# Electronic States and Defects in Non-Crystalline and Nano-Crystalline Alternative Transition Metal Delelectrics

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**additional support: DTRA and SRC**

## outline

**(i) high-k dielectrics - '*atomic physics'*****

**(ii) *local site symmetries* - *strong d-state correlation***
**Hund's rule - high-spin *d-state occupancy***

**(iii) *relative energies* of valence and conduction states scale with *neutral transition metal atomic energies***

**(vi) O-atom vacancy - traps - many electron theory**

**limiting factor - device performance and reliability including radiation hardness**

# introduction to many electron theory

## ground and first excited states of the H-atom

**Schrodinger equation - neglects electron spin (relativistic effect)**

**energy levels from Schrodinger equation agree with Bohr model, and experiment to within *a very small* fraction of an eV**

→ **2s and 2p, etc. at same energy**

→ **$h\nu$ (1s to 2p) ~ 13.6 [1-1/4]**

→ **10.2 eV or 121.6 nm (UV)**

**at high resolution***

**i) 2p level split: spin-orbit effect**

**many electron theory predicts**

***WW2 radar electronics**

→ **$2p_{3/2}$ - $2p_{1/2}$**

→ **$4.5 \times 10^{-5}$ eV- $\Delta\nu$ ~ 10.9 GHz**

→ **$\lambda$ = 2.7 cm (micro-wave)**

**small difference,**

**but significant with respect to getting it right**

## many electron wave functions

***ground state*** $1s^1 2p^0$ **to** ***excited state*** $1s^0 2p^1$

**term symbol:** $^{2S+1}L_J$

**L - total orbital angular momentum, S - total spin, and**
**J - maximum value of L+S - other J values *stepped down* by 1**

➔**ground state**

$1s^1 2p^0$: **L = 0, S = 1/2, and J = 1/2**

$^2S_{1/2}$ **with J =** $+1/2, -1/2$**, or**

$^2S_{1/2,-1/2}$ **(doubly degenerate)**

➔**excited state**

$1s^0 2p^1$: **L = 1, S = 1/2, and J = 3/2**

$^2P_{3/2}$ **with J values of** $+3/2$ **and** $+1/2$

**with spin-orbit splitting**

# atomic state symmetries 4- to 8-fold coordination

**spherically harmonics - *SO3* symmetry- filled core levels**

**lower symmetries for valence shell electrons**

| $SO_3$ | J | to | $O_h$ | $T_d$ |
|---|---|---|---|---|
| s | 0 | → | $A_{1g}$ | $A_1$ |
| p | 1 | → | $T_{1u}$ | $T_2$ |
| d | 2 | → | $E_g + T_{2g}$ | $E + T_2$ |
| f | 3 | → | $A_{1u} + T_{1u} + T_{2u}$ | $A_2 + T_1 + T_2$ |
| g | 4 | → | $A_{1g} + E_g + T_{2g} + T_{1u}$ | $A_1 + E_g + T_2 + T_1$ |

**basis set for *Si, Ge, III-V's, $Si(GeO_2)$, $Si(Ge)_3N_4$*, Hf high-k's**

**$A_{1g}$ and $B_{1g}$ - non-degenerate d-states - $dz^2$ and $dx^2$-$y^2$**

**$A_{2g}$ - non-degenerate d-states – dxz (or dyz , dxy)**

**E - doubly degenerate d-states - $dz^2$, $dx^2$-$y^2$**

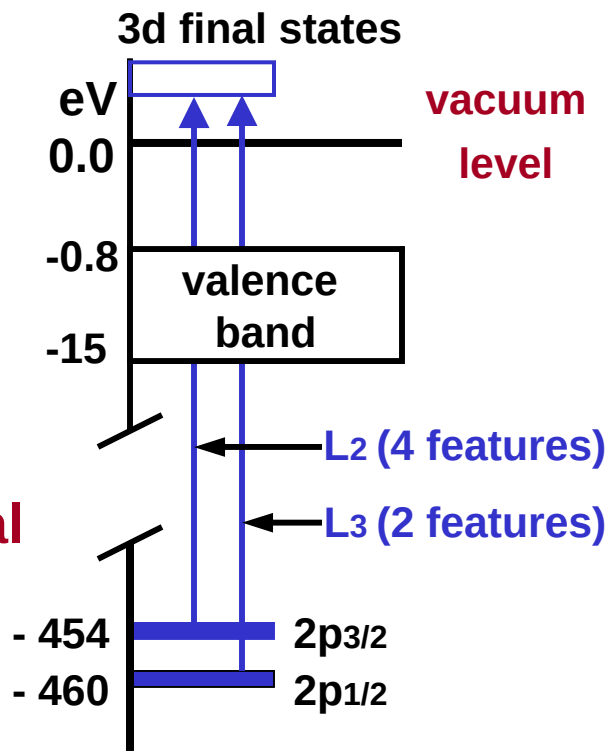
**$T_1$ - triply degenerate p-states - px, py, pz**

**$T_2$ - triply degenerate d-states - dxy, dxz, dyz**

# $L_{2,3}$ spectra $2p^6 2d^0$ to $2p^5 3d^1$ + ($2p^6 4s^0$ to $2p^5 4d^1$)satellite octahedral $Ti^{4+}$

## charge transfer multiplets theory applied to $SrTiO_3$*

$Ti^{4+}$ in $SrTiO_3$, and $TiO_2$ *Oh* octahedral




**ideal octahedral symmetry: $Ti^{4+}$ site**

**i) number of transitions same for *Oh* and *SO3*, *easier* to "count in *SO3***

**initial state**

**$2p^6 2d^0$: L = 0, S = 0, J =0**

**$^{2S+1}L_J = {}^1S_0$ (L = 0)**

**final state**

**$2p^5 2d^1$**

**L = 3, S = -1/2 + 1/2 = 0**

**$^{2S+1}L_J = {}^1F_{3,2,1}$ (L = 3)**


*F.M.F. de Groot et al, Phys. 42, 928 (1990);Phys. Rev. 42, 5459 (1990).

*F. de Groot, A. Kotani, *Core level spectroscopy of solids* (Boca Raton, CRC Press, 2008).

# $L_{2,3}$ spectra $2p^6sd^0$ to $2p^53d^1$

**irreducible representation (IR)/ground state; $A_{1g}$**

**$A_{1g}$ is a one-dimensional symmetric "d-like" state**

**final states must have "p-like" $T_{1u}$ symmetries**

**$< A_{1g} \mid T_{1u} > = 0$, equivalent to $\Delta L = \pm 1$**

ground state

| $SO_3$ | J | to | $O_h$ |
|---|---|---|---|
| s | 0 | → | $A_{1g}$ |
| p | 1 | → | $T_{1u}$ |
| d | 2 | → | $E_g + T_{2g}$ |
| f | 3 | → | $A_{1u} + T_{1u} + T_{2u}$ |
| g | 4 | → | $A_{1g} + E_g + T_{2g} + T_{1u}$ |

triply degenerate final states
different $m_l$ and $j$

3 states

+

3 states

= 6 spectral features

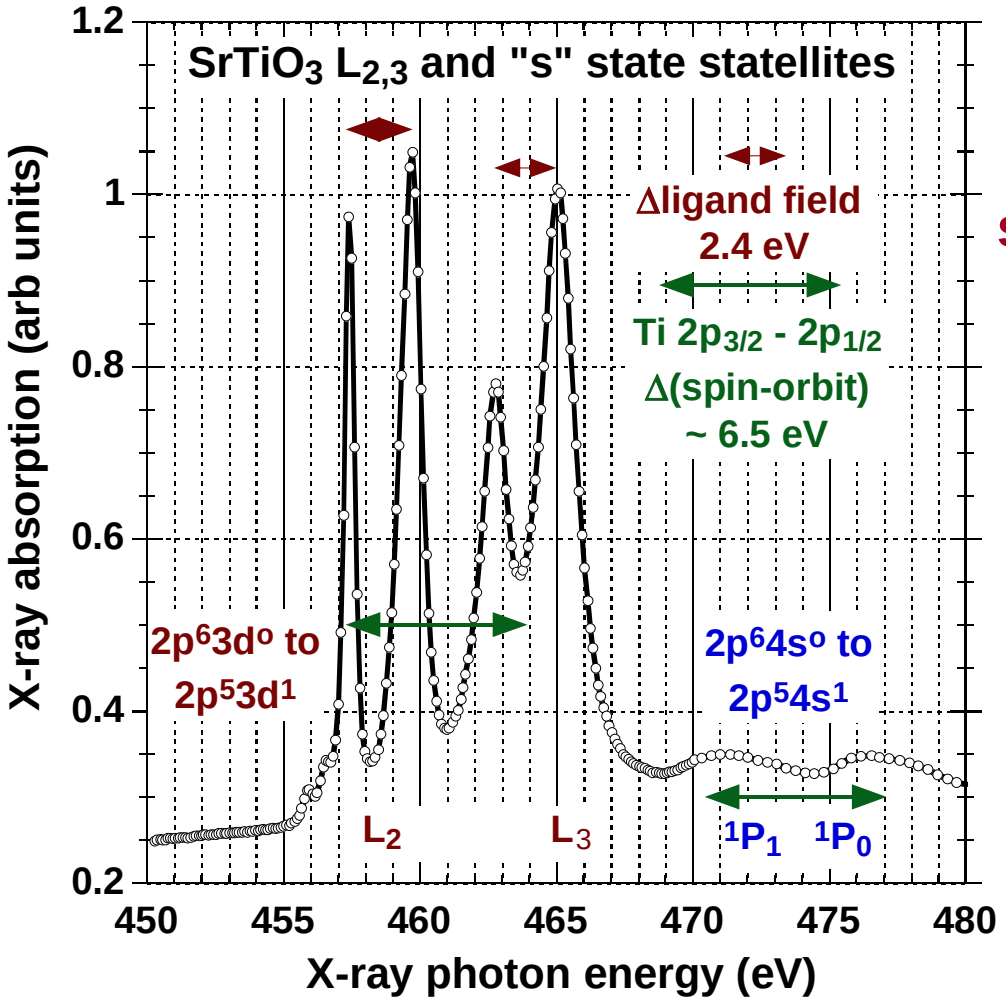
# $L_{2,3}$ $SrTiO_3$

## $Ti^{4+}$ – ideal octahedral symmetry, $O_h$

**large energy difference between Ti atomic 3d and 4s states (-11 eV and - 6 eV, respectively) expect and observe 6 features**

**$L_{2,3}$ spectra $2p^6sd^0$ to $2p^53d^1$**

**4 features in $L_2$ ($2p_{3/2}$) 2 in $L_3$ ($2p_{1/2}$)**



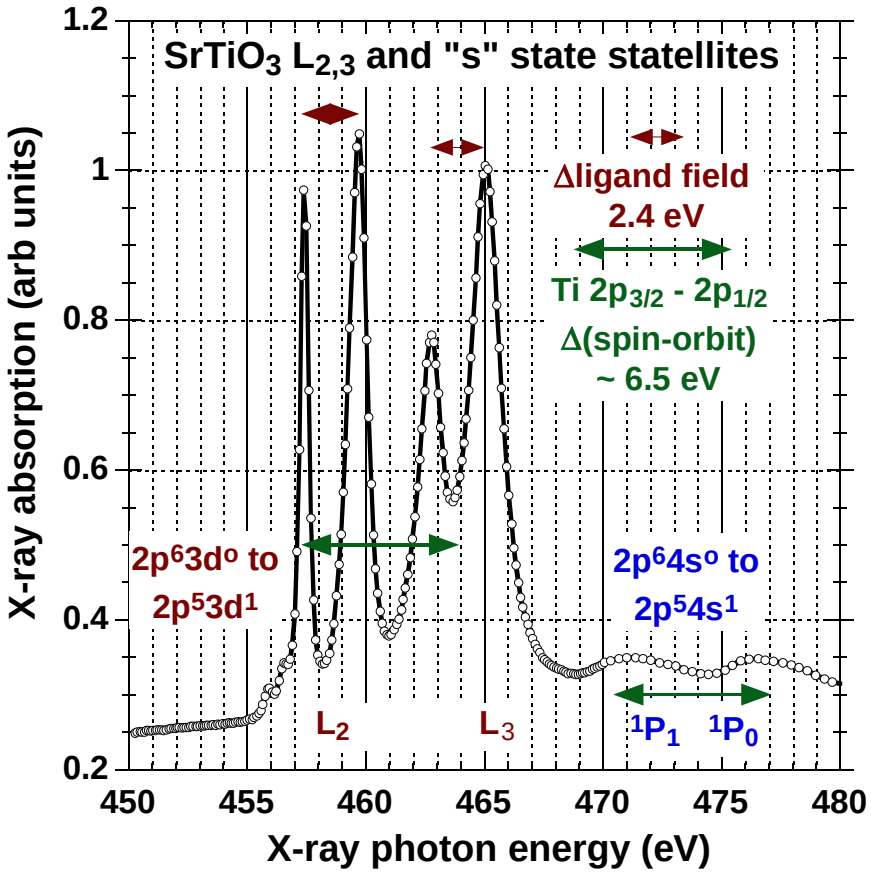

**satellite features $2p^64s^0$ to $2p^54s^1$**

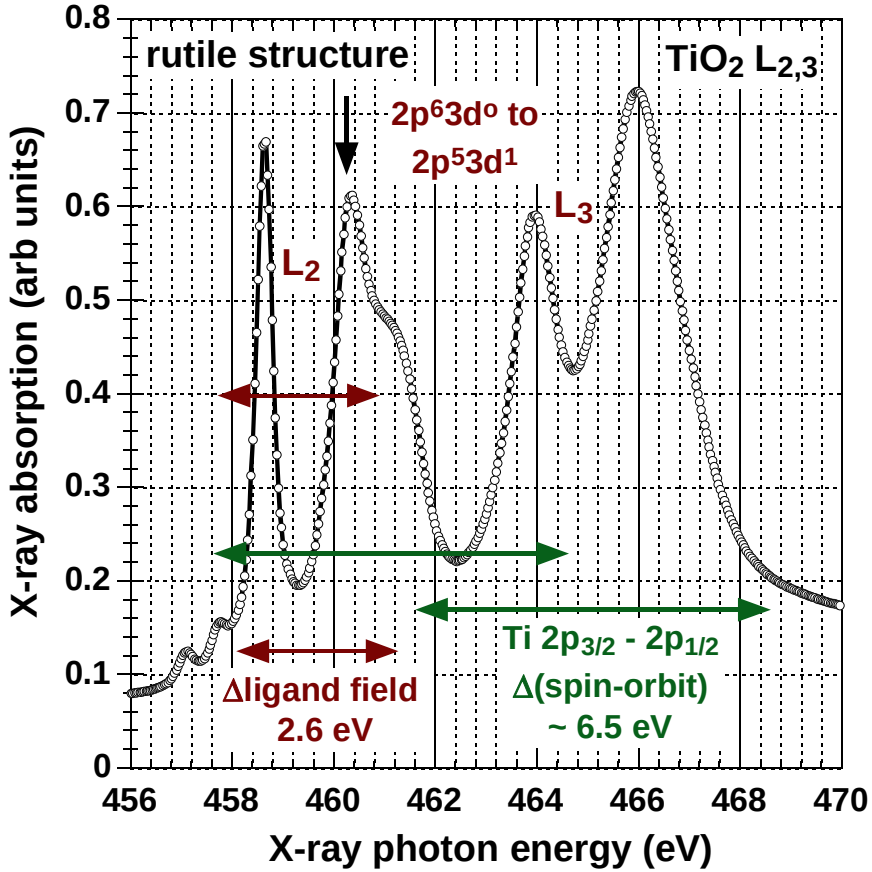
**X-ray photon energies > $L_{2,3}$ correlates with difference of 5 eV between 3d and 4s Ti atomic states**

# primitive unit cell distortion in $TiO_2$ grown on Ge template

## elongation of unit cell in z-direction

## removes 2 fold degeneracy of $e_g$ feature in $L_2$



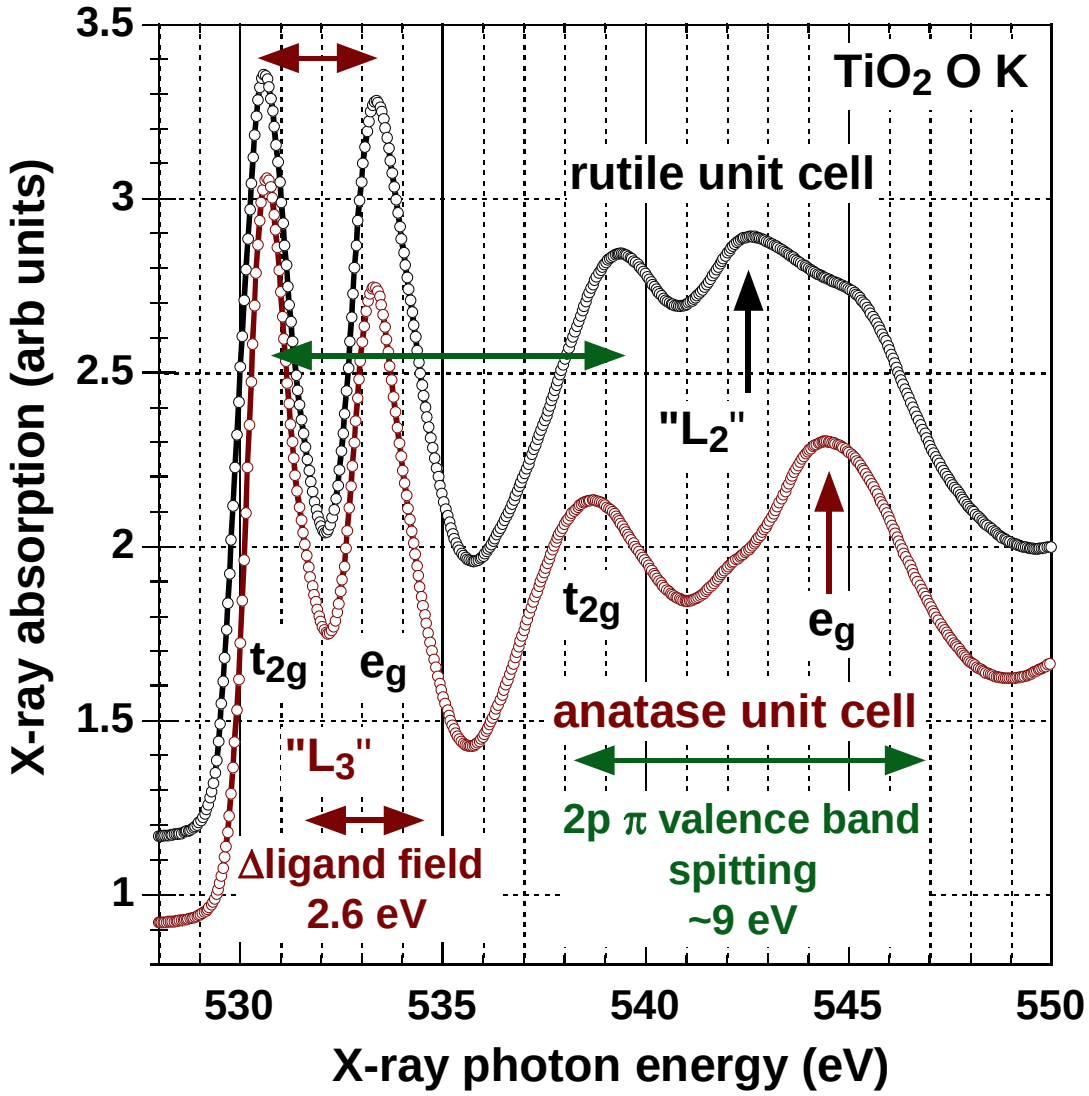




**ideal octahedron -- *Oh* symmetry**

**tetragonal distortion elongated in z-direction**

# differences in $L_{2,3}$ between rutile and anatase unit cells

## "transported" to O K edge, and then into visible, vacuum ultra-violet (VUV) spectra as well




(i) corrects previous interpretations of de Groot et al. conduction band is not joint DOS from Ti and Partial DOS!!*

(ii) connection between $L_{2,3}$ and OK implications for band edge defects

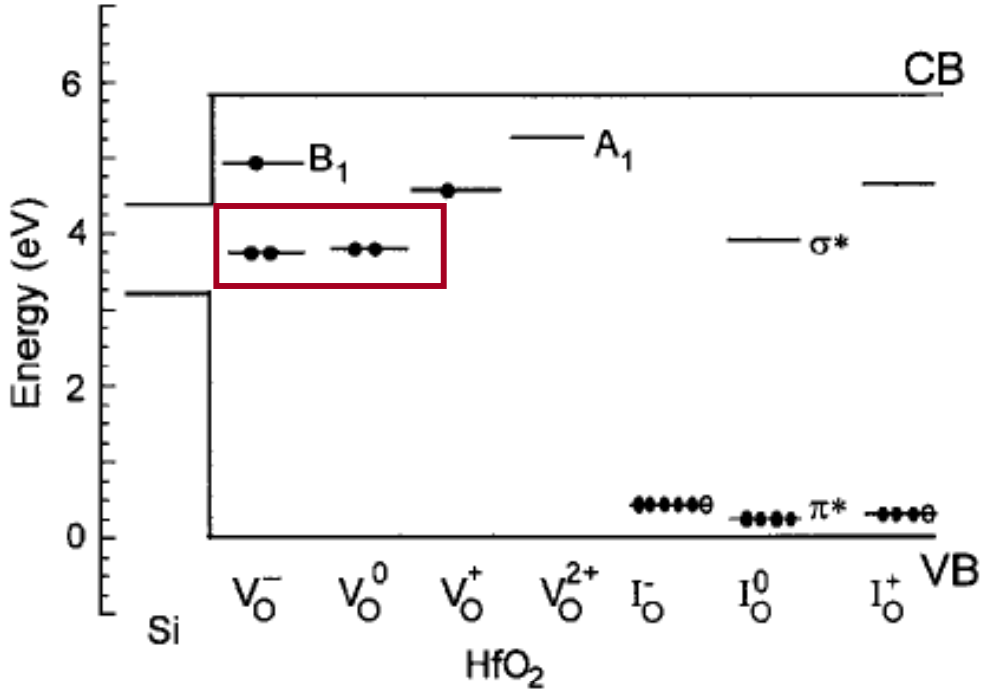
* deGroot wrong!!

**introduction to O-vacancy issues**

**many body theory gives proper interpretation of experiments,**
**other theories do not**

**Robertson, Shlugger, etc...**

**O-vacancy theory $HfO_2$, $ZrO_2$**



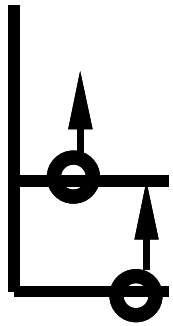

**many electron theory**

**ground state**

**$^3F$ $^3T1g$ J = 1/2,3/2**

**high spin occupancy**

**$d^2$ state**



**schematic representation of $d^2$ occupied states**

**three serious problems**

**➔double or low-spin occupancy of Hf(Zr) d-states**

**R,S ignored Hund's rules, and H Bethe 1929!!**

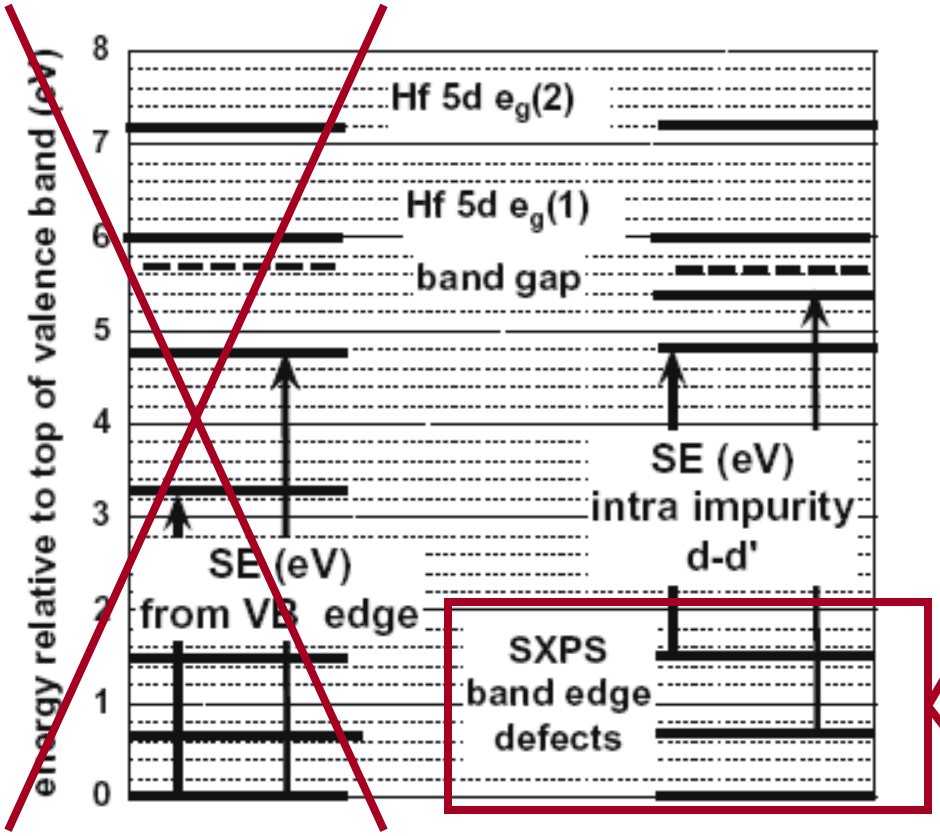
**encouraged incorrect interpretation of SE,**

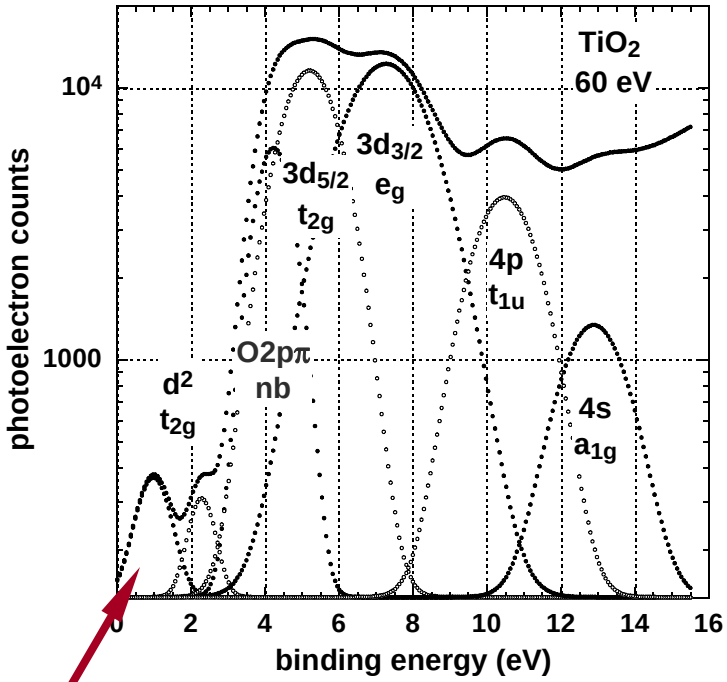
**UCB and ISMT groups**

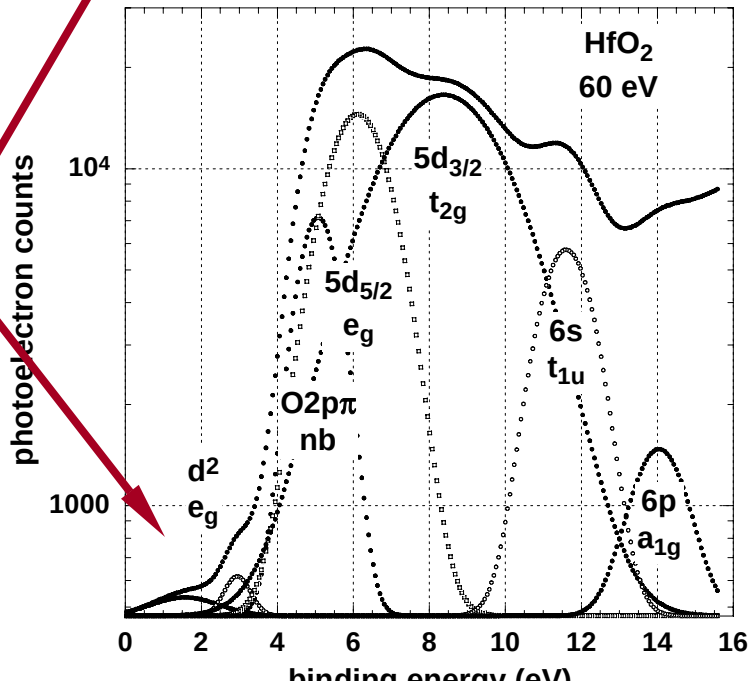
**➔ignored NCSU group**

**valence band spectra**

# UCB and ISMT assigned SE features wrt to top of valence band




**SXPS results confirm R,S had ground state at wrong energy**

**medium range order (SRO) in $SiO_2$**

**MRO associated with d-states - non-degenerate A's, B's, doubly degenerate E's, and triply degenerate p-like $T_1$'s and d-like $T_2$'s**

**this is what makes $SiO_2$, and potentially $GeO_2$, and their oxynitrides unique with respect to band edge defect states**

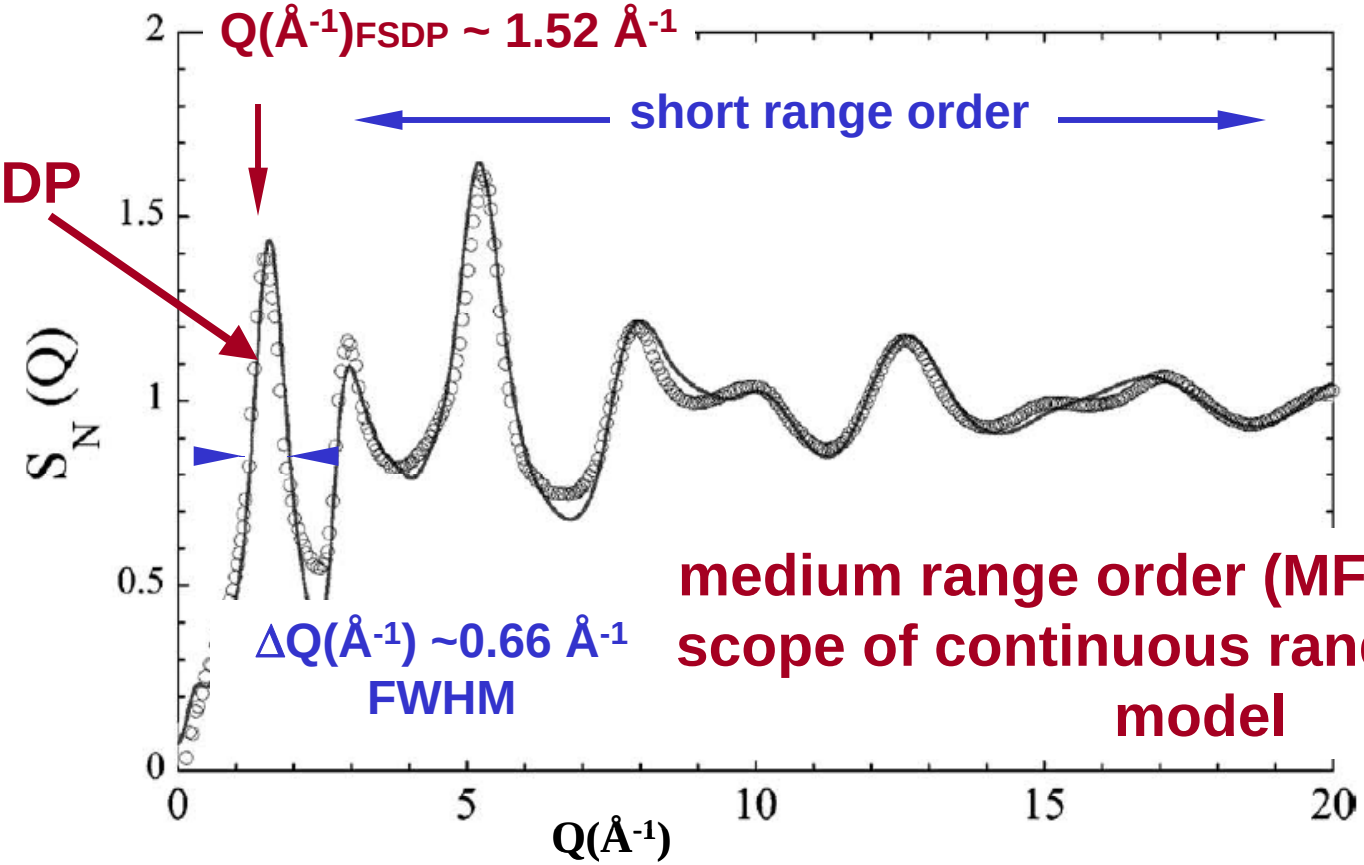
**prelude to rest of story**

**major accomplishment is this fundamental intrinsic connection between many electron theory, synchrotron X-ray spectroscopy and defects**

**➔dielectrics with band edge $A_{1g}$ "s-like" states OK, only positive charge after radiation dosing – $SiO_2$**

**➔$HfO_2$, etc. with $e_g$ or $t_{2g}$ - O-vacancy/negative ion electron traps – negative charge after radiation dosing**

# first sharp diffraction peak* in structure factor, $S_N$, for $SiO_2$




**medium range order (MFO) is beyond scope of continuous random network model**

**$S_N(Q)$ is Fourier transform of diffraction intensity**

**two MRO length scales**

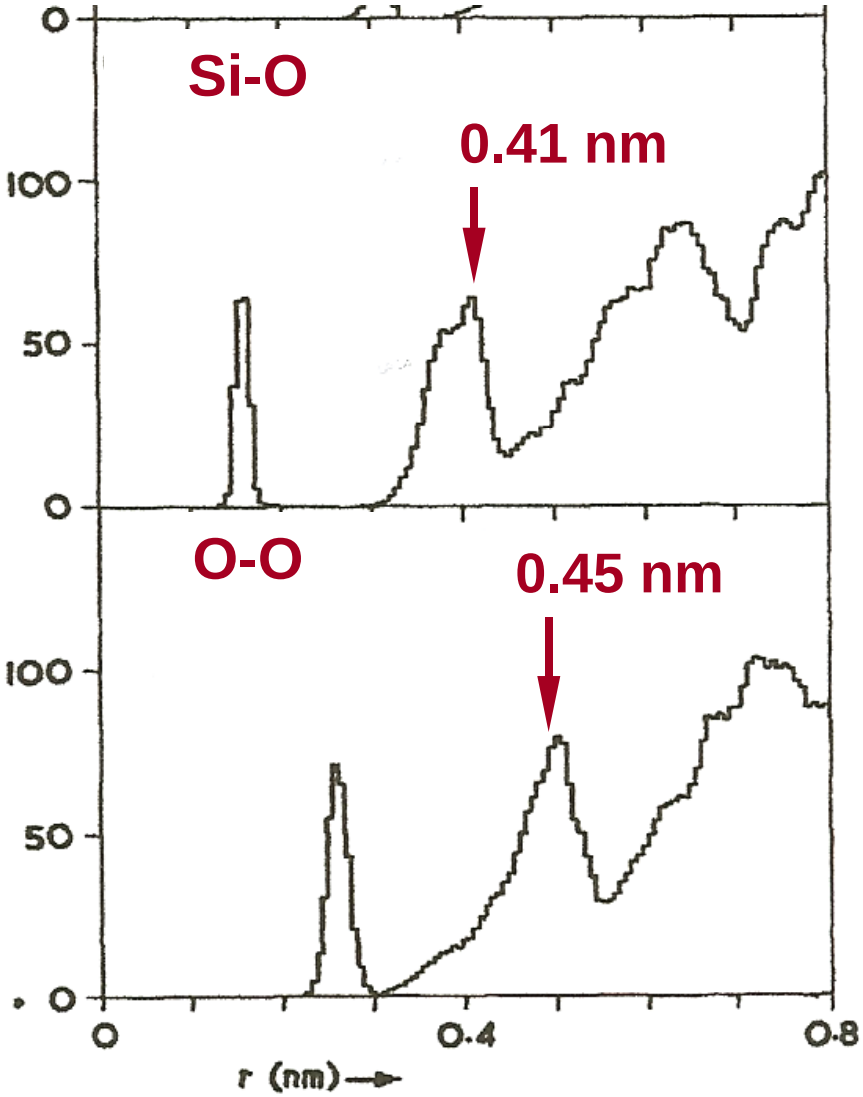
**peak position: correlation length, $\lambda_{corr} \sim 2\pi / Q(Å^{-1})$, ~0.4 nm**

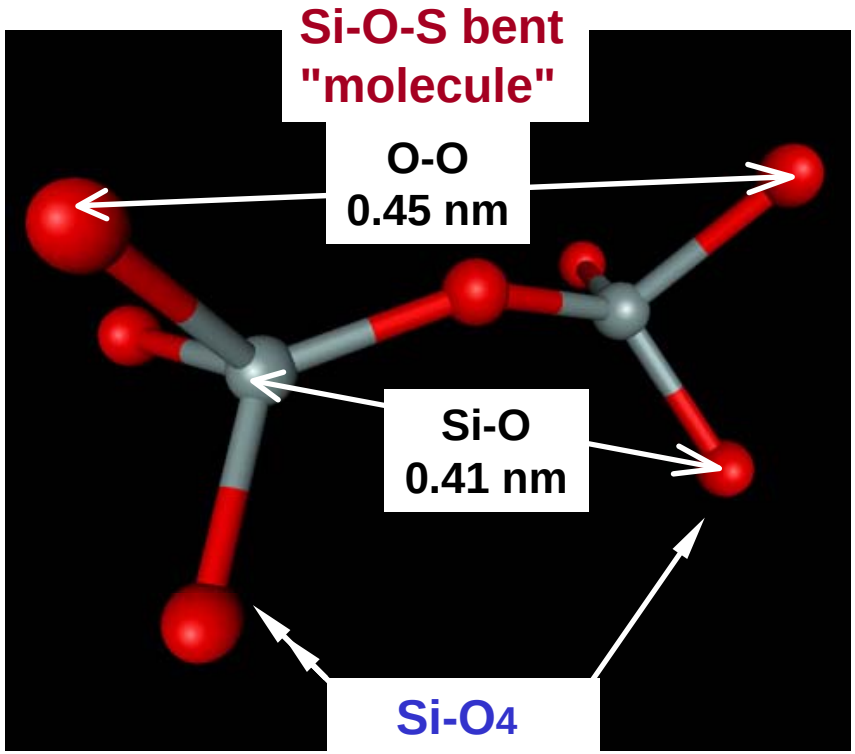
**FWHM: coherence length ~ $\lambda_{coh} \sim 2\pi / \Delta Q(Å^{-1})$, ~0.95 nm**

*J Du & LR Corrales, Phys Rev B 72, 092201 (2005).

# $S_N(Q)$* and Bell and Dean** saw it "brushed it off!!"

## Si-O 3rd and O-O 4th neighbor distances not predicted by CRNs




$\lambda_{corr} \sim 2\pi / Q(Å^{-1})$, ~0.4 nm

intra-six member ring

$\lambda_{coh} \sim 2\pi / \Delta Q(Å^{-1})$, ~0.95 nm

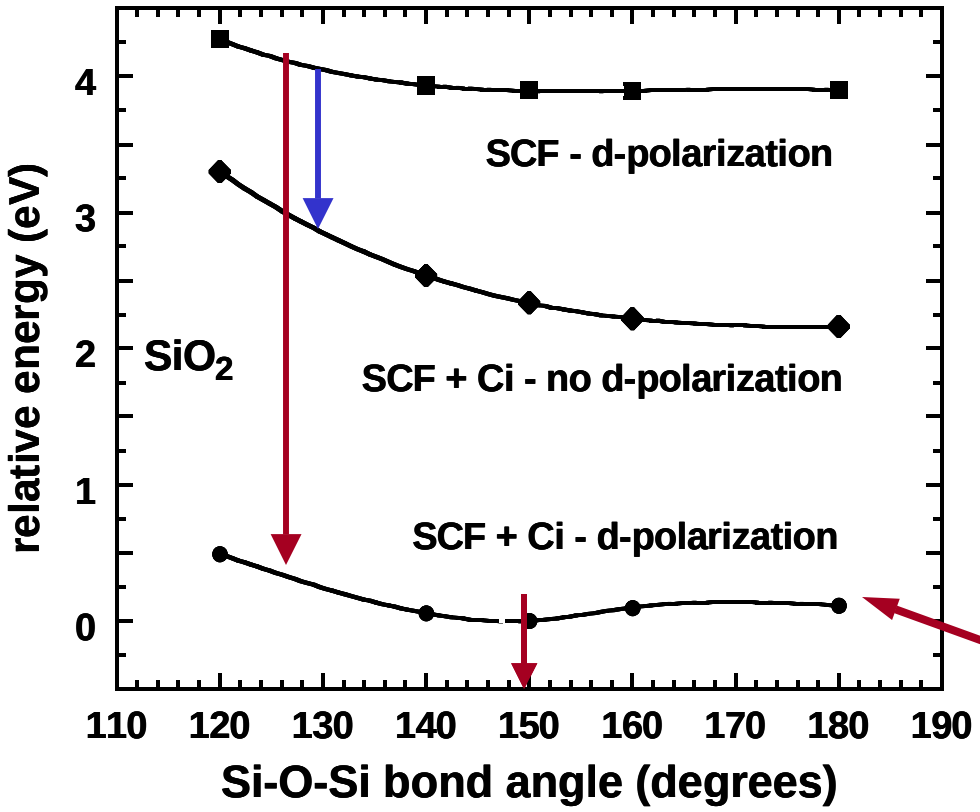
connected 6-member rings

*J Du & LR Corrales, Phys Rev B 72, 092201 (2005).

**RJ Bell and P Dean, Philos. Mag. 25 (No. 6) 1381-1398 (1972).

# relative energy vs Si-O-Si bond angle

## Si-Si distance fixed - 0.31 nm - O'Keefe and Hyde (1978)




**Hartree-Fock (SCF) with gaussian d-orbitals (polarization) on Si**

**SCF + configuration interaction (CI) optimization (no d-orbitals)**

**SCF + CI with d-orbitals**

$SiO_2$ - 19±2° i) N-L* 17±2° ii) M-W** >30°

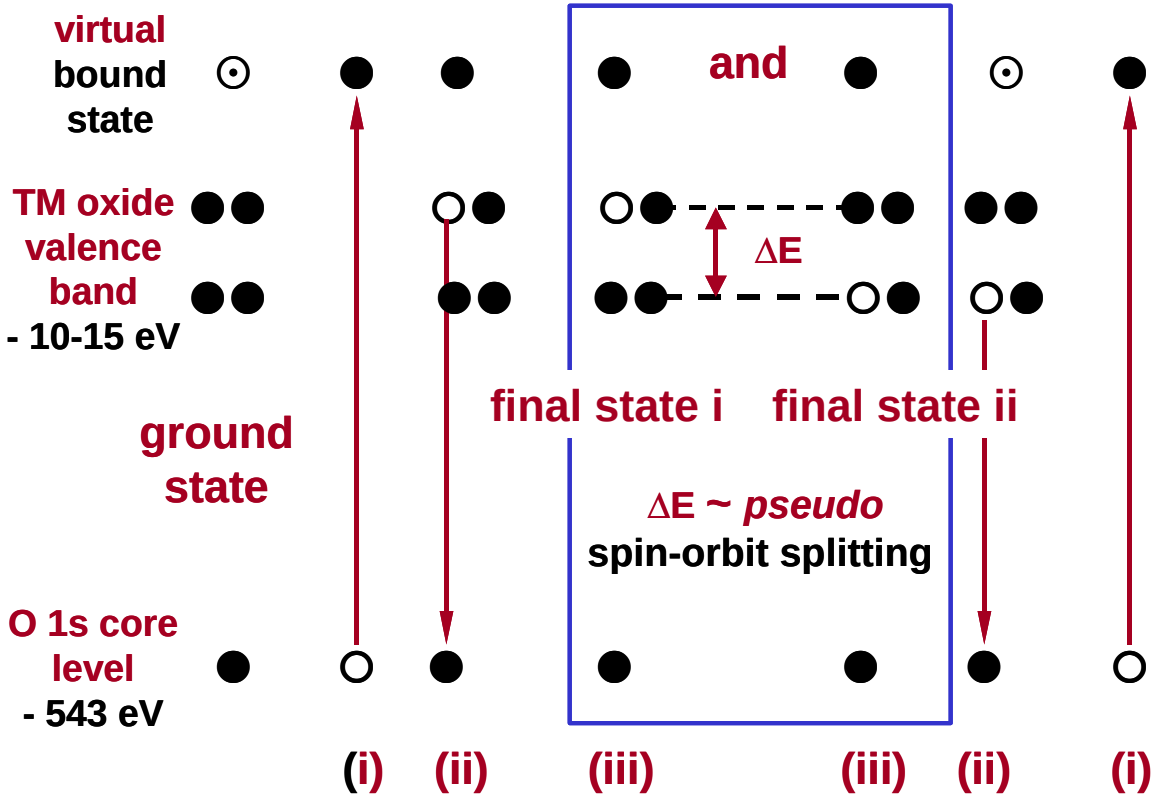
$GeO_2$ - 11.5±1.5° i) N-L* 15±2°


i) N-L*- J. Neufeind and K.-D. Liss, Bur Bunsen Phys Chem 100, 1341 (1996).

ii) M-W** - R.L. Mozzi and B.E. Warren, J. Appl. Cryst. 2, 164 (1969).

# O K edge excitations - coherent process for $SiO_2$ OK edge

## (i) x-ray excitation to to virtual bound state and
## (ii) 1s core hole filling form O 2p $\pi/\sigma$ valence band states



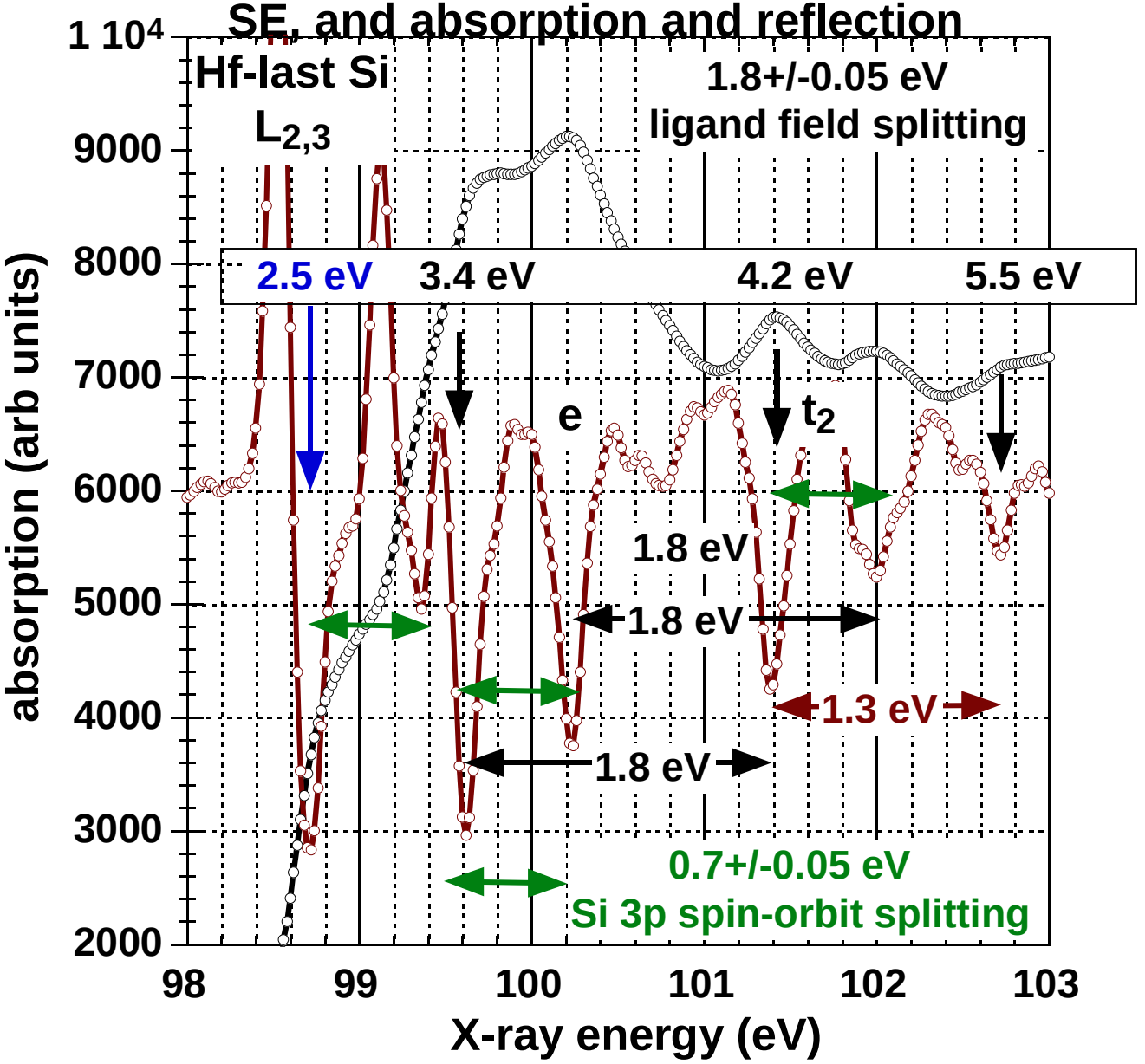

**microscopic process basis for relationships between $L_{2,3}$ and visible/VUV spectra**

**explains difference in spin-orbit splittings in $L_{2,3}$, and pseudo-spin orbit splittings in O K edge spectra**

**for Si $L_{2,3}$ crystal field splitting of 1.8 eV is greater than S-O of 0.7 eV, whereas for $ZrO_2$ - spin-orbit, and pseudo spin orbit (13 eV and 10 eV) are greater than crystal field, ~3.5 eV**

# relative energies of features in 2nd derivative of Si $L_{2,3}$

**when "transported" to visible/VUV energy scale, correspond to features in SE, and absorption and reflection**



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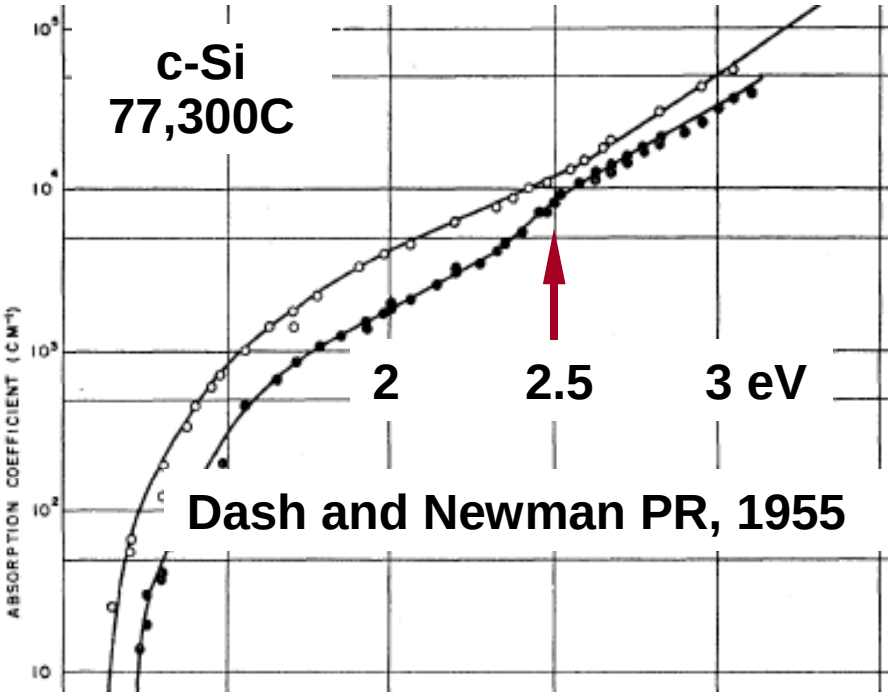
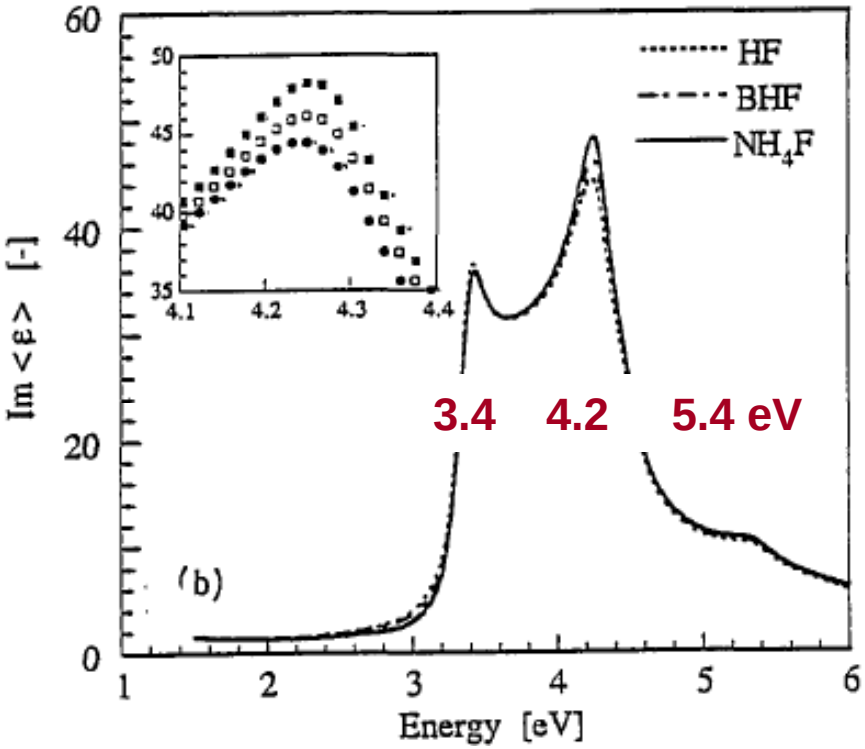



Dash and Newman PR, 1955




**2.5 eV is direct gap**

**1.1 eV is indirect gap**

**phonon-assisted for symmetry**

**stronger transitions – d-states!!**

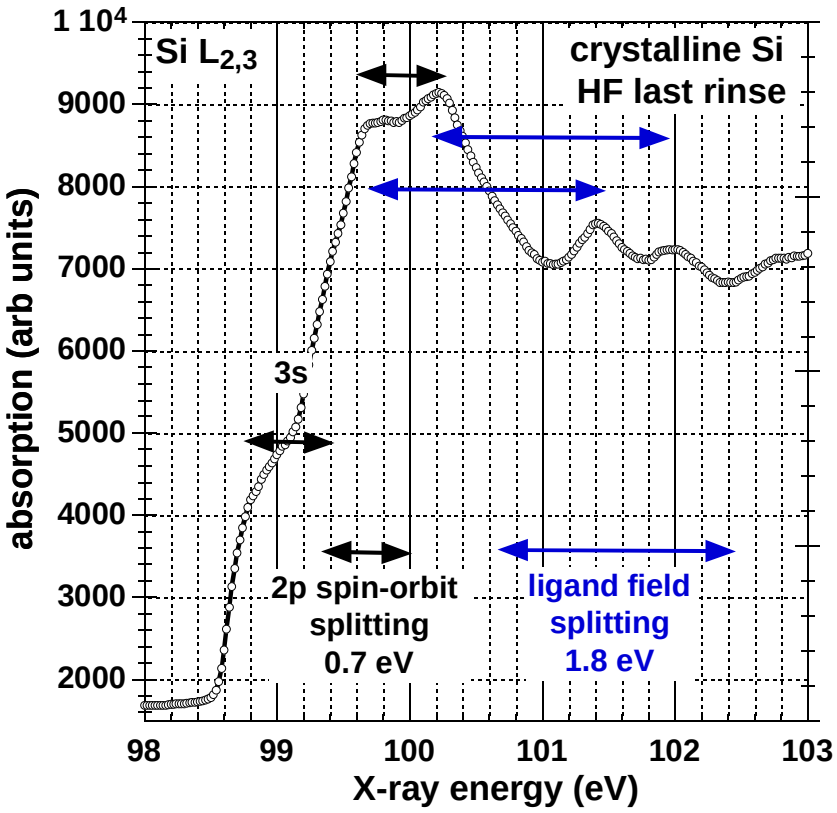
**in reflection spectroscopic ellipsometry**

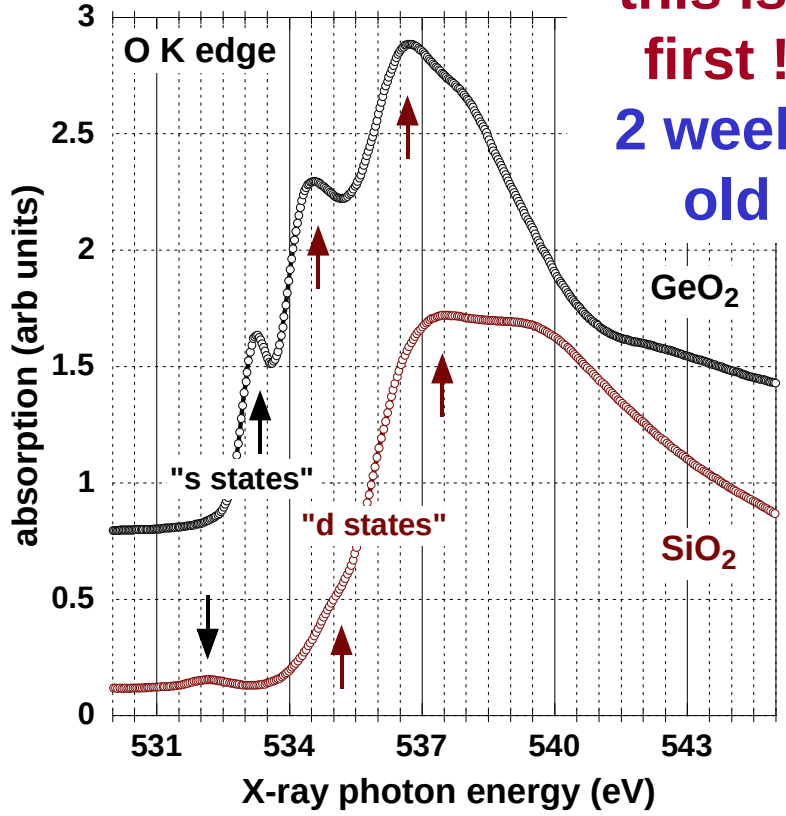
**Yasuda and Aspnes JOSB, 1994**

# relevance to electrical performance and reliability, including rad-hardness of $SiO_2$

**Si "s-like" one-dimension $A_{1g}$ features are at conduction edges of crystalline-Si and non-crystalline $SiO_2$**

**and remote plasma deposited $GeO_2$ (a first!!)**

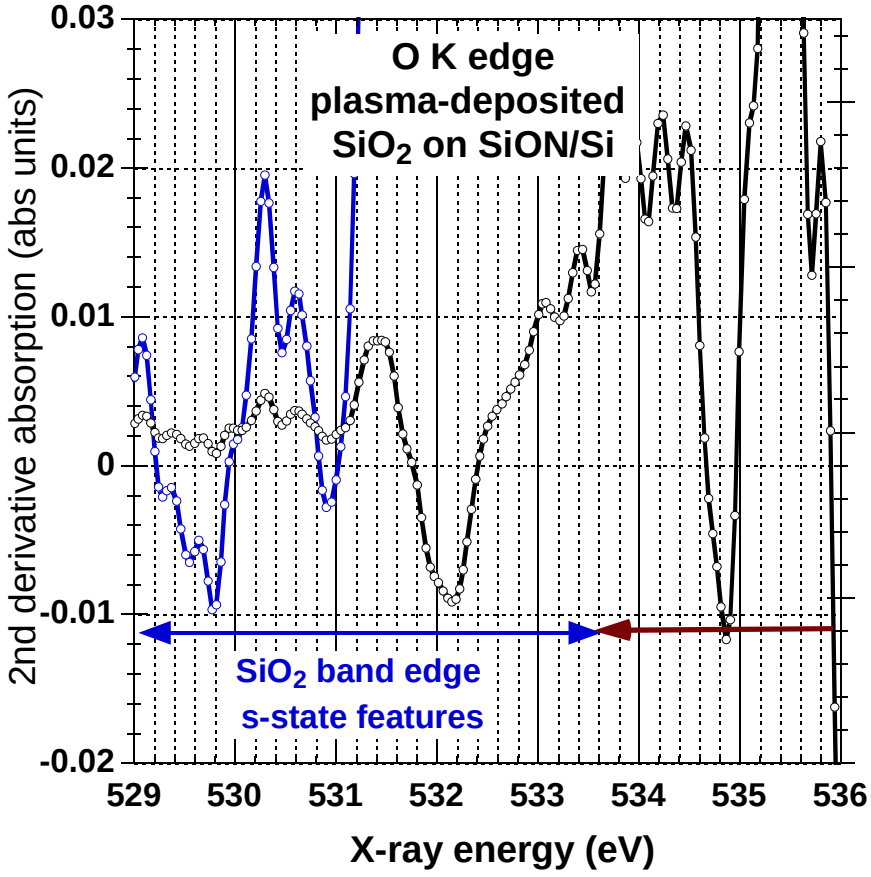


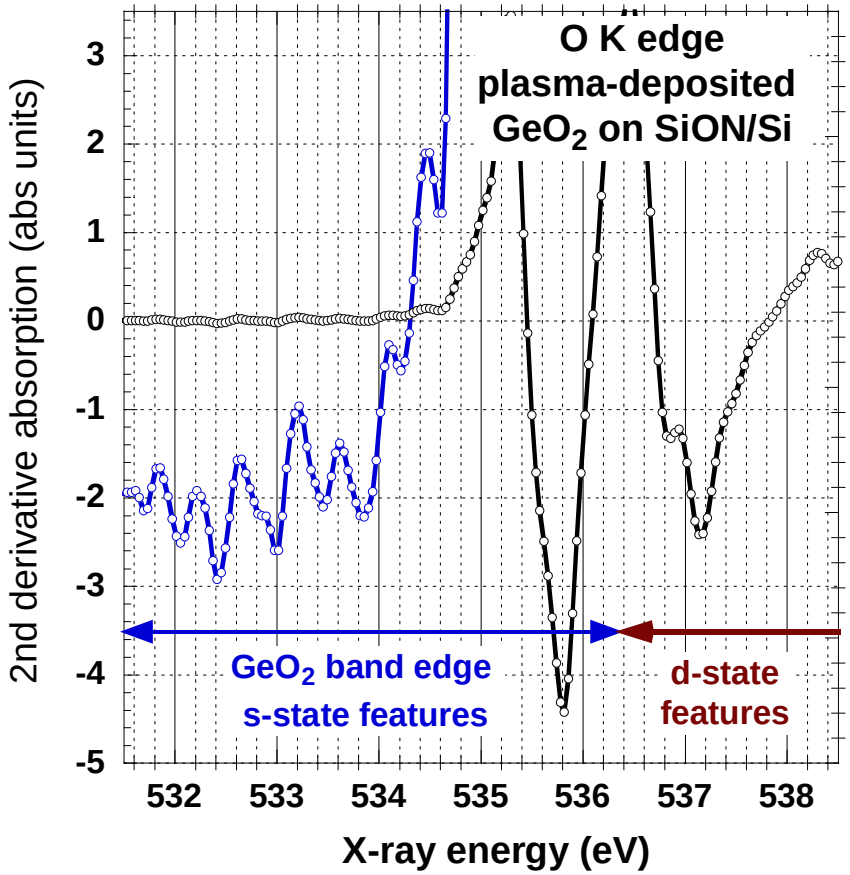




**this is a first !! 2 weeks old**

**"s-states" $SiO_2/GeO_2$ more stress resistant than Hf-or Lu, La based high-k dielectrics – in which band edge states have d-character**

# relative energies of "s-state" band edge and higher energy "d-state" features are approximately the same in $SiO_2$ and $GeO_2$




**O-atom vacancy defects are in middle of gap!!**

**this makes $SiO_2/GeO_2$ special**

**no band edge traps, or negative trapping after X-ray, γ-ray stress**

**application to experimental results**

**i) defect suppression in**

**thin $HfO_2$ - compare 2 nm and 4 nm thick films**

**relationship to trap-assisted tunneling**

**ii) defects in HfSiON ternaries**

**compare with C-V characteristics**

# reminder: soft X-ray photoelectron spectroscopy valence band spectrum for nano-grain $HfO_2$

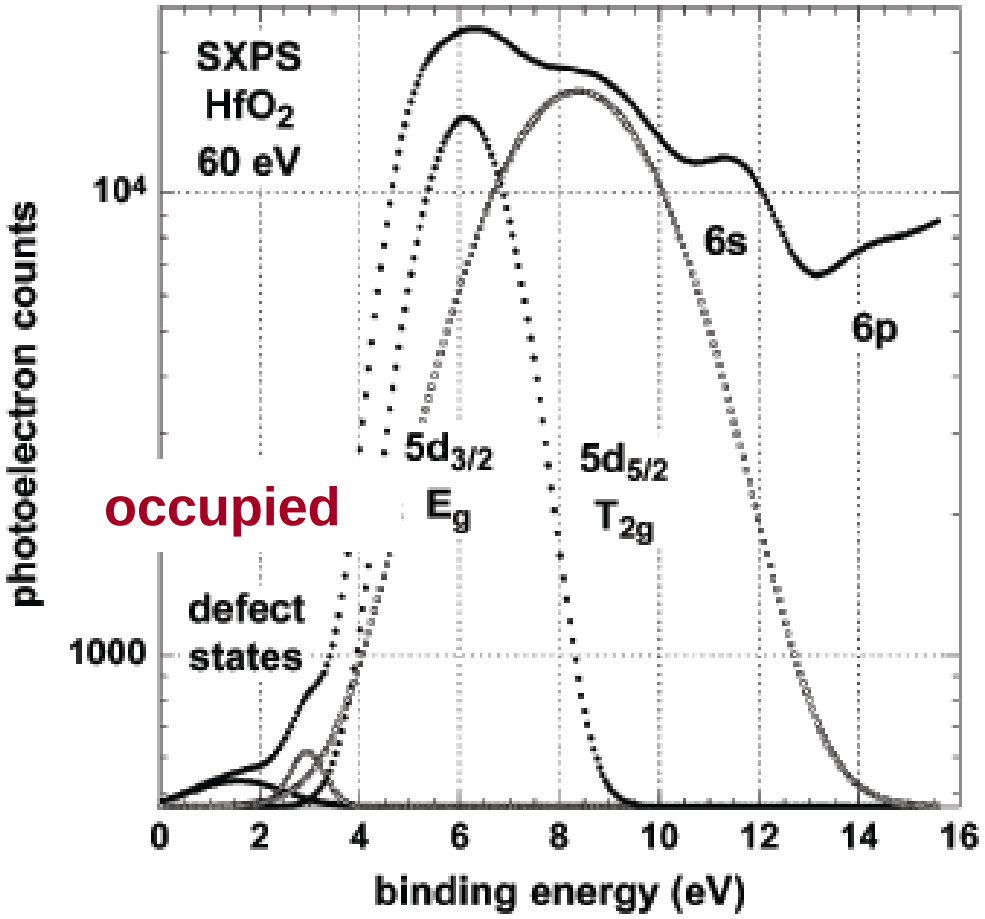



Fig. 5. SXPS valence band spectrum for nano-crystalline $HfO_2$: 5d-state and defect features are identified.

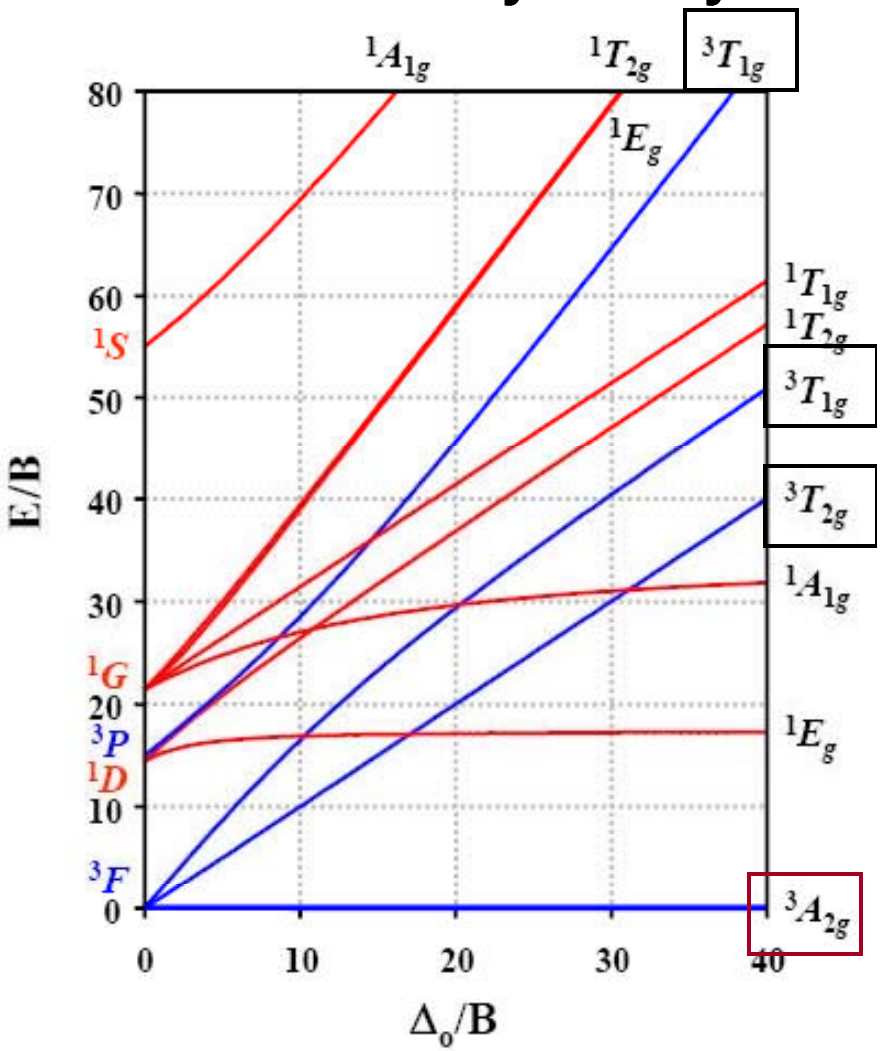
**O-vacancy electron states – 2 electrons/removed neutral O-atom**

**lowest energy states is high spin $d^2$ that can be on any one of four Hf atoms that border vacancy**

**excited states (d to d') are near conduction band are electron traps**

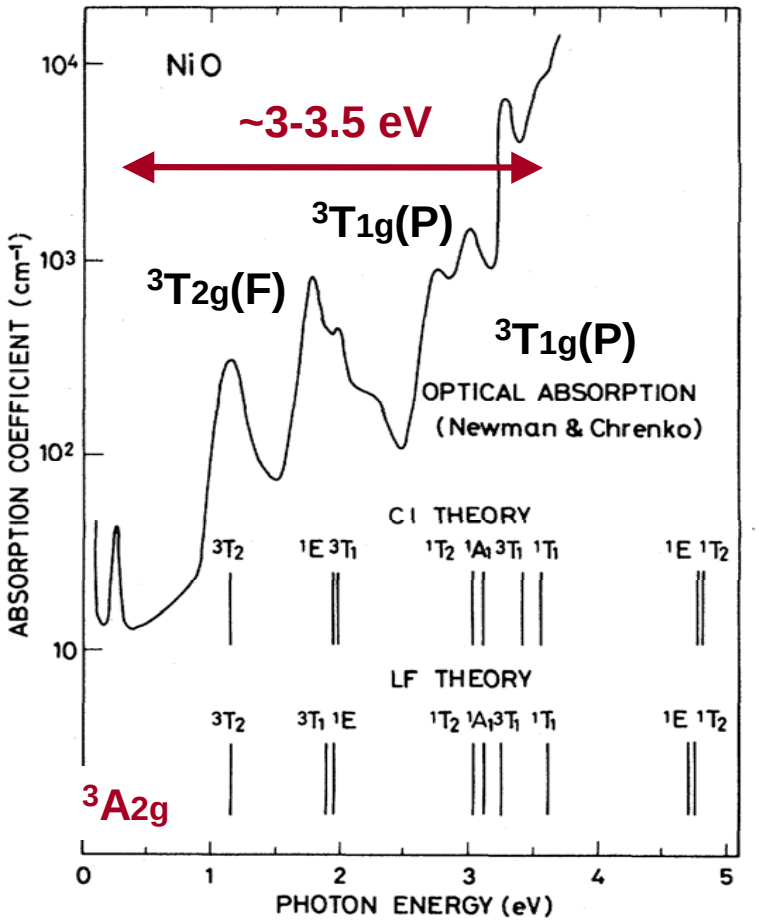
# Tanabe-Sugano diagram

**$d^2$ state occupancy and *Oh* cubic symmetry**




ground triplet ‘s’ state $^3A_{2g}$ to 3 triplet excited ‘p’-states, $^3T_{2g}$, $^3T_{1g}$ and $^3T_{1g}$

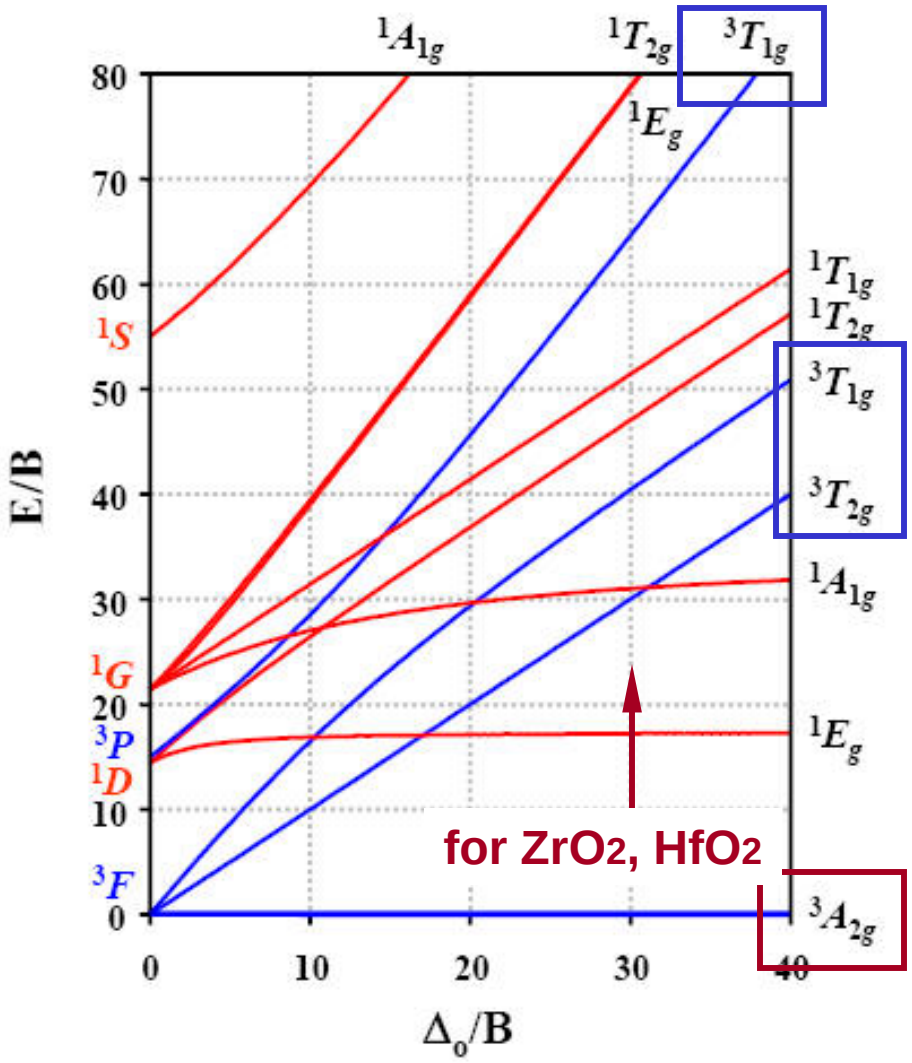
# NaCl structured NiO



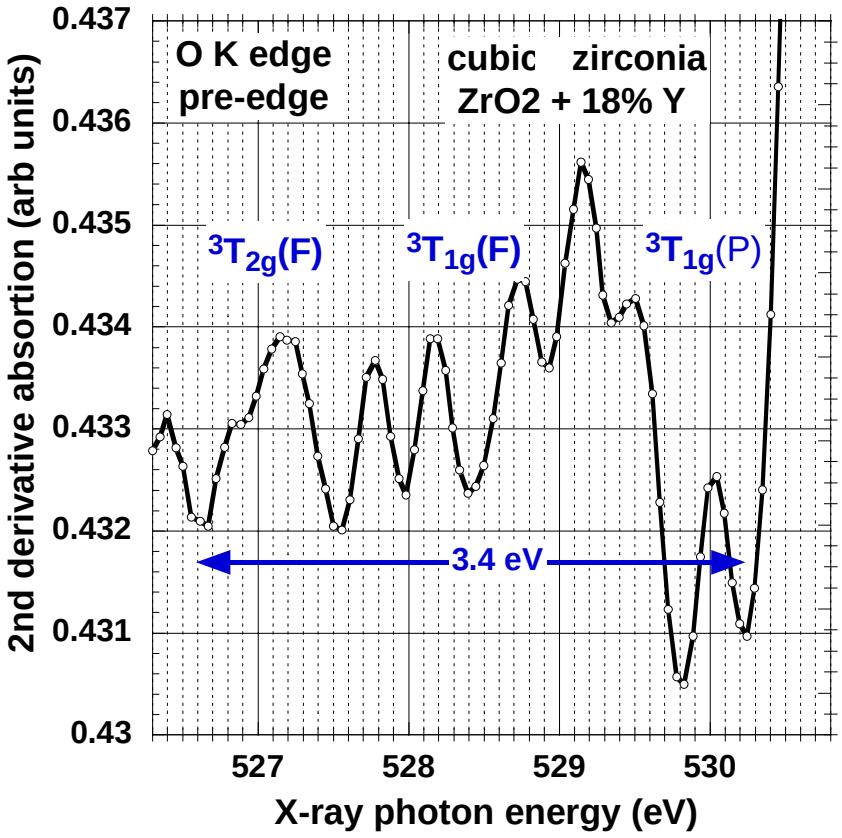

**Tanabe-Sugano diagrams also apply to d-d' transitions for O-atom vacancy defects, and negative ion states**

A Fujimori, et al., PR B30, 967 (1984).

## same Tanabe-Sugano diagram and energy scale applies to $d^2$ O-atom vacancies in Y, Or, Hf oxides, and NiO in NaCl crystals




E/B ~ 60-70 ~3 -3.5 V

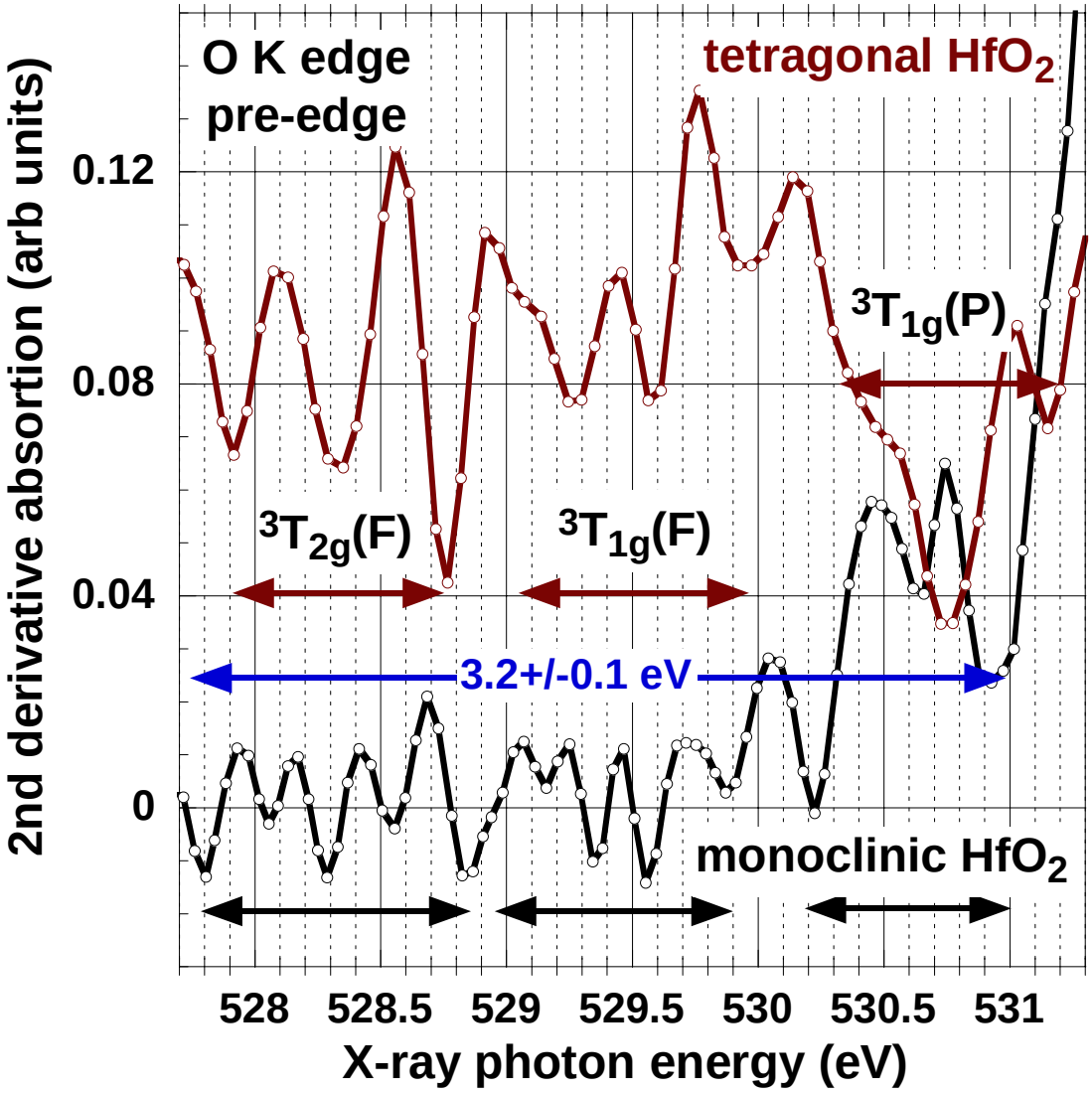



**triplet character of states**

**3 three states with small splitting, ~0.5 eV,**

**different values of J, also ~same spectral width**

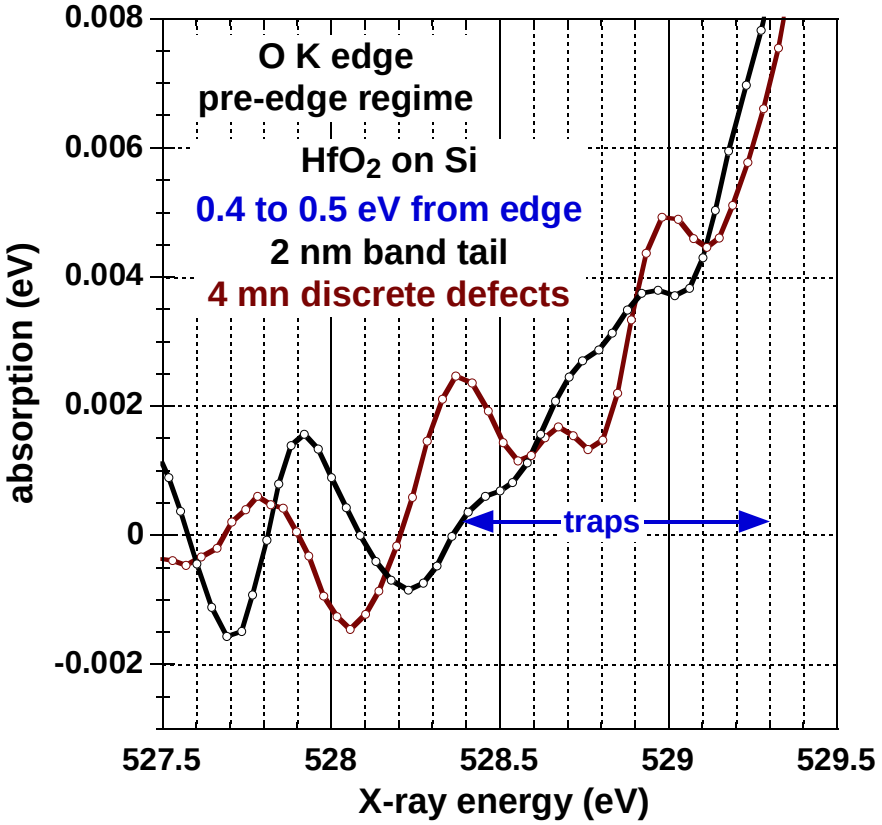
# multiplicity and symmetry of features is determined by symmetry of the primitive unit cell

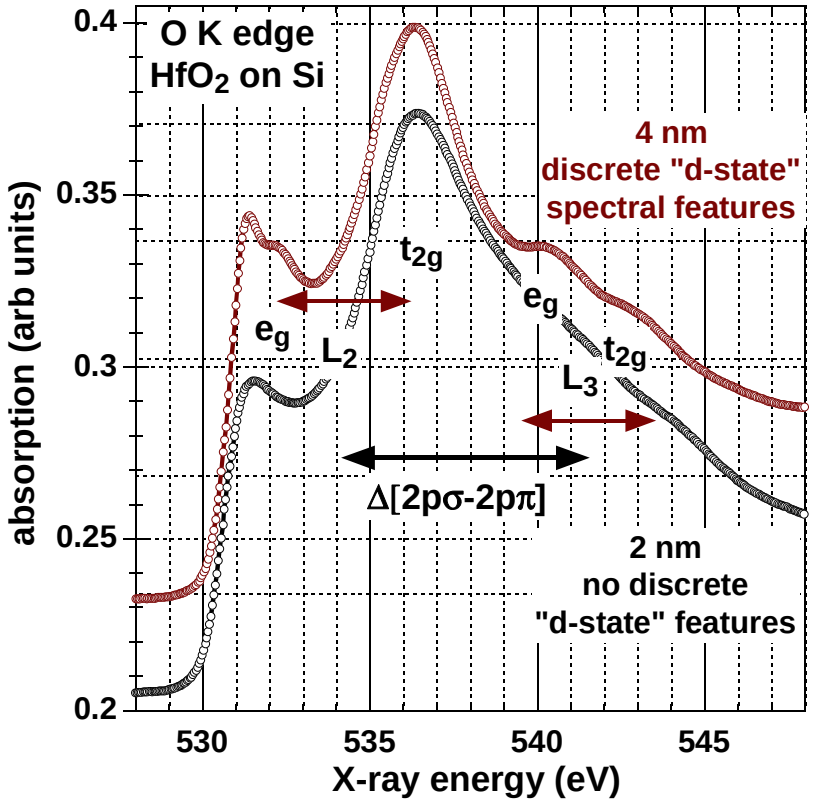



**tetragonal nano-grains**
**relatively high symmetry**
**3 sets of triplets**

**monoclinic nano-grains**
**reduced symmetry**
**more features**
**mixing of triplet and singlet states**

# differences in O-vacancy band edge defects, and "d-state" features in OK edge spectra that correlate with film thickness



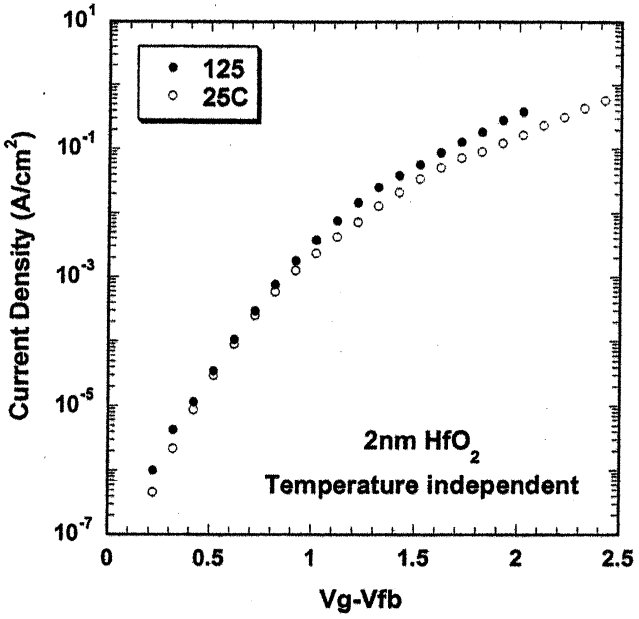

**discrete character of defects and "d-state" features depends on unit cell size**

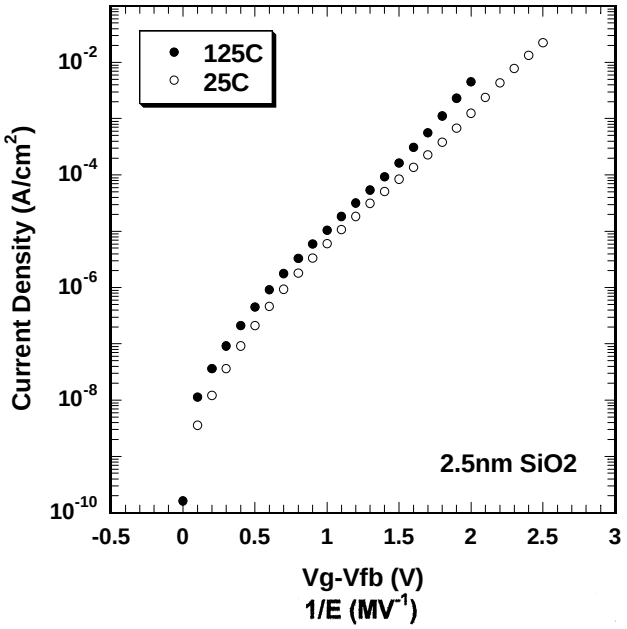
**physical thickness of nano-grain films constrains extended unit cell to be less than film thickness**

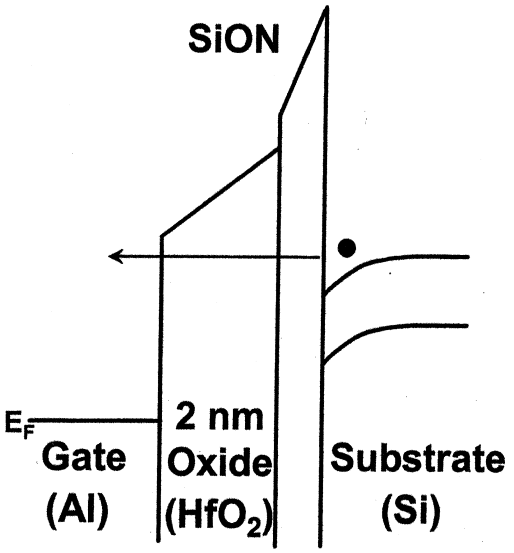
**2 nn thick films to less than critical size of ~ 3.0-3.5 nm necessary for cooperative Jahn-Teller distortions**

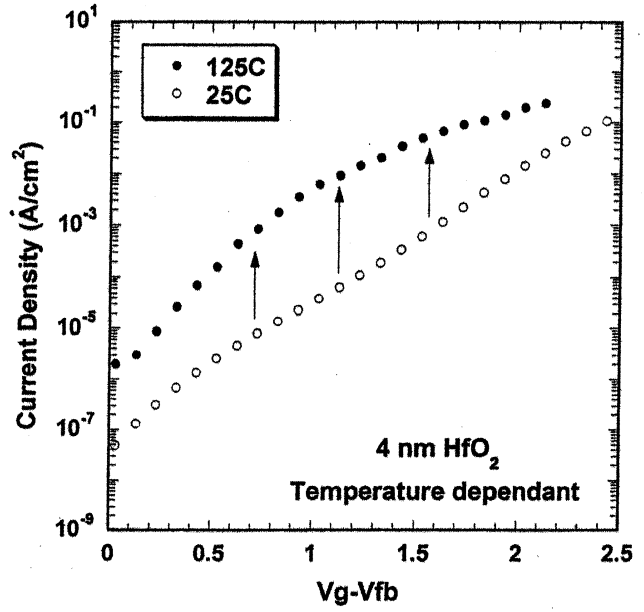
# differences in J-V correlate with differences in

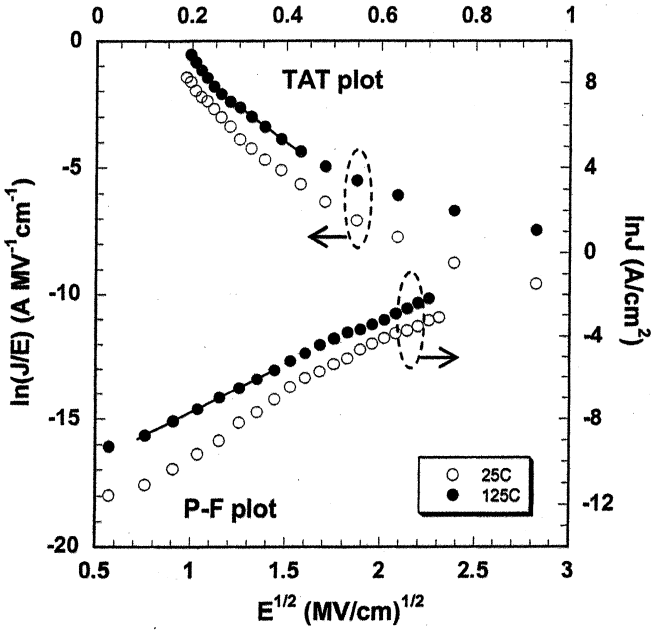
## conduction band edge and band edge defect states (O-vacancies)

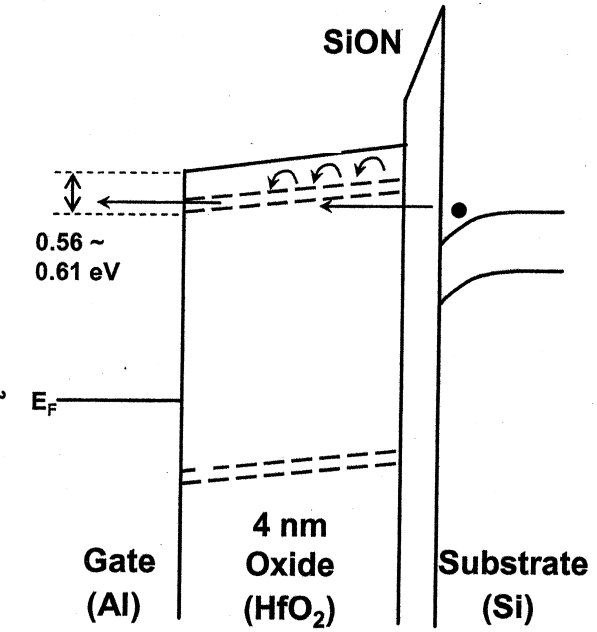


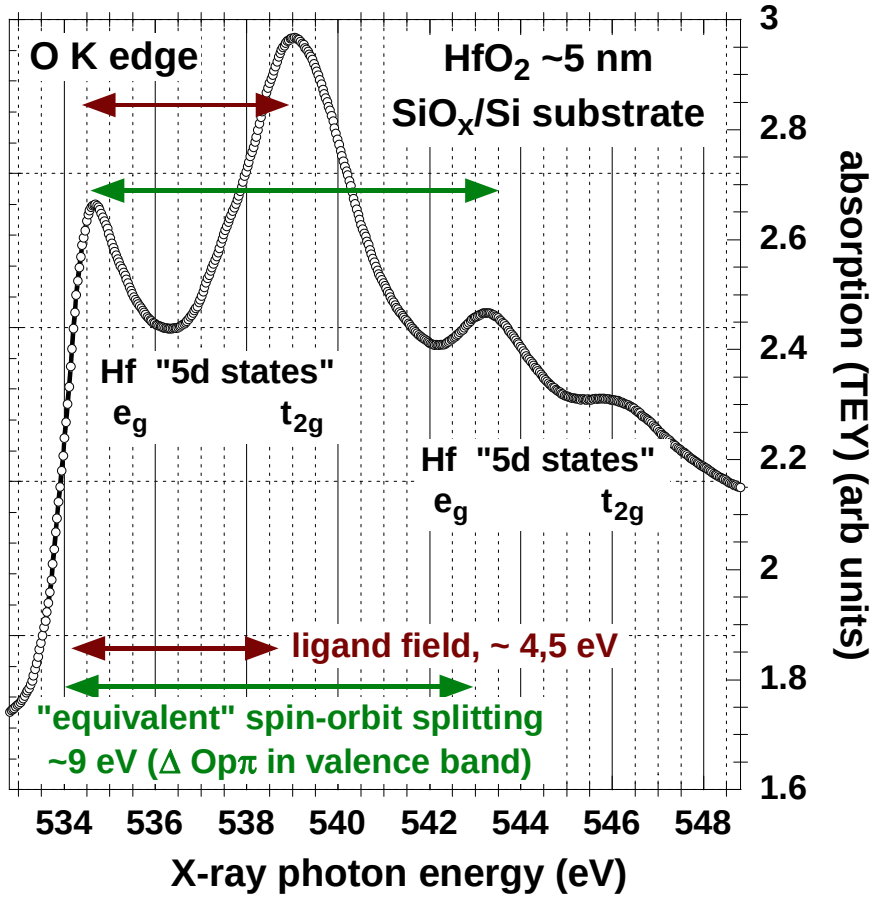



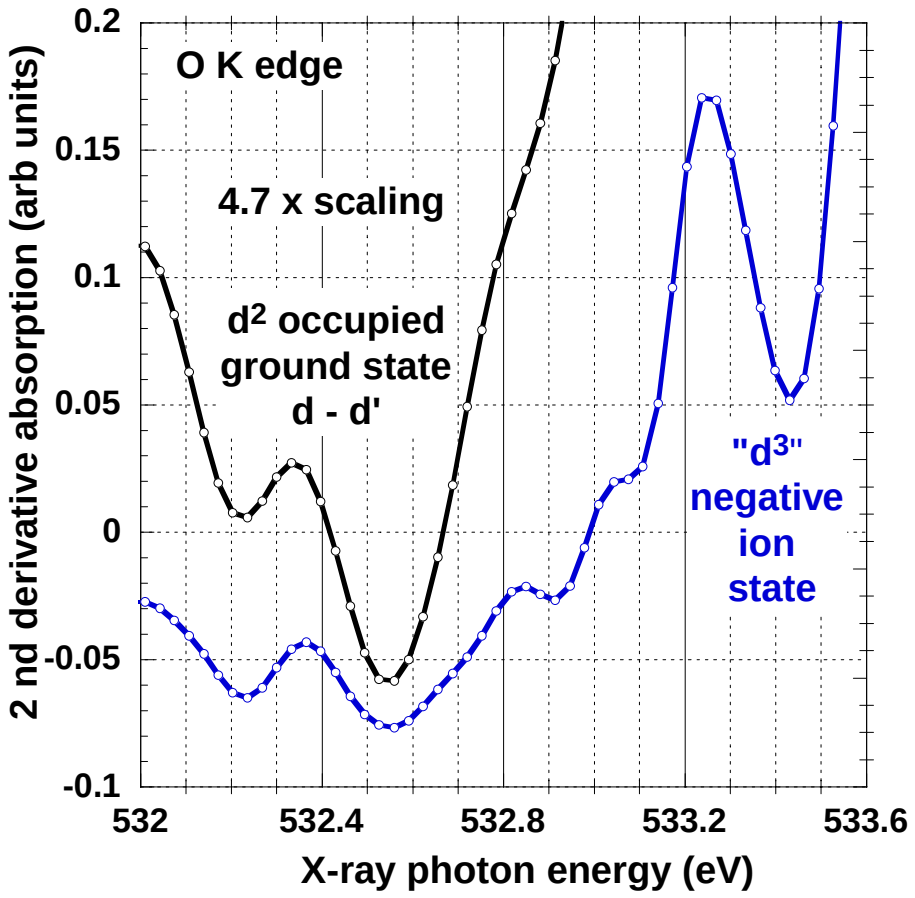



# TEY (total energy yield) SSRL BL 10-1

## X-ray absorption spectroscopy - XAS

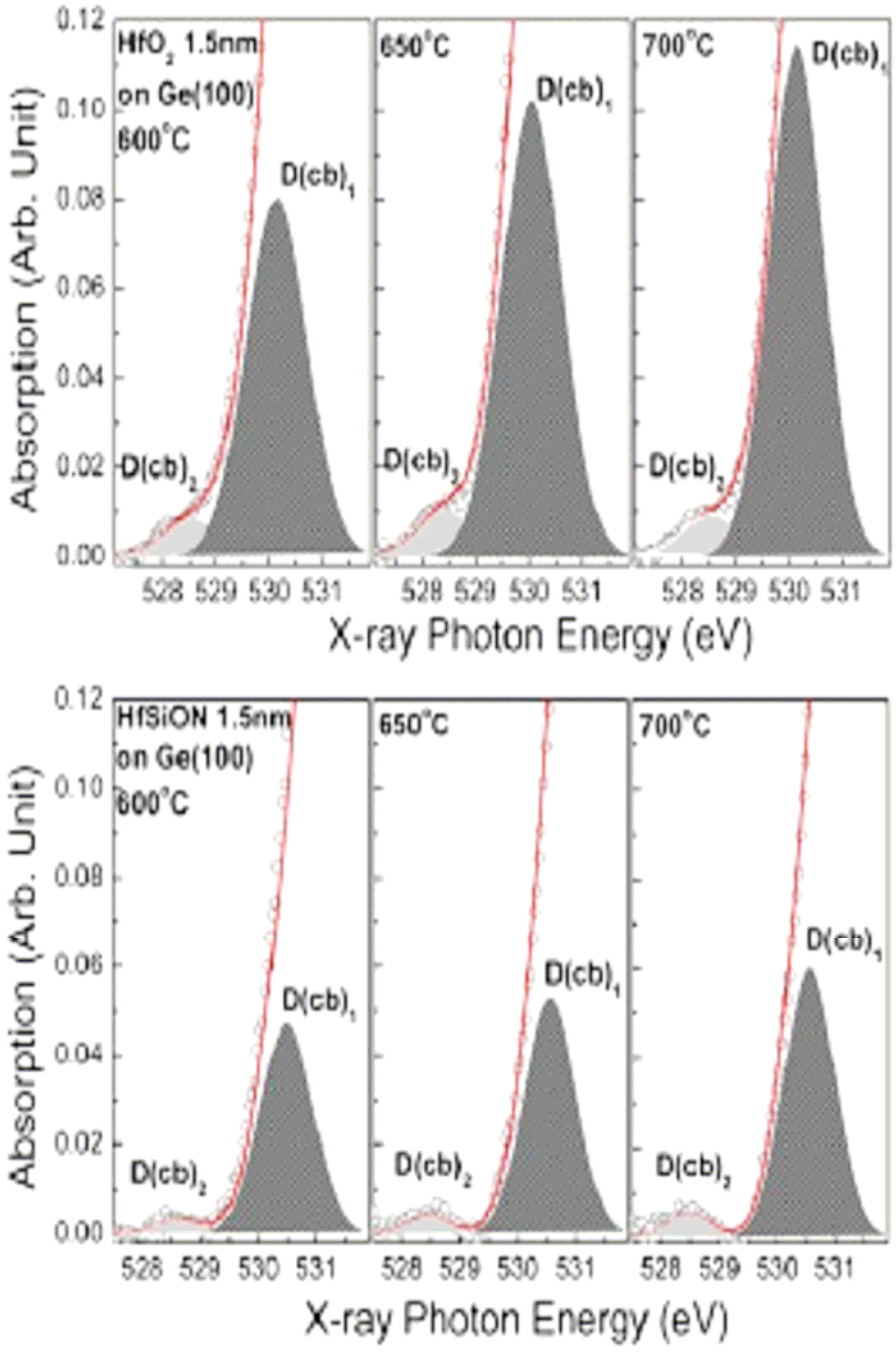
## negative ion states additional shallow traps closer to conduction band edge




**virtual bound states in conduction band**

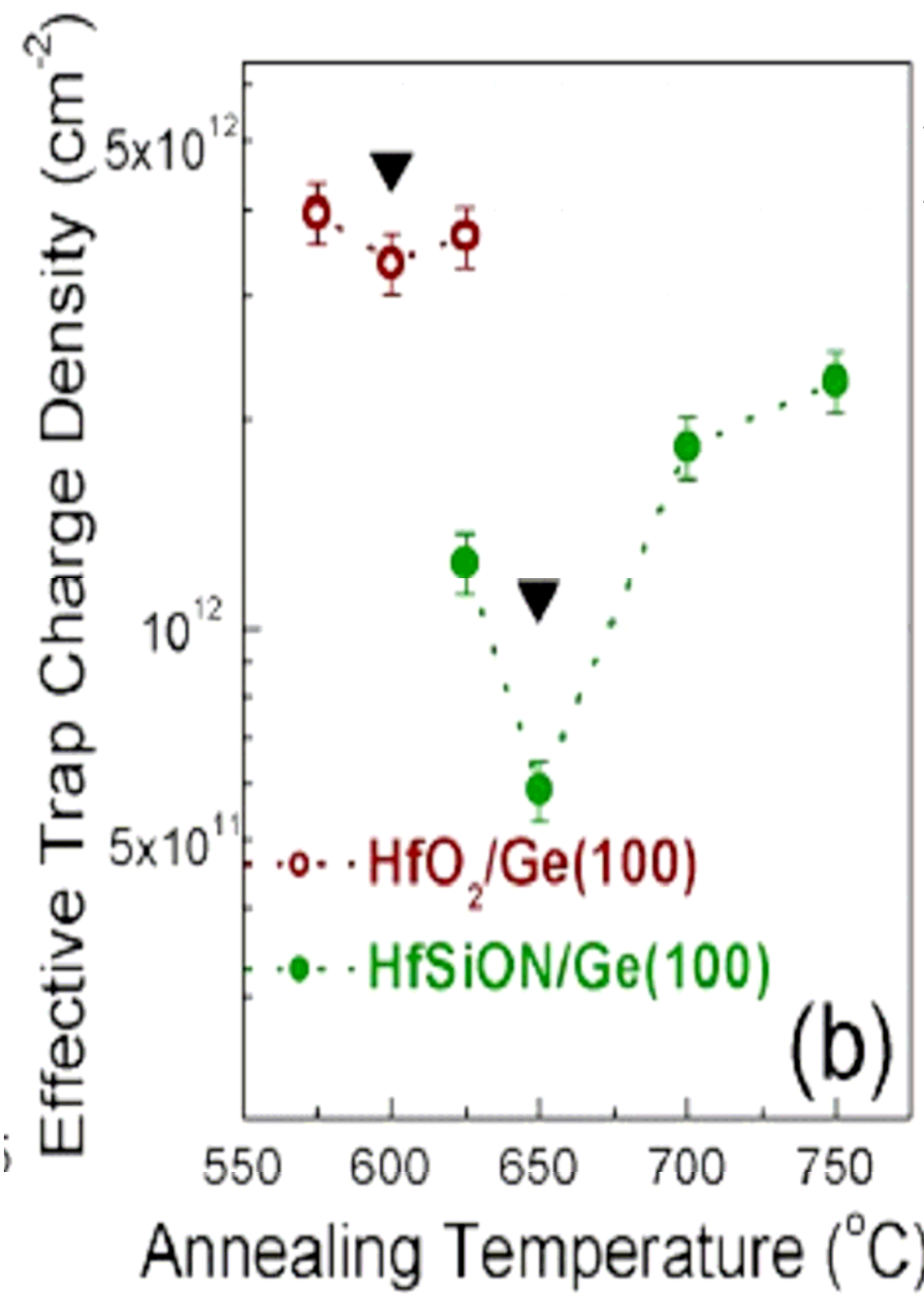
**pre-edge region virtual bound states intra-$d^2$ O-vacancy and $d^3$ negative ion state**




**(a) Thermal evolution of the O $K_1$ spectra for both $HfO_2$ and HfSiON over a narrow energy region below doubly-degenerate Hf 5d conduction band edge states as a function of PDA temperature.**

**two deconvoluted peaks, labeled D(cb)1 and D(cb)2, indicate the defect states determined by Gaussian fits of the XAS O K1 edge spectra.**

**lower density of defects by spectroscopy for HfSiON than $HfO_2$ - confirmed by CV**




**Capacitance-voltage (CV) for *n*-MOSCAPS 5nm HfSiON on *n*-type Ge (100**

**lowest trap density same as Saraswat's (Stanford Univ) best**

**HfSiON on Si - X-ray stress similar to $SiO_2$ no negative fixed charge as in $HfO_2$**

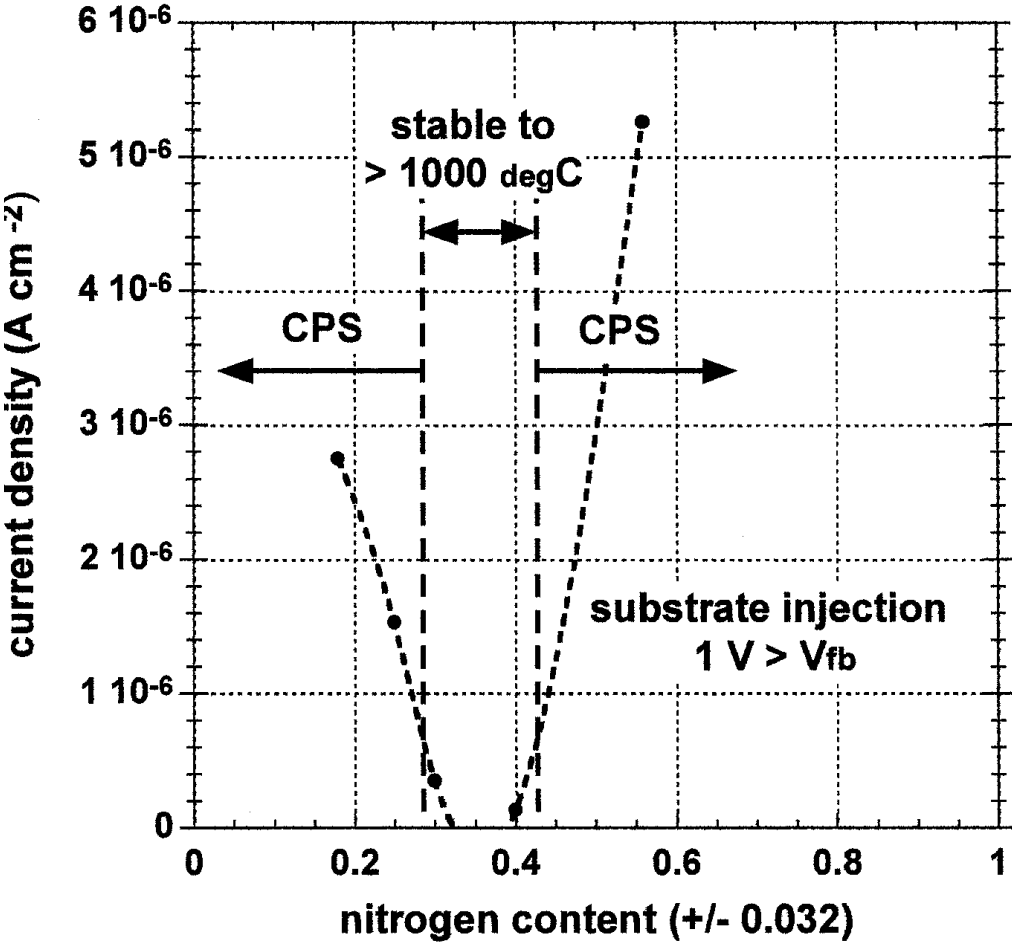
**defects lower than in $HfO_2$ agrees with XAS**

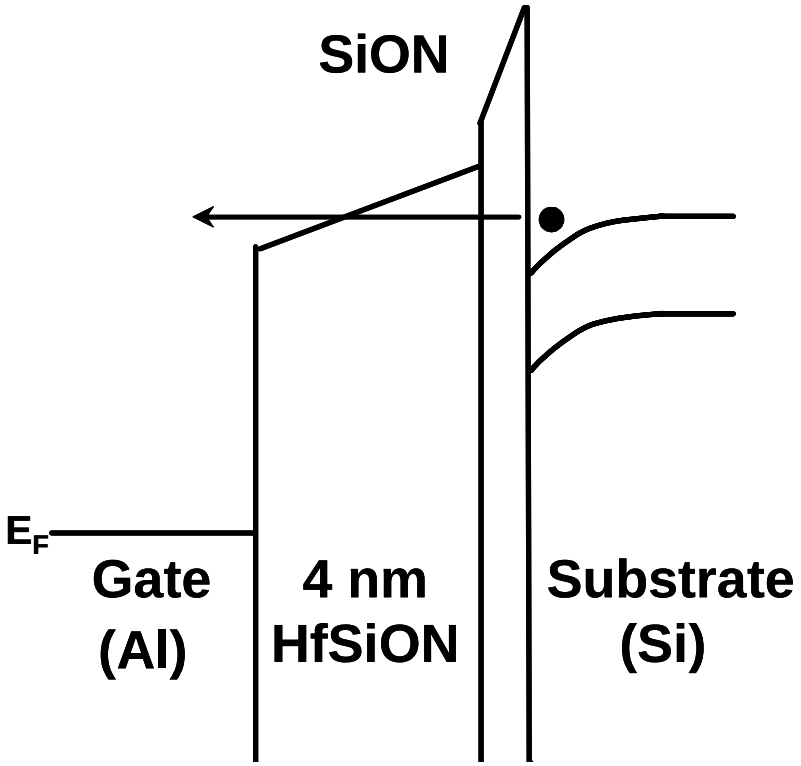
# $(HfO_2)_{0.3}(SiO_2)_{0.3}(Si_3N_4)_{0.4}$

**chemically-controlled composition stable to > 1000°C**

**defect generation - X-ray stress**

**"$SiO_2$ look alike with a higher dielectric constant ~10-11, and a 5000 fold decrease in leakage current !!**




**HfSiON (Si) requires SiON IRT**

*AFOSR, Vanderbilt MURI Jim Felix, Dan Fleetwood,....

**this review presentation is dedicated to**

**i) Isaac Besuker and Victor Pollinger -- my mentors and friends within the Jahn-Teller theoretical chemistry community,**

**and**

**ii) Rick Garfunkel for his *much appreciated critique* of a "bad" SRC review presentation a few weeks ago**
**this improved talk is my response to his critique**

**medium range order (SRO) in $SiO_2$**

**MRO associated with d-states - non-degenerate A's, B's, doubly degenerate E's, and triply degenerate p-like $T_1$'s and d-like $T_2$'s**

**this is what makes $SiO_2$, and potentially $GeO_2$, and their oxynitrides unique with respect to band edge defect states**

**major accomplishment is this fundamental intrinsic connection between many electron theory, synchrotron X-ray spectroscopy and defects**

**➔dielectrics with band edge $A_{1g}$ "s-like" states OK, only positive charge after radiation dosing – $SiO_2$**

**➔$HfO_2$, etc. with $e_g$ or $t_{2g}$ - O-vacancy/negative ion electron traps – negative charge after radiation dosing**