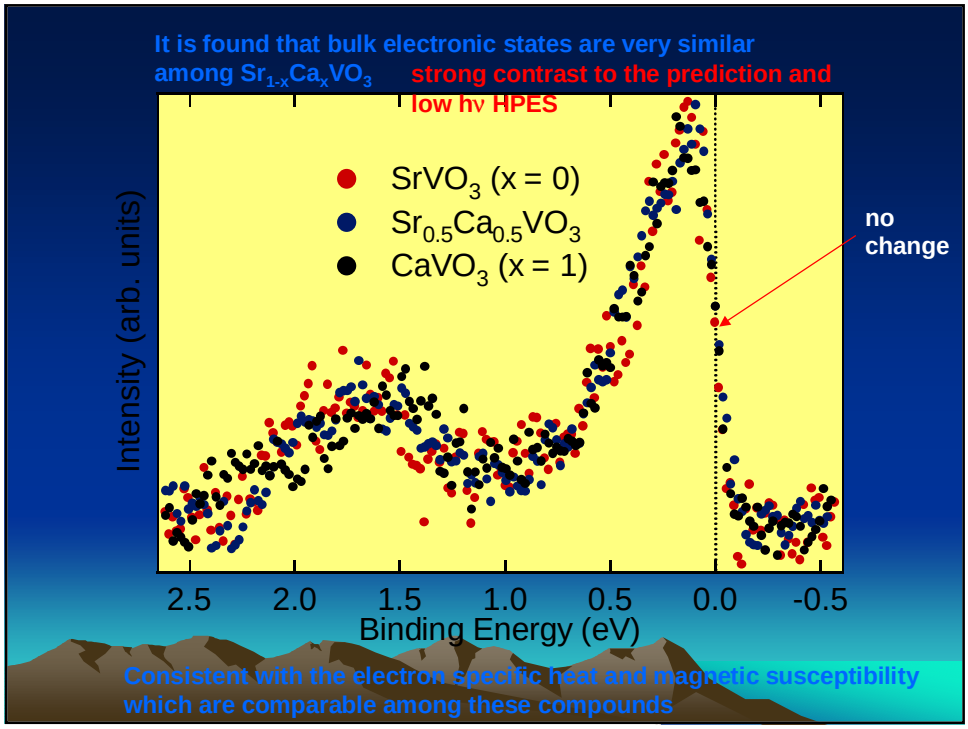
increased bulk sensitivity at higher hv

mean free path reduces down to 21.2 ev

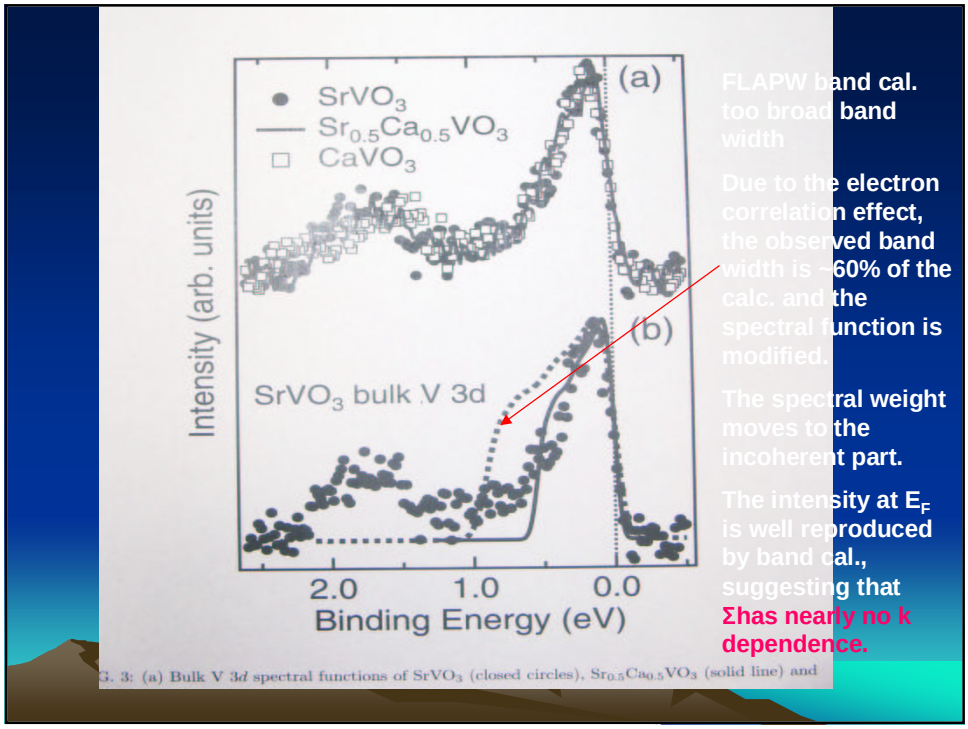
A.Sekiyama et al. cond-mat/0206471

Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on

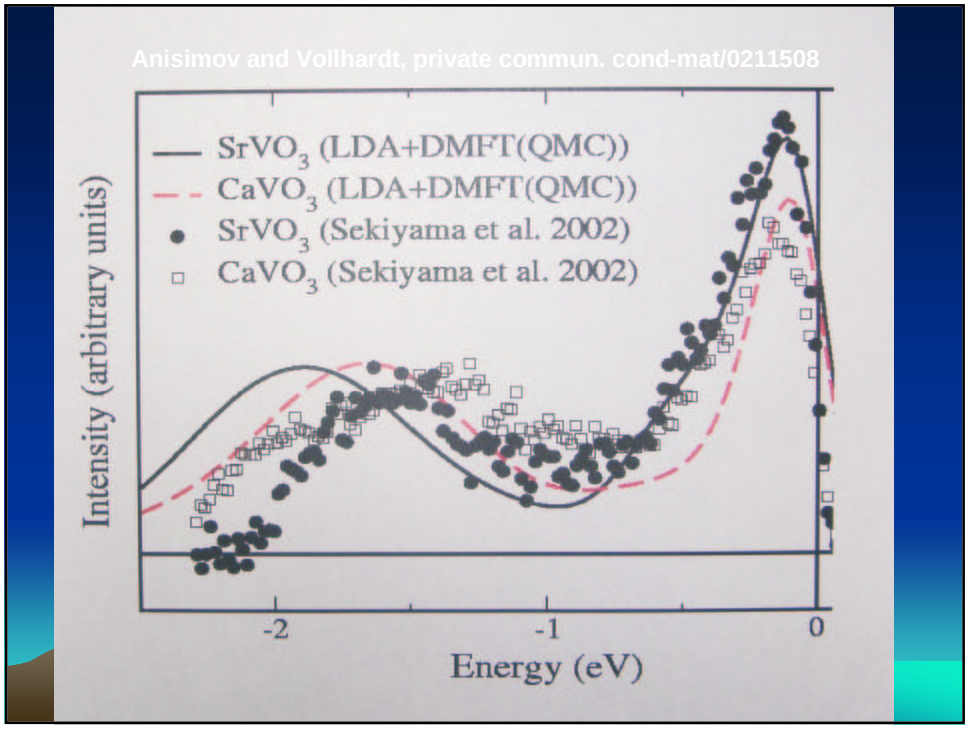




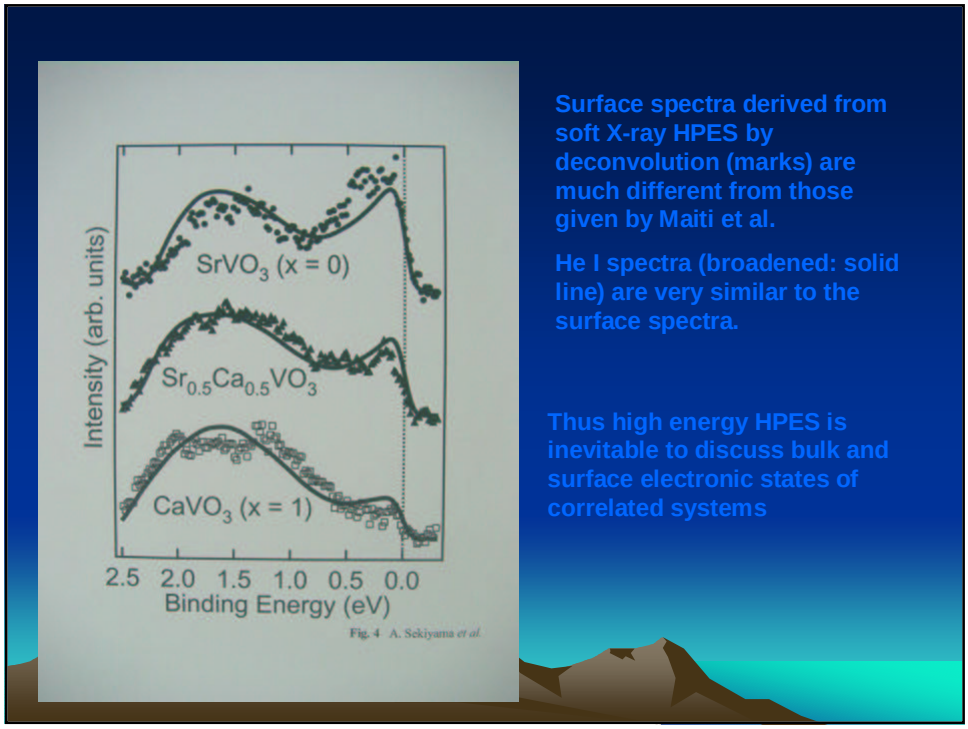
Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on

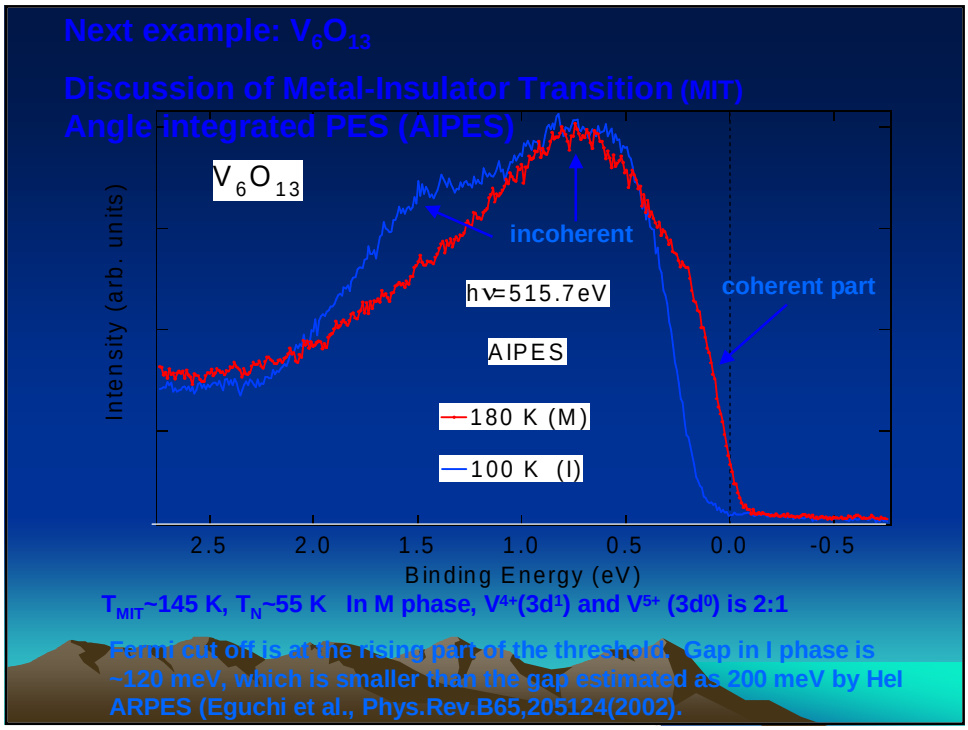


G. 3: (a) Bulk V 3*d* spectral functions of $SrVO_3$ (closed circles), $Sr_{0.5}Ca_{0.5}VO_3$ (solid line) and



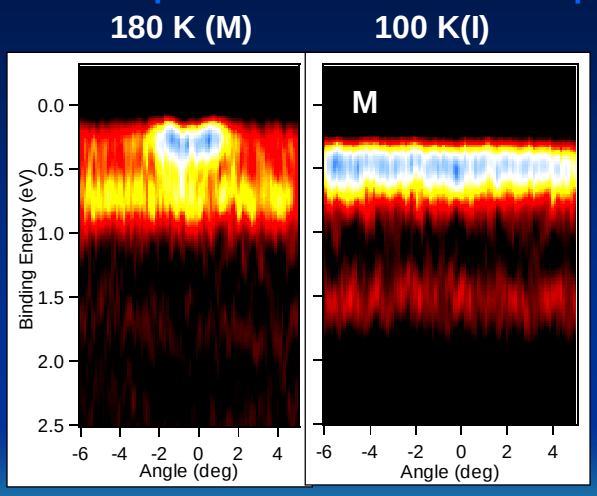
Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on





Condition for high energy ARPES
high resolution in energy & θ (Δθ<±0.2°)
photon **wave vector q=2π/λ**
hν=1,000eV • λ • 12A • q=0.52A^{-1}
q$_\perp$=0.37A^{-1} for θ=45° incidence
k$_B$=π/a =0.63(1.05)A^{-1} for a=5(3)A
q$_\perp$ • 30(18)% of 2k$_B$
photoelectron
k$_\perp$=0.51(A^{-1})(E$_K$(eV))$^{1/2}$sinθ
E$_K$=1,000eV • k$_\perp$=16.1 sinθ
q$_\perp$=0.37A^{-1} • sinθ=0.37/16.1=0.023
θ • 1.3°(k$_\perp$=0 electron emission offset)
2k$_B$ (1.26A^{-1}) ⇔ 4.4°
angular resolution
Δθ=0.2° • Δk$_\perp$=0.056(A^{-1}) • 0.045*2k$_B$

Both dispersive coherent peak and non-dispersive incoherent peak are observed in the M phase



move to the 2nd subject

In Yb compounds, Kondo peak is accessible by HPES whereas Kondo tail is accessible in Ce compounds

- In the case of Ce compounds, RPES technique is applicable, which is not effective in Yb compounds.
- However, the cross section of Yb 4f is large even in the soft X-ray region.
- Thus in both cases, bulk sensitive soft X-ray PES is feasible

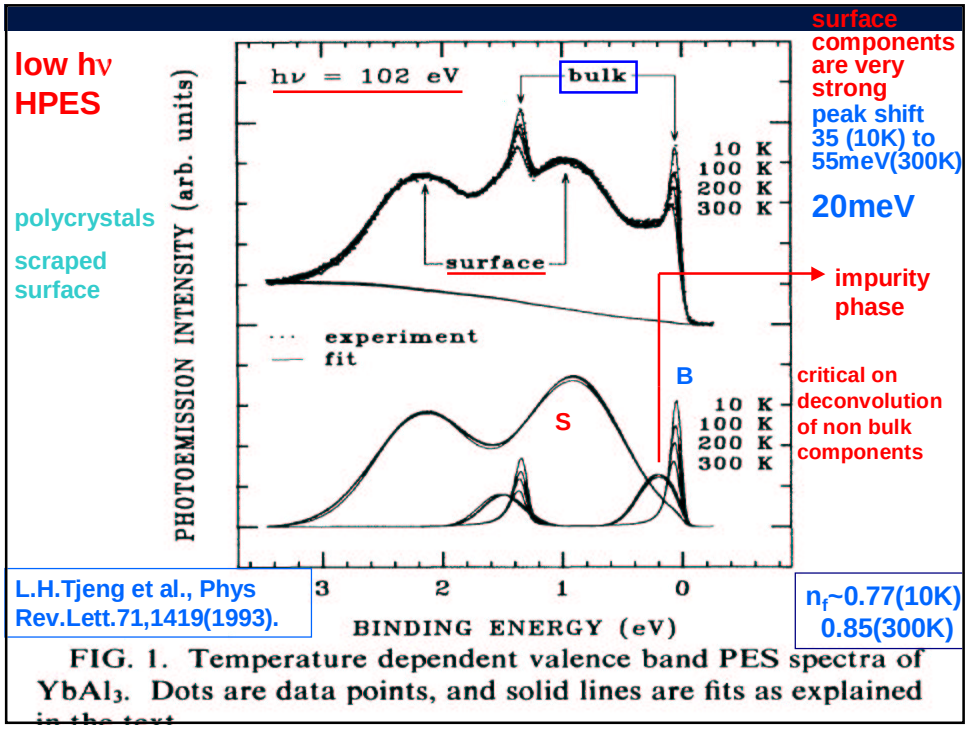
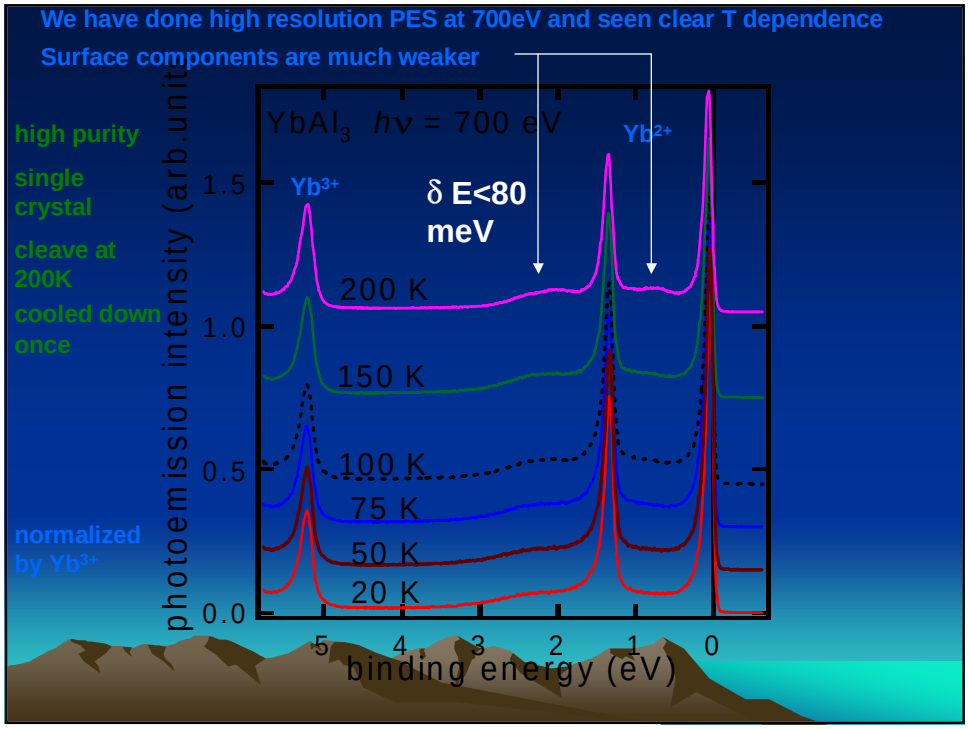
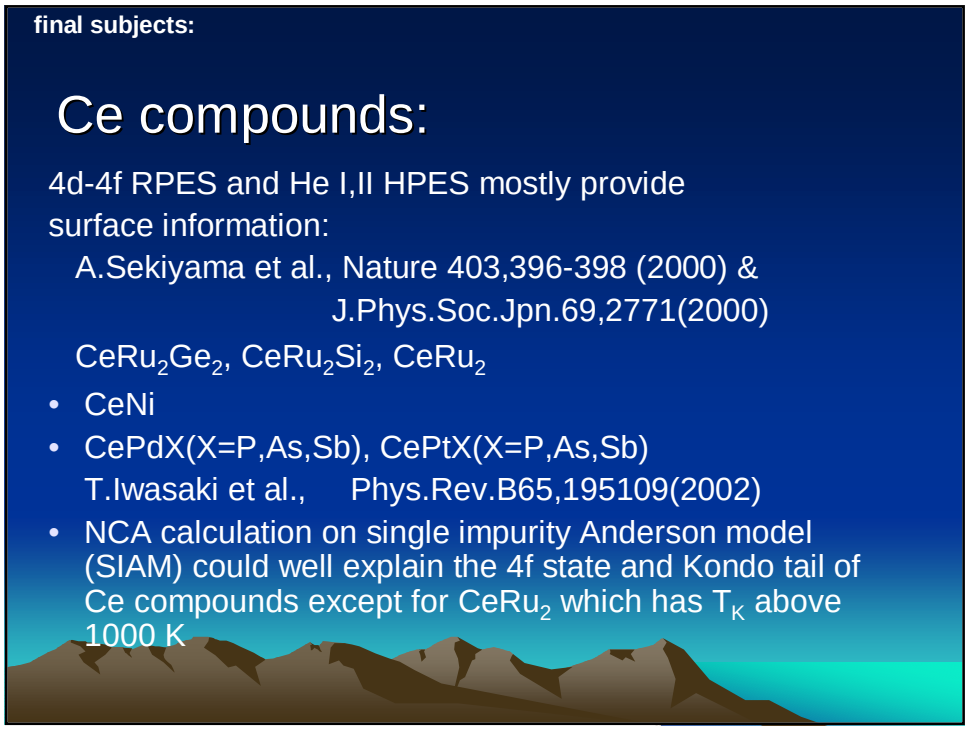


FIG. 1. Temperature dependent valence band PES spectra of $YbAl_3$. Dots are data points, and solid lines are fits as explained in the text.

Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on

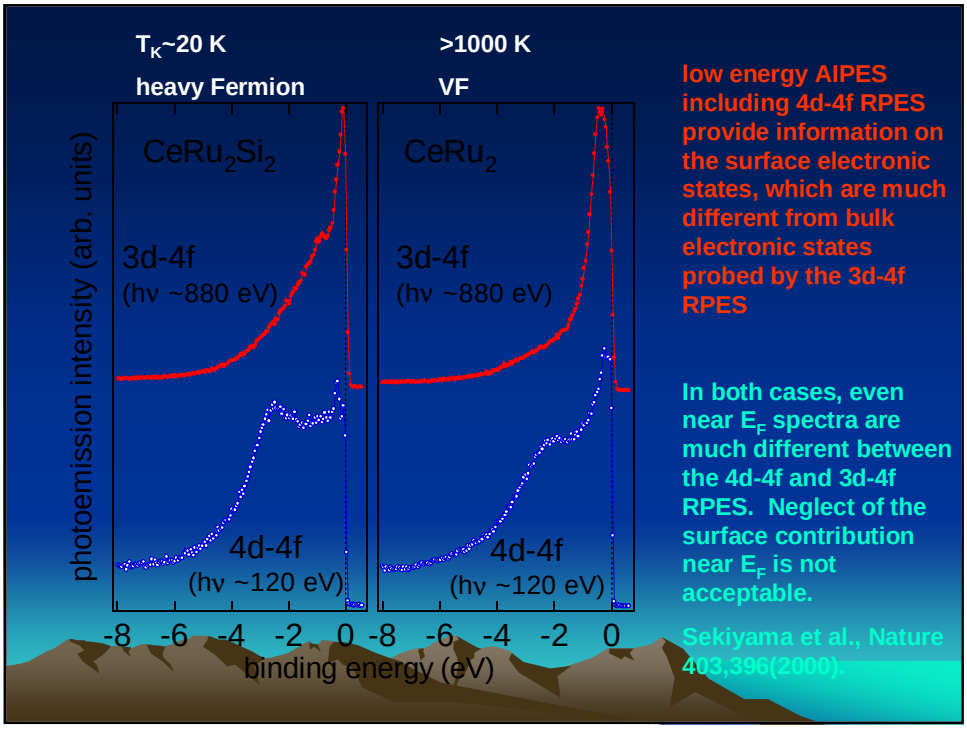




In very low T_K systems, one may think that the surface localized 4f states are not much different from the bulk electronic states, which are already localized to some extent.

One may also claim that the spectra near the E_F are not much influenced by the surface effects, because the surface states are located in the deeper E_B.

These speculations are not well grounded.

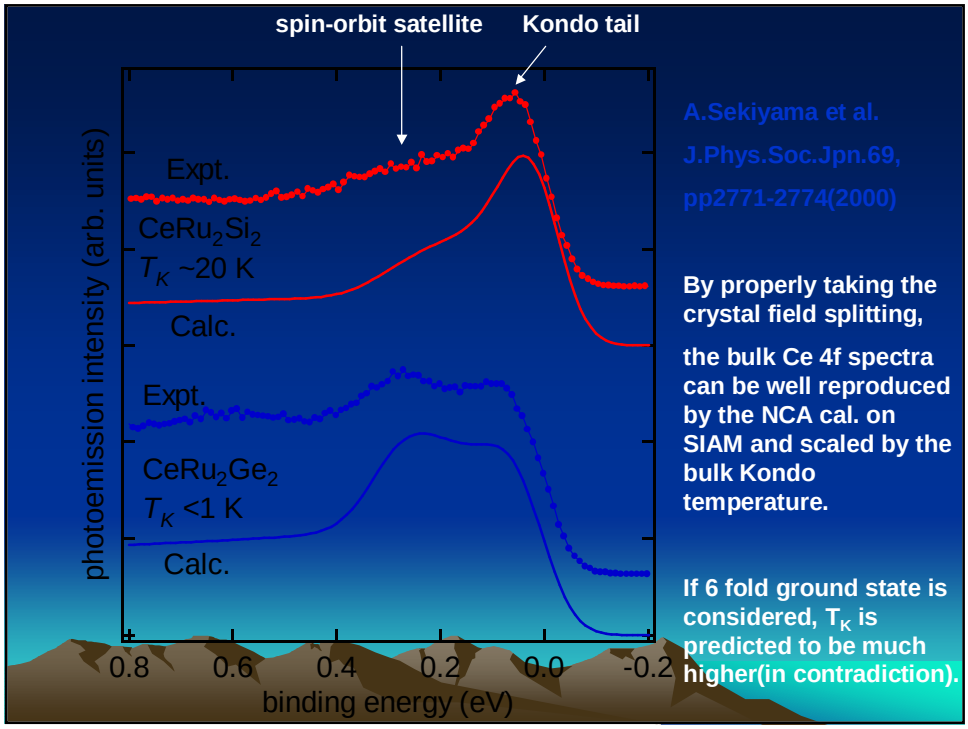


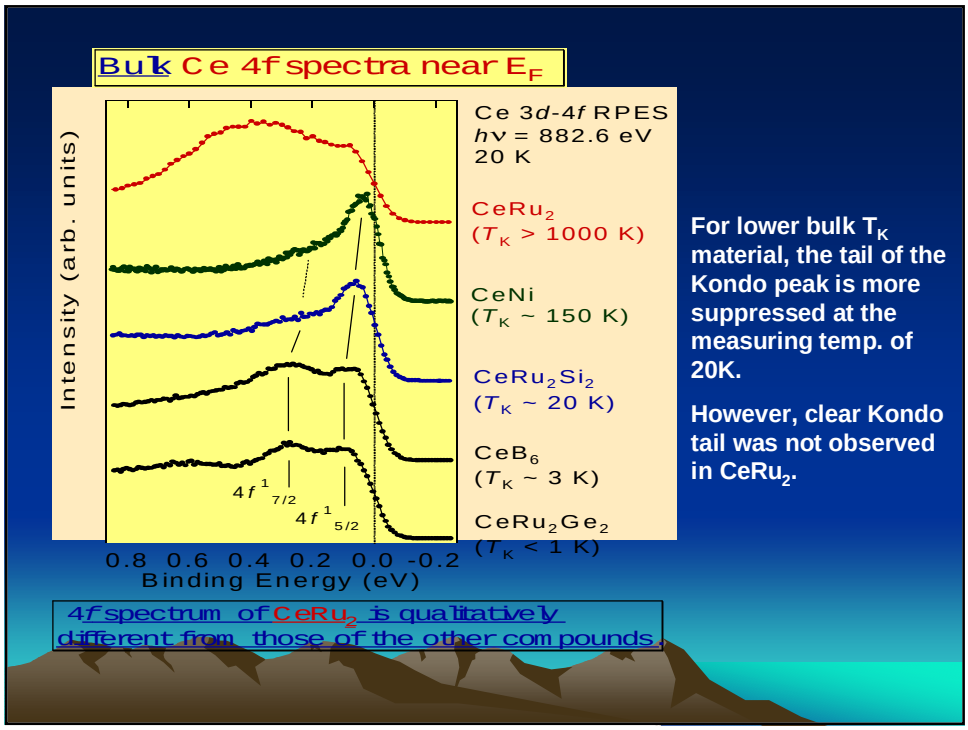
low energy AIPES including 4d-4f RPES provide information on the surface electronic states, which are much different from bulk electronic states probed by the 3d-4f RPES

In both cases, even near E_F spectra are much different between the 4d-4f and 3d-4f RPES. Neglect of the surface contribution near E_F is not acceptable.

Sekiyama et al., Nature 403,396(2000).

Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on





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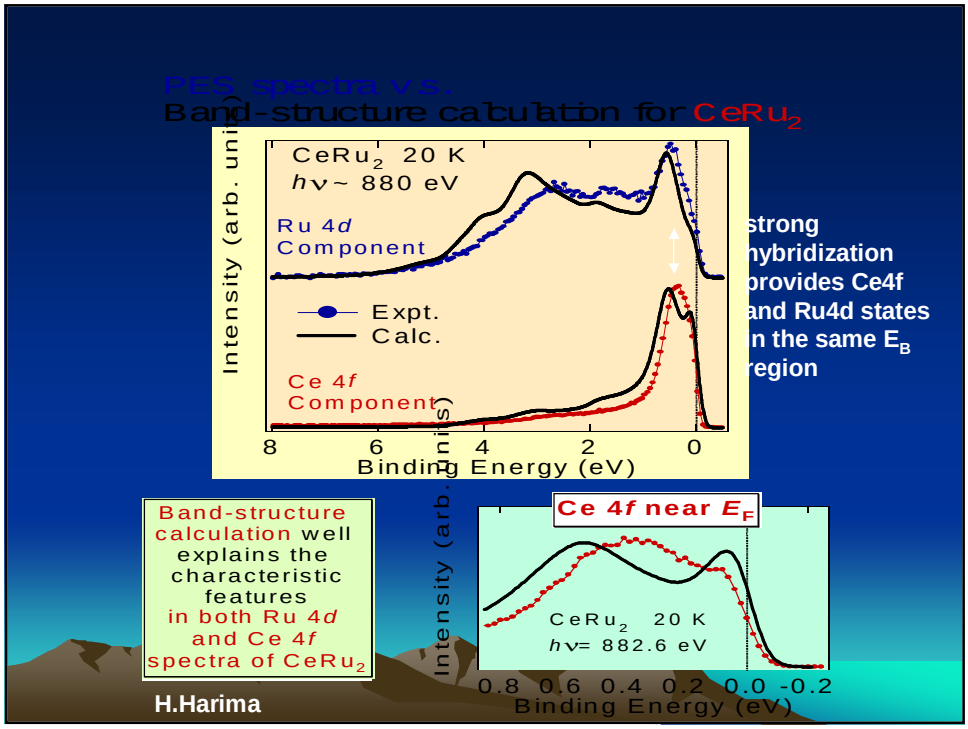
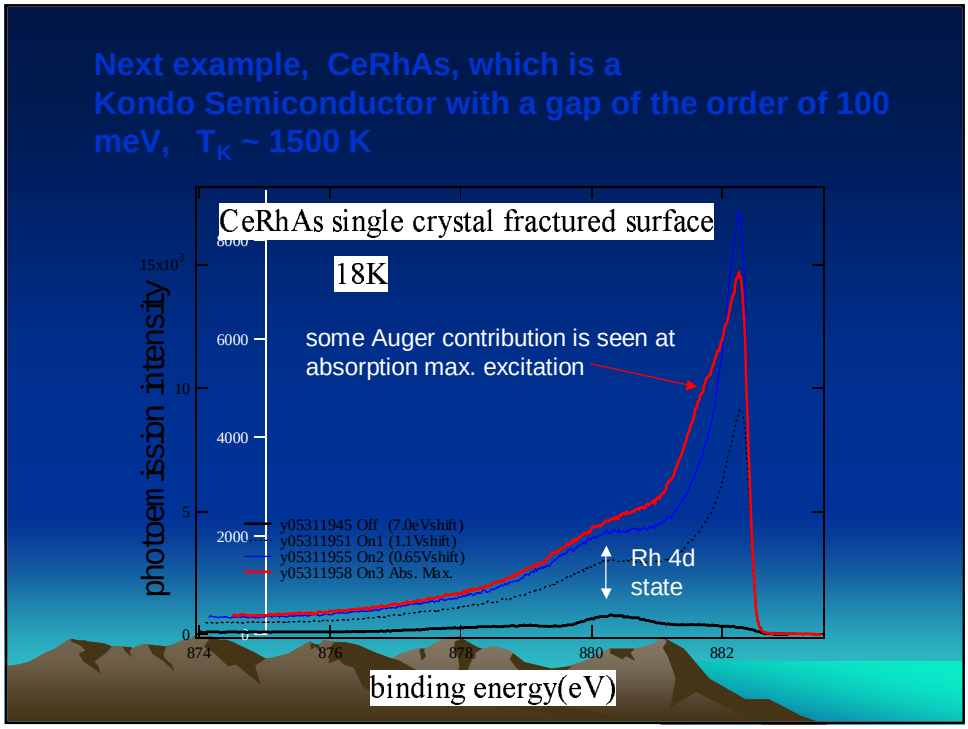


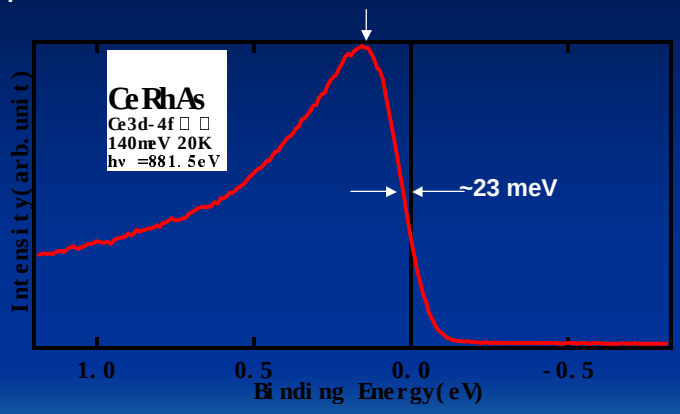


Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on

Excitation below Abs. maximum

peak is located at 140 meV possibly due to an opening of the gap

The peak in the case of CeNiSn and CePdSn is much closer to E_F (~50 meV) in our experiment



middle point is shifted back slightly and suggests an opening of a gap

spin-orbit satellite is hardly observable near 0.3 eV↔strong contrast with low hv HPES

PHYSICAL REVIEW B **66**, 155202 (2002)

Direct observation of the Ce 4*f* states in the Kondo semiconductor CeRhAs and related compounds: A high-resolution resonant photoemission study

Kenya Shimada,[1] Kenichi Kobayashi,[2] Takamasa Narimura,[2] Peter Baltzer,[1] Hirofumi Namatame,[1] Masaki Taniguchi,[1,2] Toshiaki Suemitsu,[3] Tetsuya Sasakawa,[3] and Toshiro Takabatake[3]

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(Received 13 May 2002; revised manuscript received 5 July 2002; published 3 October 2002)

Ce 4*f* derived states at the Fermi level (E_F) of the isostructural single crystals CeRhAs, CeRhSb, and CePtSn were observed directly by means of high-resolution ($\Delta E = 18$–20 meV), low-temperature (10–12 K) photoemission spectroscopy with a photon energy of $h\nu = 126$ eV. The Ce 4*f* spectrum for the Kondo semiconductor CeRhAs exhibited no peak structure near E_F, and its spectral intensity decreases monotonically above the binding energy ~90 meV, thereby forming a large gap structure. The spectrum of the semimetal CeRhSb is enhanced above ~120 meV, but decreases steeply above ~13 meV, which indicates the existence of a narrow pseudogap at E_F. A clear crystal field excitation at ~27 meV, and a weak Kondo resonance at E_F, were found in the metal CePtSn.

Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on

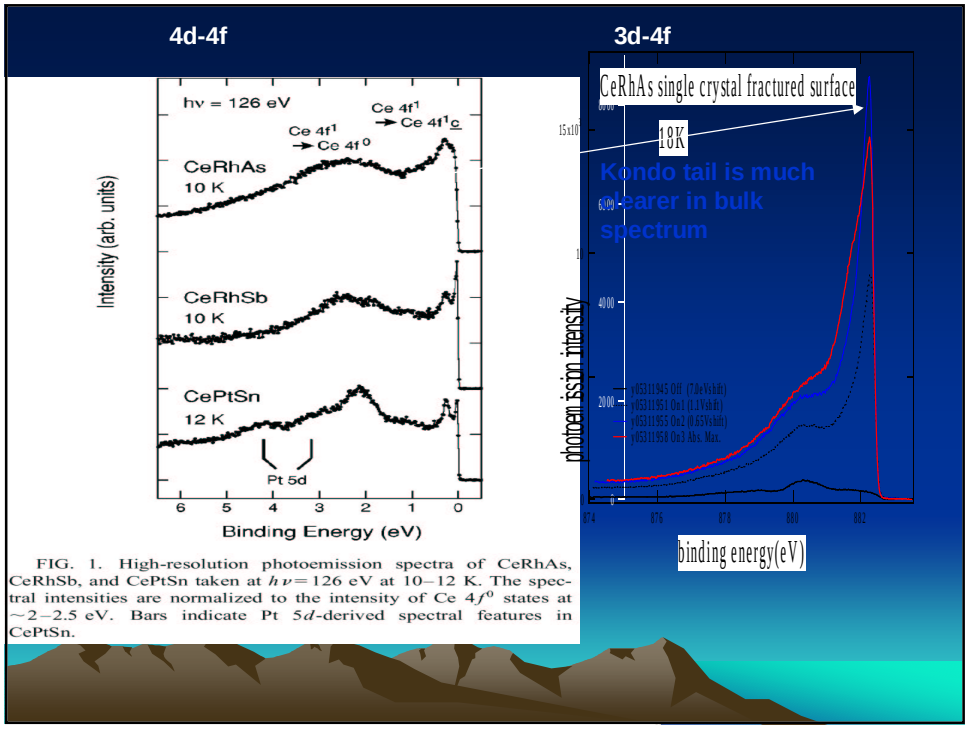

FIG. 1. High-resolution photoemission spectra of CeRhAs, CeRhSb, and CePtSn taken at $h\nu = 126$ eV at 10–12 K. The spectral intensities are normalized to the intensity of Ce $4f^0$ states at ~2–2.5 eV. Bars indicate Pt $5d$-derived spectral features in CePtSn.

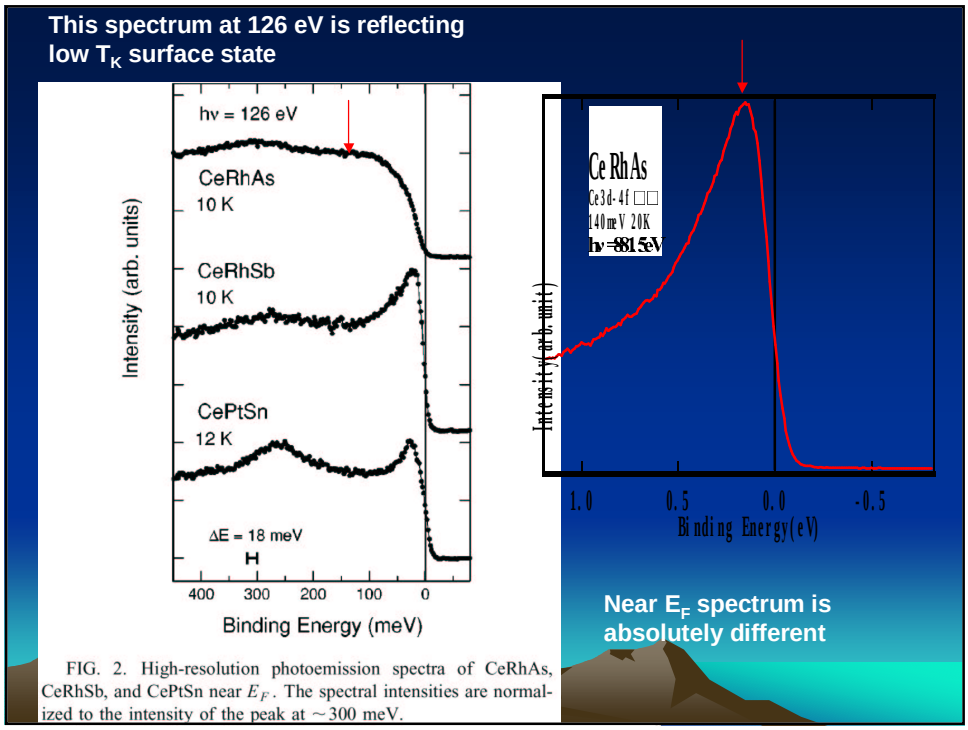

FIG. 2. High-resolution photoemission spectra of CeRhAs, CeRhSb, and CePtSn near E_F. The spectral intensities are normalized to the intensity of the peak at ~300 meV.

Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on

very low T_K system with very small $\rho V^2(E_F)$

PHYSICAL REVIEW B, VOLUME 65, 195109

High-resolution resonance photoemission study of Ce*MX* (*M*=Pt, Pd; *X*=P, As, Sb)

T. Iwasaki, A. Sekiyama, A. Yamasaki, M. Okazaki, K. Kadono, H. Utsunomiya, and S. Imada
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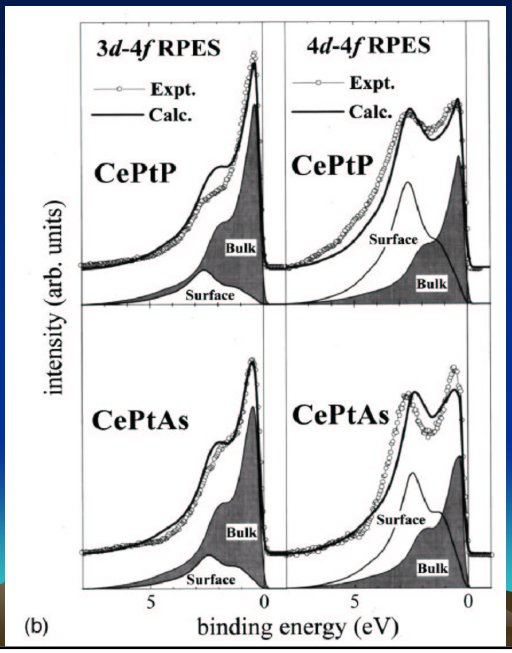
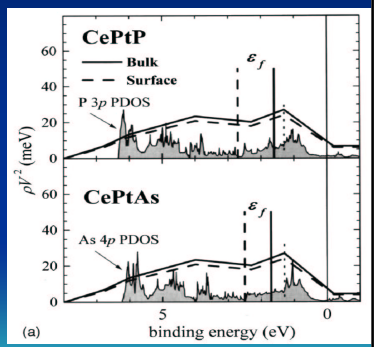
More quantitative analyses are done for CePtX and CePdX (X: P, As, Sb)

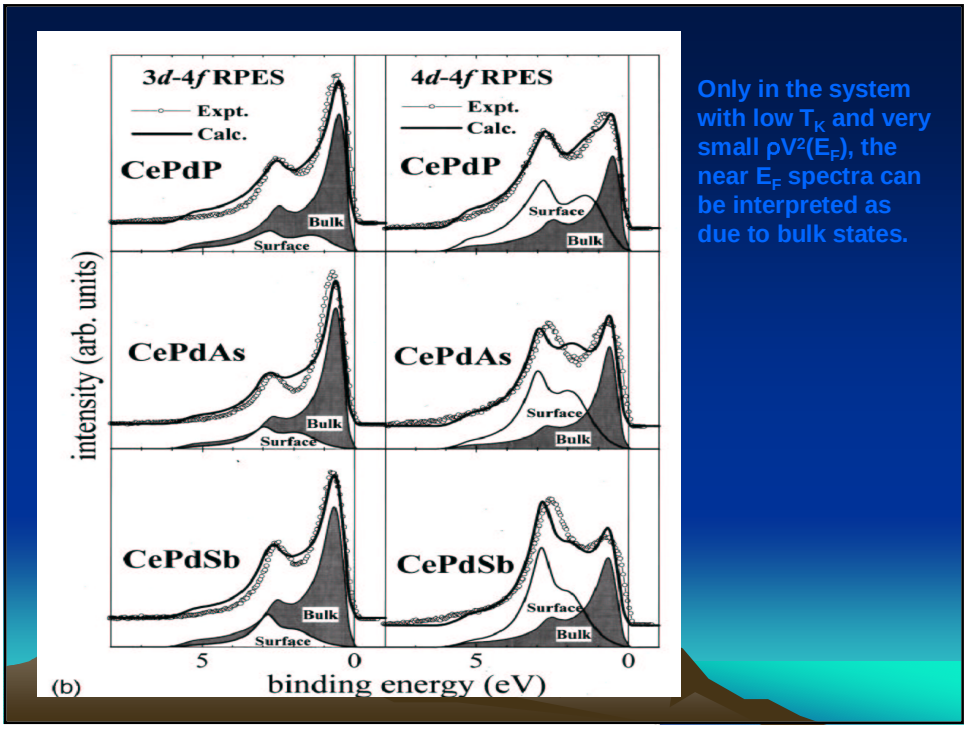


Bulk/surface weight is much higher for the 3d RPES than for 4d RPES



Hybridization decreases toward E_F because of the decreased PDOS of conduction band

Photoemission spectroscopy of correlated electron systems by the soft X-ray excitation revealing genuine bulk electronic structures: Examples of Sr1-xCaxVO3, V6O13, YbAl3, YbInCu4 and so on



Only in the system with low T_K and very small $\rho V^2(E_F)$, the near E_F spectra can be interpreted as due to bulk states.

Summary

- Soft X-ray high resolution photoemission spectroscopy (both angle integrated and resolved) can provide very important information on bulk electronic states of RE and TM compounds
- Feasibility of soft X-ray ARPES for band mapping and Fermiology is demonstrated for the first time
- Re-examination of electronic structures of many correlated electron systems by this technique is inevitable