

Materials Specific Calculations for f-electron systems

- Traditional Approaches:
 - f-core
 - f-band
- Compare with experimental results



Depending on system, all variations of f-core, f-band or combinations thereof were found.

From Localised States to DMFT

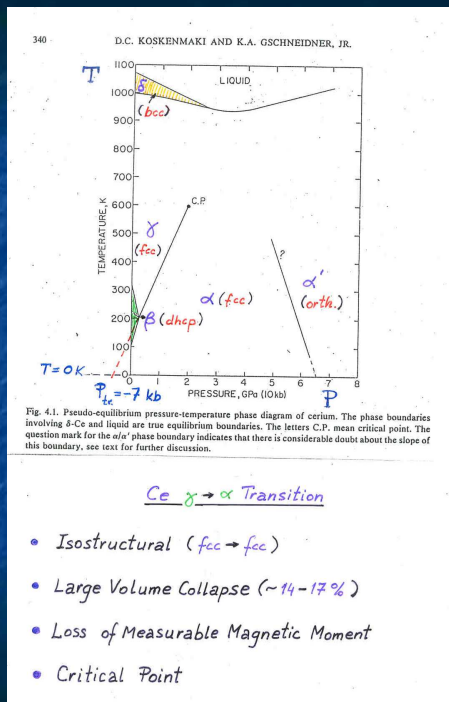
- Localised States in correlated d & f electron systems can be described in LSD (with Self-Interaction-Correction)
- Dynamics of Localised States to be described with DMFT or D CPA and Self-Interaction-Corrected LSD states as trial wave functions

Self-Interaction-Correction

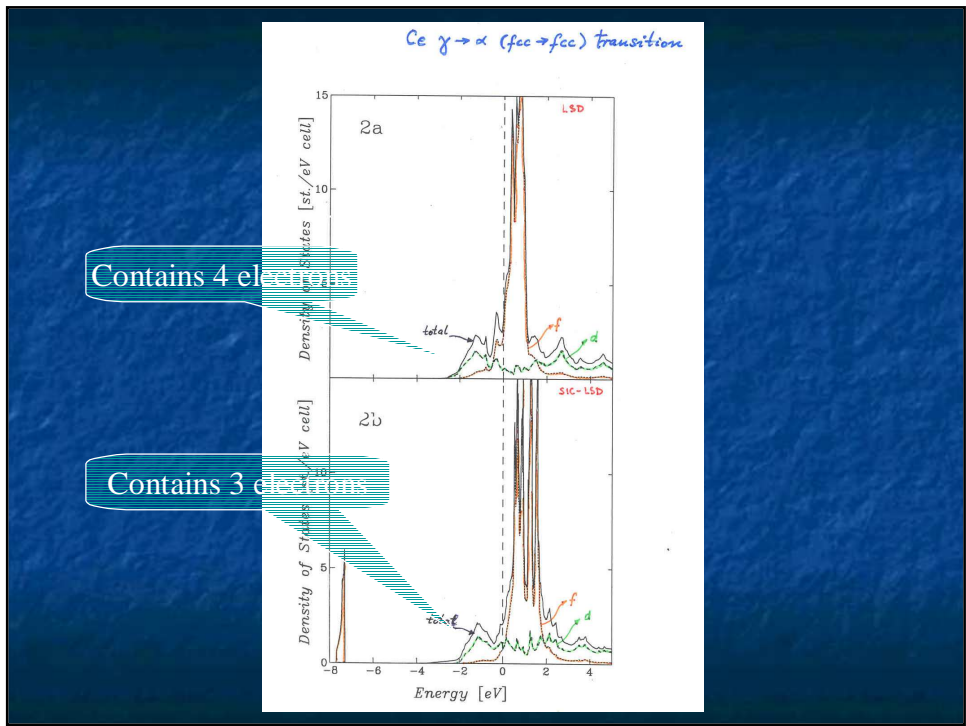
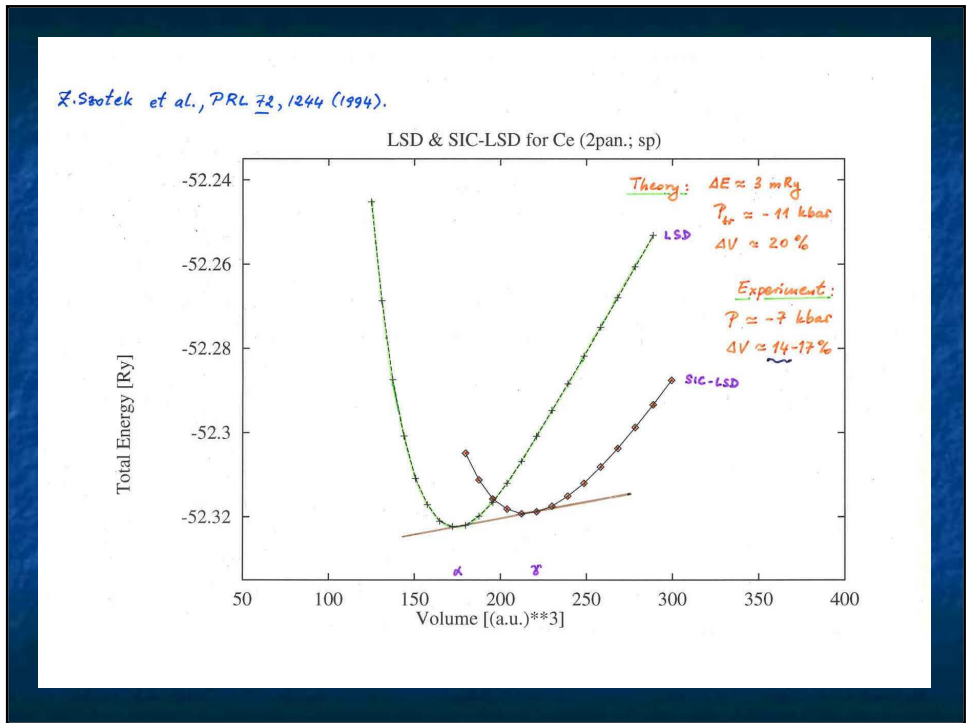
$$E^{SIC-LSD}[n] = E^{LSD}[n] - \sum_{\alpha} \delta_{\alpha}[n_{\alpha}]$$

$$\delta_{\alpha}[n_{\alpha}] = E^{XC(LSD)}[n_{\alpha}] + E^H[n_{\alpha}]$$

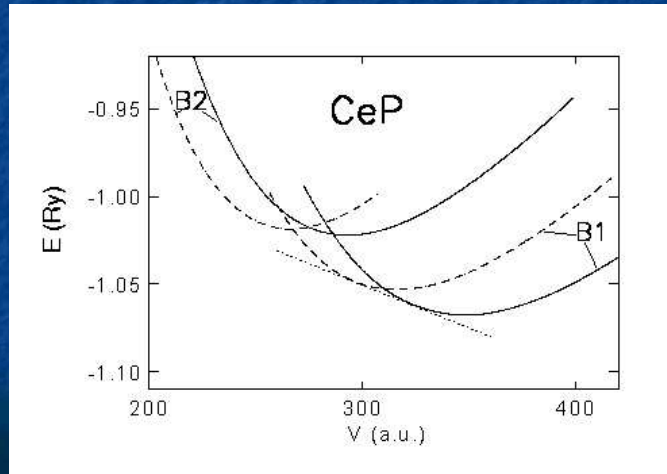
- Corrects Local-Spin-Density (LSD) for spurious self-interaction.
- Is sizeable for a localised electron, i.e. when an electron spends a long time on a particular site.
- It reduces to the LSD for delocalised electrons.



f-electron Materials: from Localised States to DMFT



Structural and localisation transitions in CeP

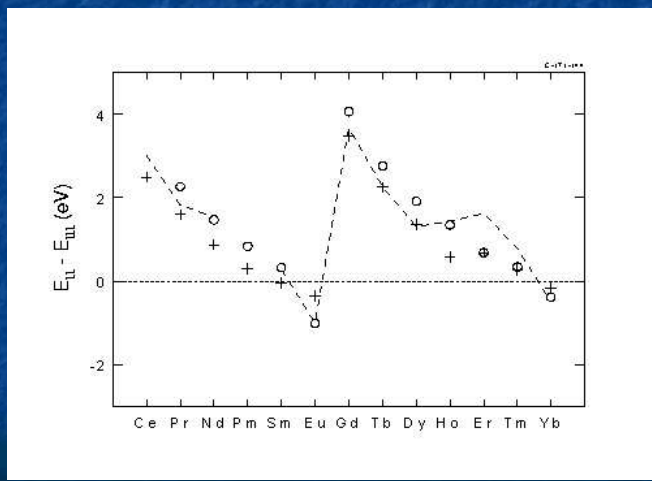


Structural and Localisation Properties of Ce Monopnictides

compound	transition	P_t (kbar)		V_h (a_0^3)		V_l (a_0^3)	
		theo.	expt.	theo.	expt.	theo.	expt.
CeN	B1(d) ! B2(d)	620	-	148	-	141	-
CeP	B1(l) ! B1(d)	71	90 ^a , 55 ^b	325	308 ^a	297	298 ^a
CeP	B1(d) ! B2(d)	113	150(40) ^a	288	285 ^a	246	247 ^a
CeAs	B1(l) ! B2(d)	114	140(20) ^c	332	315 ^c	265	274 ^c
CeSb	B1(l) ! B2*(l)	70	85(25) ^d	400	398 ^d	353	354 ^d
CeSb	B2*(l) ! B2*(d)	252	-	311	-	295	-
CeBi	B1(l) ! B2*(l)	88	90(40) ^e	427	399 ^e	376	360 ^e
CeBi	B2*(l) ! B2*(d)	370	-	317	-	304	-

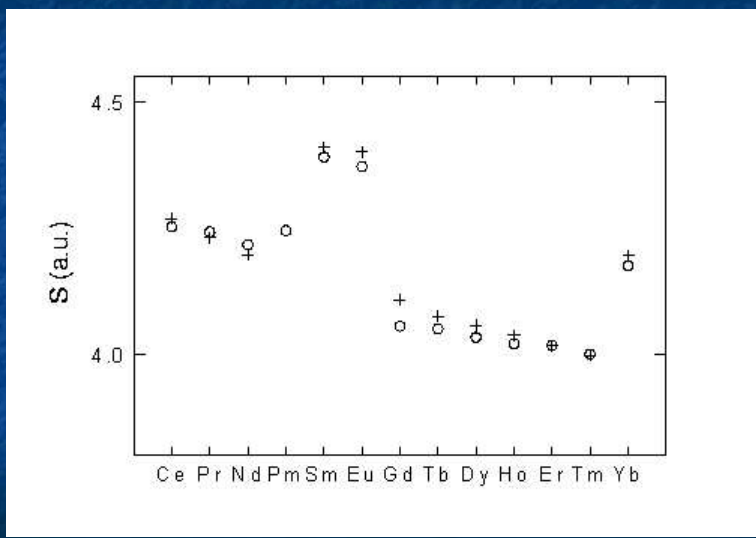
A. Svane, Z. Szotek, W. M. Temmerman, J. Lægsgaard and H. Winter,
 J. Phys.: Condens. Matter 10 (1998) 5309-5325

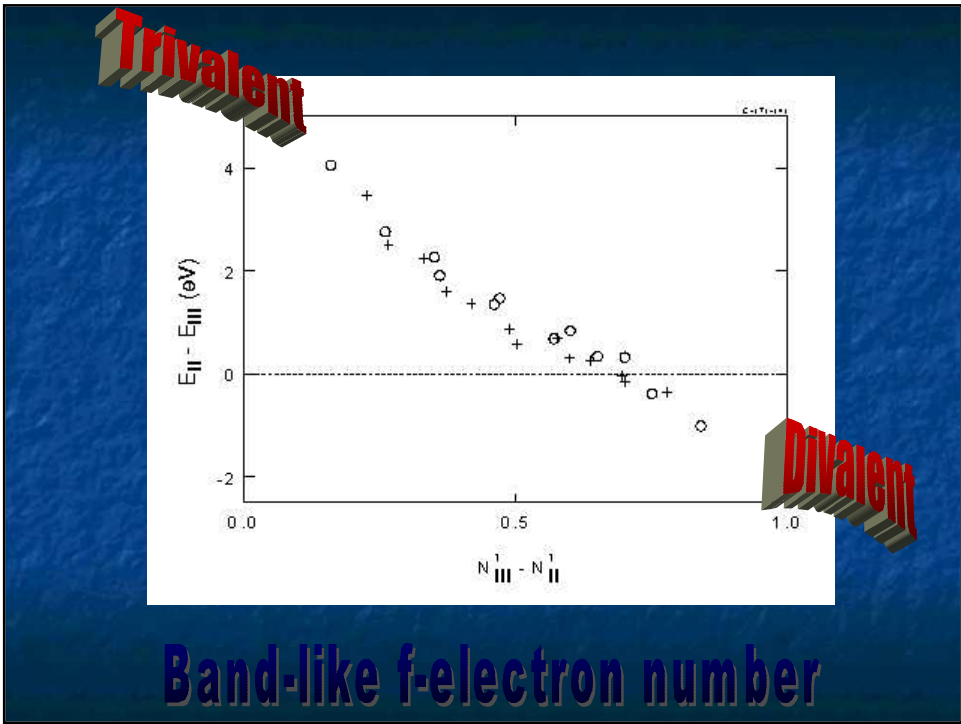
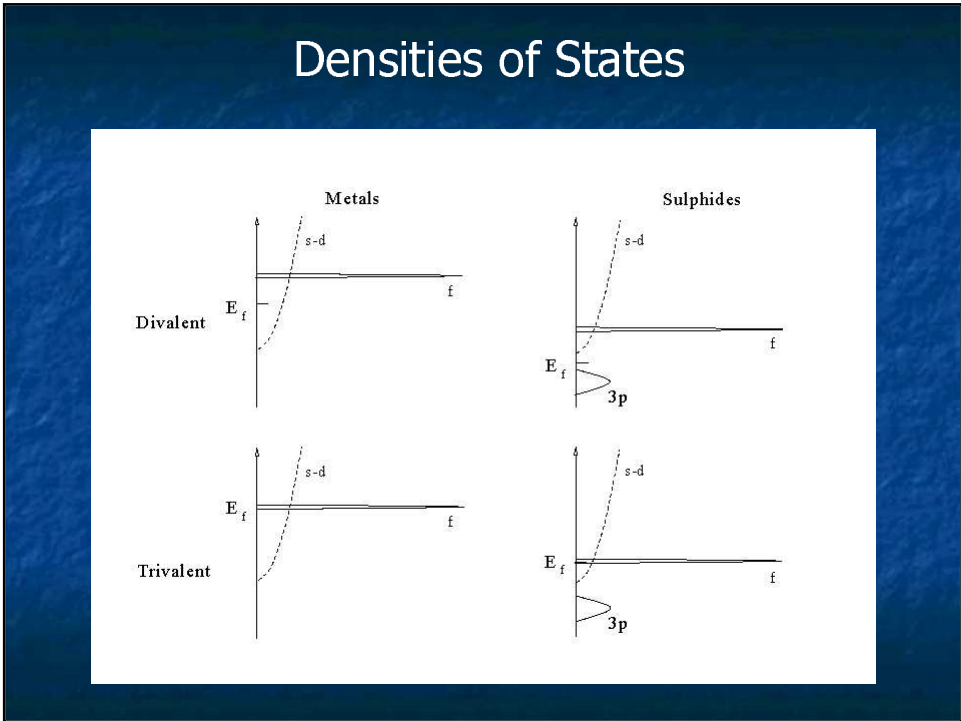
$$N_{\text{valency}} = Z - N_{\text{core}} - N_{\text{SIC(LOC)}}$$



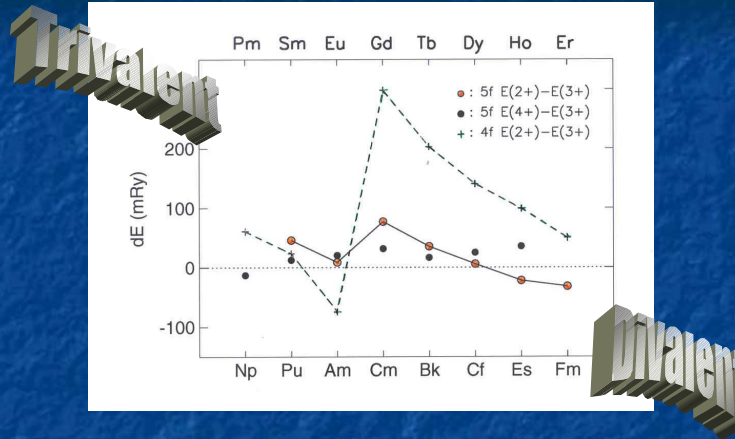
P. Strange, A. Svane, W.M. Temmerman, Z.Szotek and H. Winter, Nature 399 (1999) 756.

Theoretical Wigner-Seitz radii of the Rare Earth Sulphides

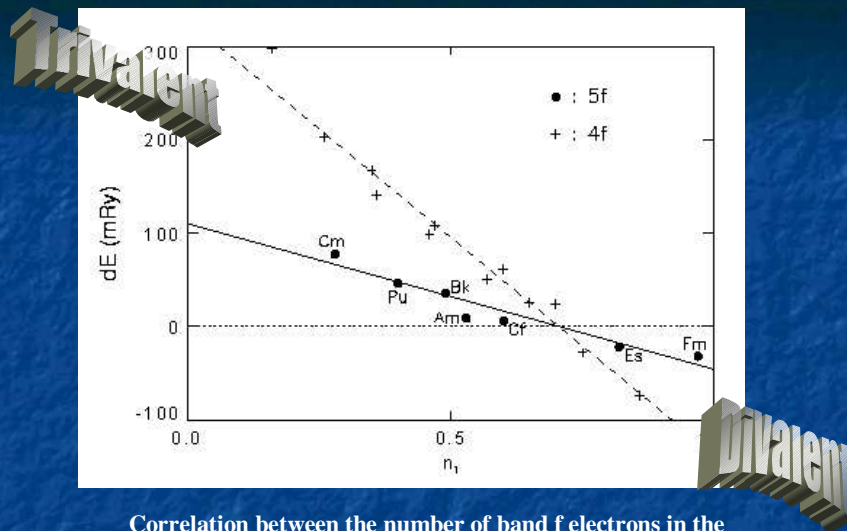




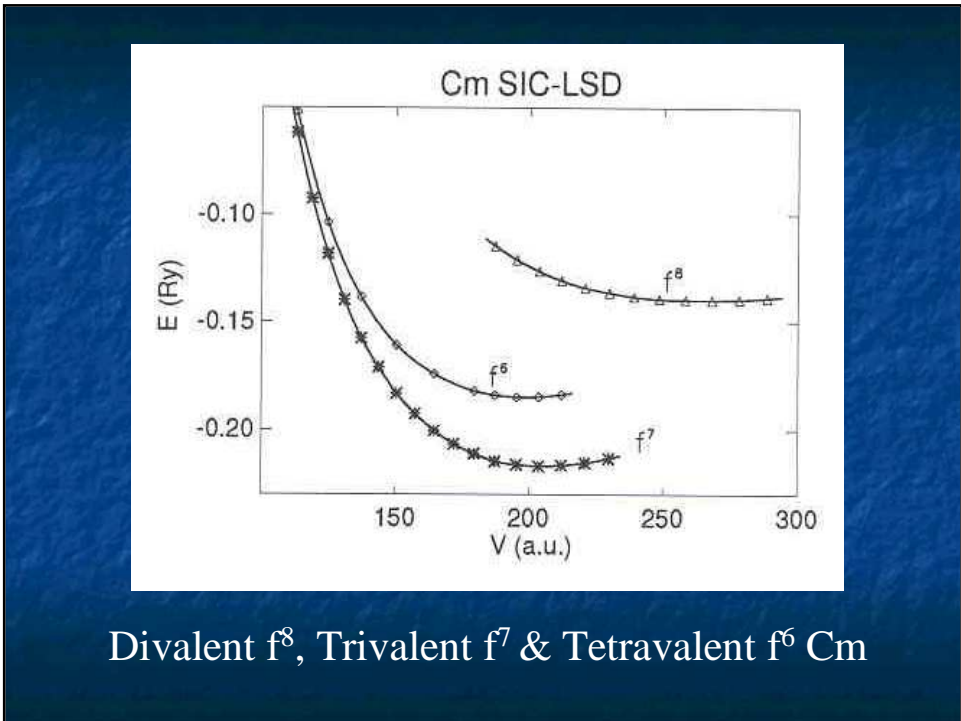
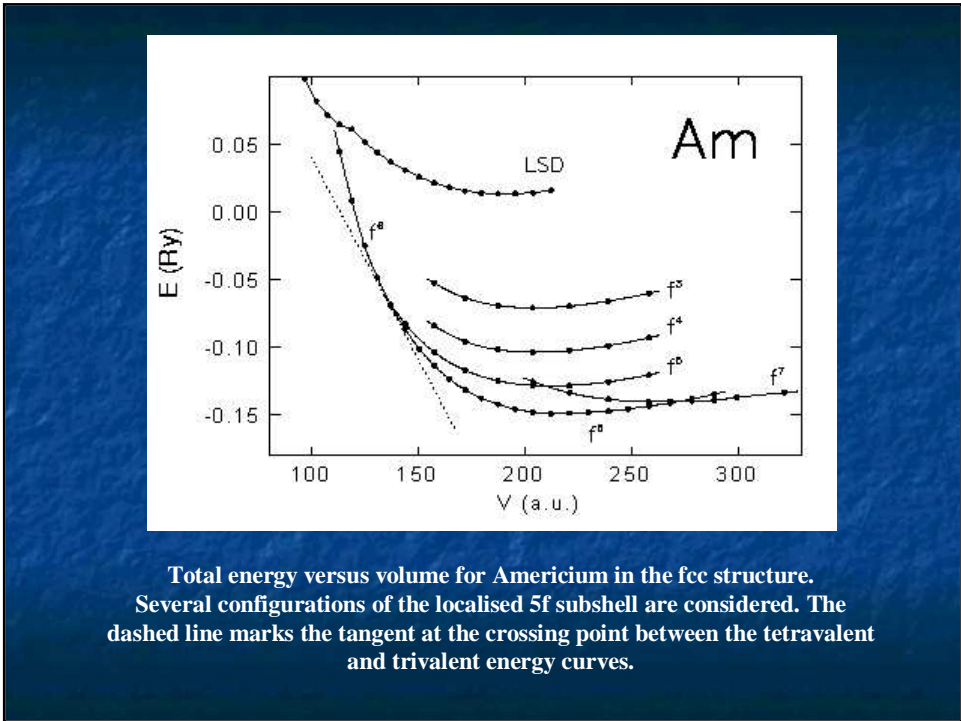
Trivalency or Divalency amongst the f systems



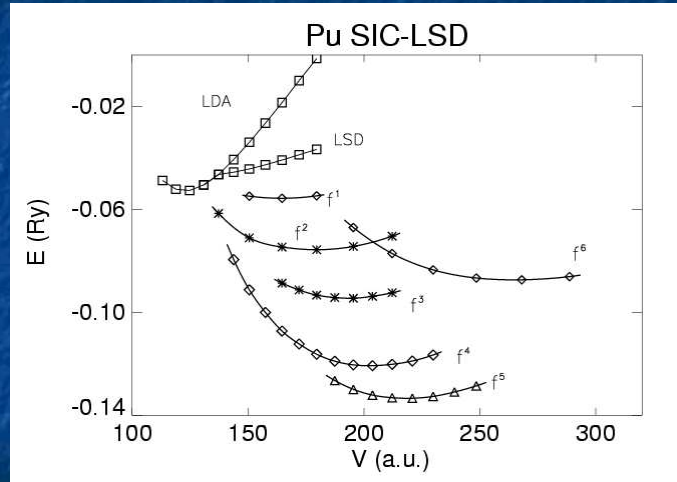
- **Rare Earths:** P. Strange, A. Svane, W.M. Temmerman, Z. Szotek and H. Winter, Nature 399 (1999) 756.
- **Actinides:** L. Petit, A. Svane, W.M. Temmerman and Z. Szotek, Solid State Communications 116 (2000) 379.



Correlation between the number of band f electrons in the trivalent configuration and the energy difference between the divalent and trivalent atomic configurations for the actinides (filled circles) and rare earths (crosses)



Pu Configurations



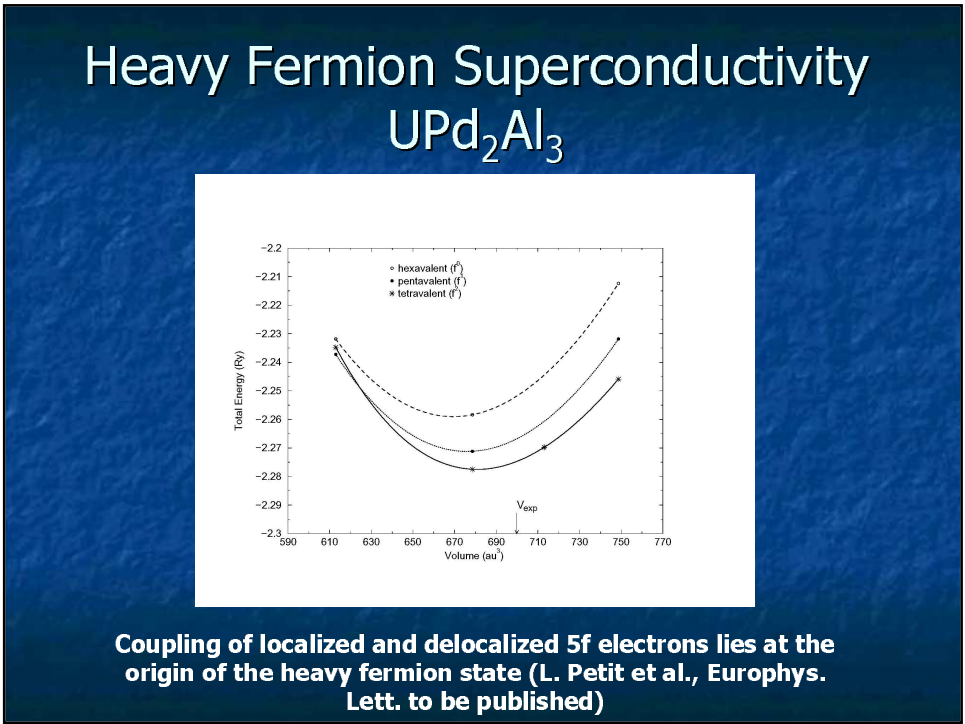
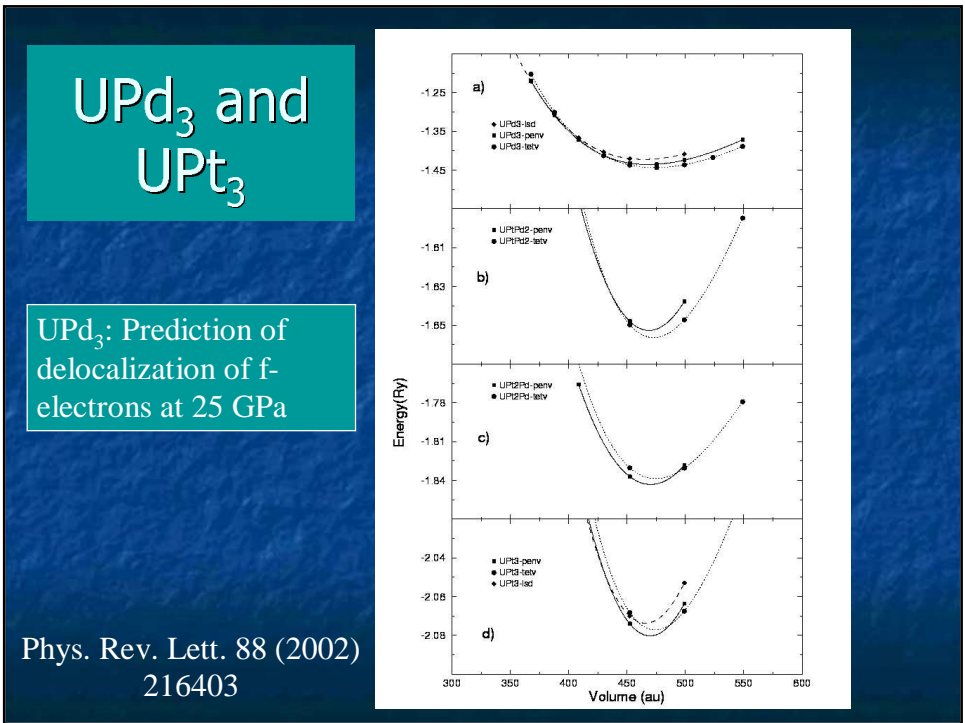
Four different localized configurations lie within 80 mRyd of the trivalent (f^5) ground state

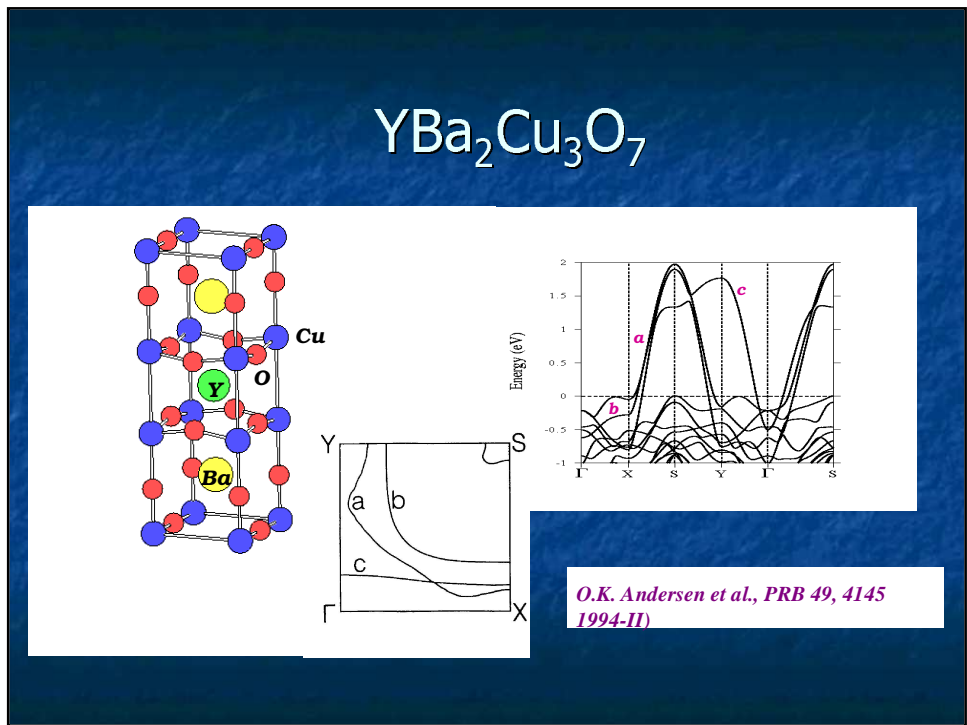
Actinide Equilibrium Volumes

For magnetic Pu solution, much improved volume from non-magnetic solution

	V_{teo} (a.u.)	V_{exp} (a.u.)	B_{teo} (GPa)	B_{exp} (GPa)	P_{teo} (GPa)	P_{exp} (GPa)
\pm -Pu	217.9(+ 30%)	168 ^a	38.4	32 ^b	15	$\gg 0$
Am	213.4(+ 8%)	198	39.5	45	43	23
Cm	204.7(+ 1.2%)	202	42.4	33(5)	70	43
Bk	199.6(+ 6%)	189	35.0	25(5)	15	32
Cf	199.5(+ 8%)	185	37.3	49(5)	30	41
Es	256.0(-4.1%)	267, 321	19.5	-	11	-
Fm	247.4	-	29.6	-	28	-

TABLE I. Calculated and experimental equilibrium volumes, V , bulk moduli, B , and f_i electron delocalization pressure, P , for the actinide elements. Experimental values are from [5], except ^a: Ref. [4], and ^b: Ref. [21]. For the theoretical estimate (upper bound) of P , see text.





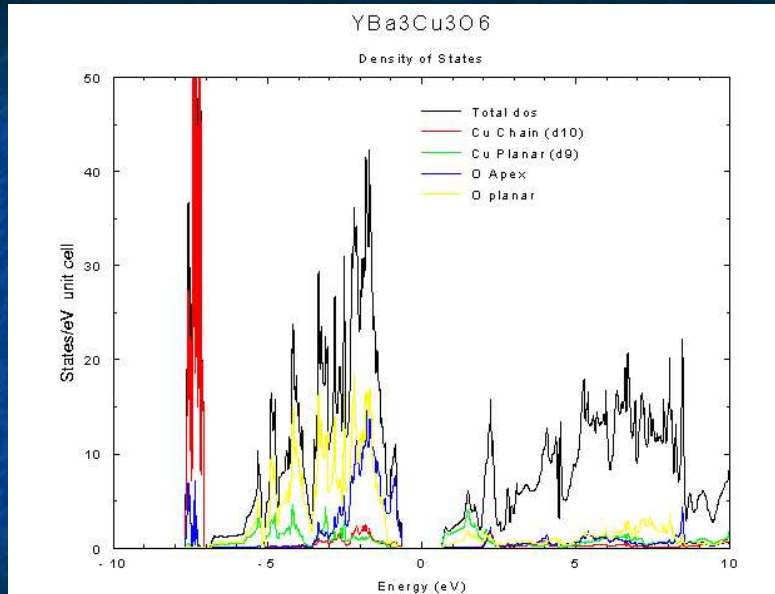
The SIC and Valencies

- **Divalent Cu:** the SIC is used to localise 9 Cu d states (d⁹) and to treat the remaining 2 Cu d states as LSD band states (Cu²⁺)
- **Trivalent Cu:** the SIC is used to localise 8 Cu d states (d⁸) and to treat the remaining 3 Cu d states as LSD band states (Cu³⁺)

SIC selects the number and symmetry of the localised states

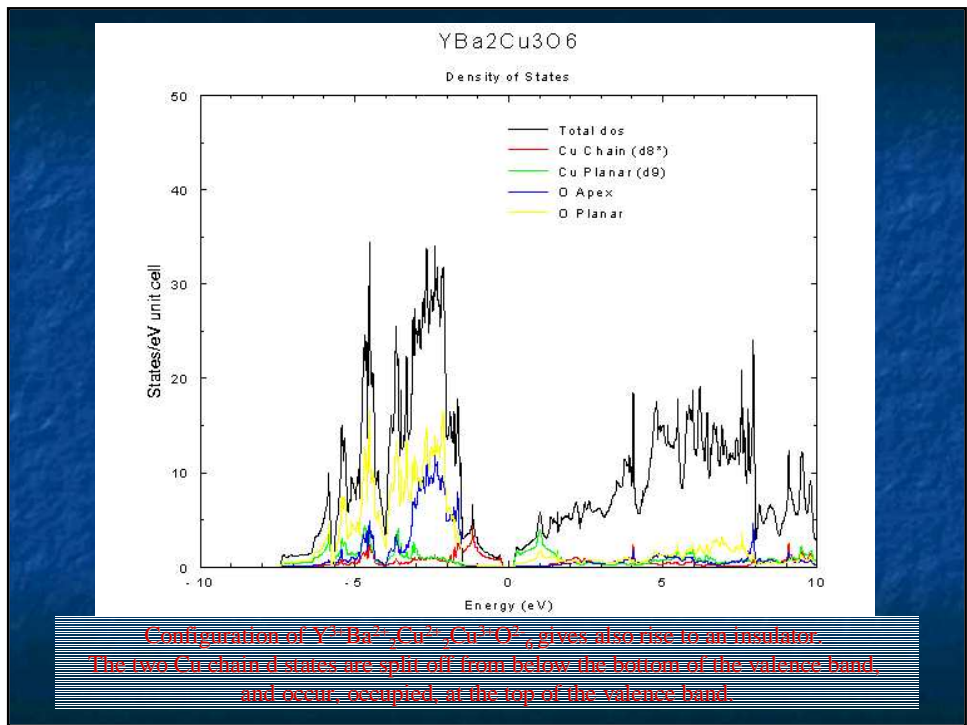
Cu Conf.	SIC Orbitals	
	Cu majority d channel	Cu minority d channel
d^{10}	5	5
d^9	5	$4 (3 (t_{2g}) + 1 (3z^2 - 1))$
d^{9*}	5	$4 (3 (t_{2g}) + 1 (x^2 - y^2))$
d^8	$4 (3 (t_{2g}) + 1 (3z^2 - 1))$	$4 (3 (t_{2g}) + 1 (3z^2 - 1))$
d^{8*}	$4 (3 (t_{2g}) + 1 (x^2 - y^2))$	$4 (3 (t_{2g}) + 1 (x^2 - y^2))$
d^0	0	0

Table 1: Different Cu configurations (Conf) corresponding to particular choices of the localized (self-interaction corrected) d orbitals on Cu-sites. The remaining Cu d states are described with LSD band theory.



ionic Configuration of $Y^{3+}Ba^{2+}_2Cu^{2+}_2Cu^{1+}O^2_{6-}$ gives rise to an insulator

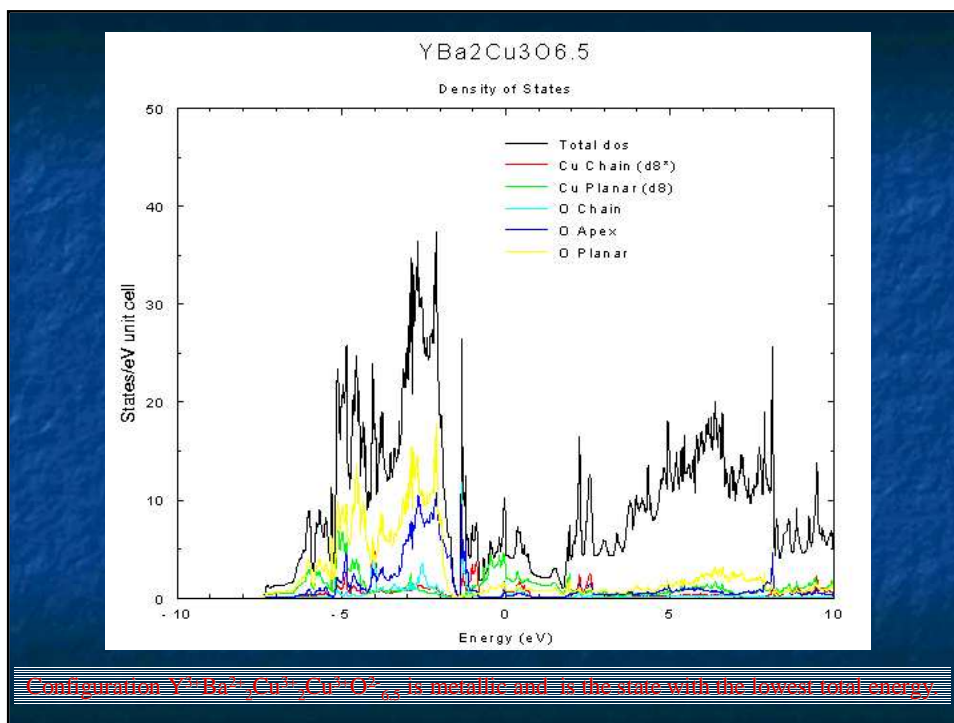
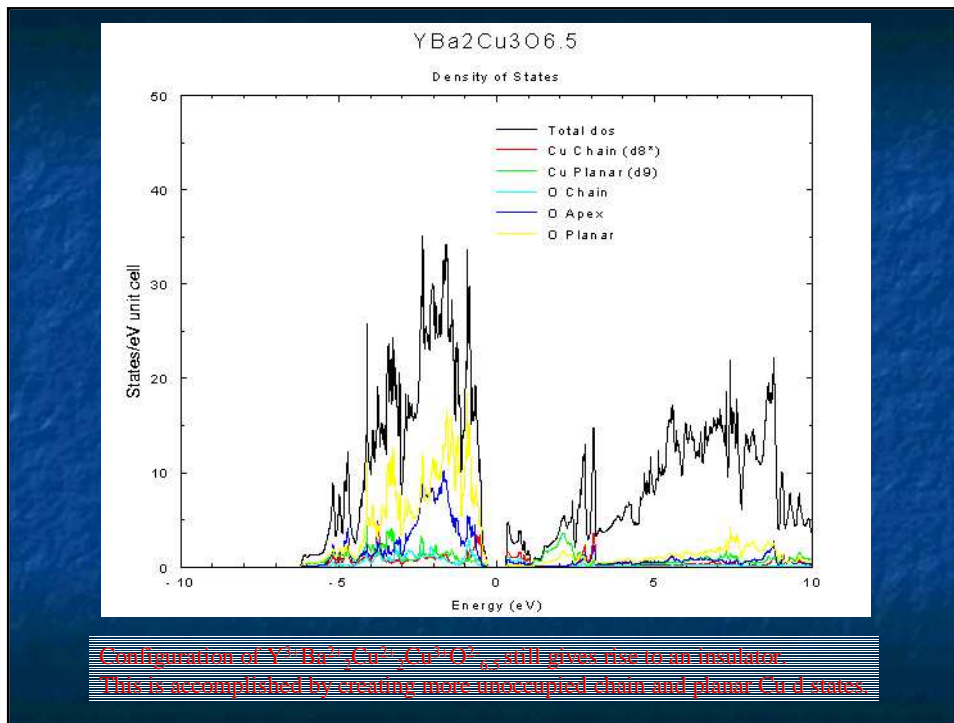
f-electron Materials: from Localised States to DMFT



$YBa_2Cu_3O_6$

SIC can change the number of valence electrons

f-electron Materials: from Localised States to DMFT



YBa₂Cu₃O_{6.5}

SIC can describe both metallic and insulating state

Metal-Insulator Transition in YBCO

The evolution in the CuO₂ plane from insulating to metallic behaviour upon oxygenation is accomplished by the delocalisation of the majority Cu_{d_{x²-y²}-O₂p_x-O₃p_y} band

TABLE II. Energy differences with respect to the lowest total energy as calculated for a variety of Cu configurations (Conf.) listed in Table I. Cu_{pl} and Cu_{ch} refer to planar- and chain-Cu respectively. The energy differences are expressed in eV per CuO₂ layer.

Conf.		YBa ₂ Cu ₃ O ₆	Gap (eV)	YBa ₂ Cu ₃ O _{6.5}	Gap (eV)	YBa ₂ Cu ₃ O ₇
Cu _{pl}	Cu _{ch}					
d ⁹	d ^{9*}	1.2	0.66	1.9	0.72	1.5
d ⁹	d ^{8*}	0.0	0.30	1.0	0.56	1.0
d ⁹	d ¹⁰	3.9	1.29			2.1
d ⁹	d ⁹	4.35				2.2
d ⁹	d ⁸	4.2				1.95
d ⁸	d ^{9*}	1.7		1.1		0.0
d ⁸	d ^{8*}	0.55		0.0		0.07
d ⁸	d ¹⁰	4.5				0.6
d ⁸	d ⁹	4.7				0.6
d ⁸	d ⁸	4.6				0.8

W.M.Temmerman, H. Winter, Z. Szotek and A. Svane, PRL 86 (2001) 2435

Apex O

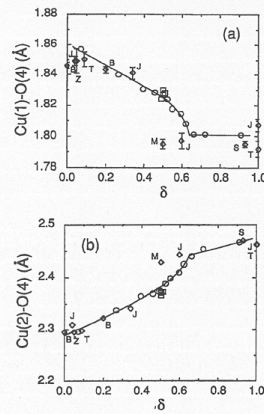


FIG. 11. Copper-oxygen bond lengths (a) Cu(1)—O(4) and (b) Cu(2)—O(4) (in Å) as a function of δ for oxygen-deficient samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Format is the same as for Fig. 5. Data marked by open diamonds are taken from the published literature as follows: J, Ref. 1; T, Ref. 52; B, Ref. 55; M, Ref. 54; Z, Ref. 56; and S, Ref. 53. Where no error bars are shown, they are nominally the size of the symbols.

J.D. Jorgensen et al., Phys. Rev. B 41 1863 (1990)

Structural Aspects of Cu valency of CuO_3

TABLE III. Bond lengths of apex O4 to Cu_{ch} and Cu_{pl} together with the valencies of the Cu_{ch} and Cu_{pl} for $\text{YBa}_2\text{Cu}_3\text{O}_6$, $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ in Å units. The only structural quantity changed in these calculations is the internal parameter determining the position of the apex O4 in the unit cell. The Δ refers to the energy difference between divalent and trivalent Cu_{ch} . Note that the Cu_{ch} becomes trivalent for a 2% reduction in the O4- Cu_{ch} (Å) bondlength. Exp. refers to the use of the experimental bondlengths and $\text{O}_{6.5}$ geom. means calculating the O_7 compound on the lattice of the $\text{O}_{6.5}$ compound.

	Bondlength O4- Cu_{ch} (Å)	Valency Cu_{ch}	Bondlength O4- Cu_{pl} (Å)	Valency Cu_{pl}	
$\text{YBa}_2\text{Cu}_3\text{O}_6$	1.813	3+	2.450	2+	exp.
$\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$	1.824	3+	2.389	3+	exp.
$\text{YBa}_2\text{Cu}_3\text{O}_7$					
$\Delta = -0.07\text{eV}$	1.850	2+	2.304	3+	exp.
$\Delta = -0.02\text{eV}$	1.831	2+	2.323	3+	-1% in bondlength
$\Delta = 0.05\text{eV}$	1.812	3+	2.342	3+	-2% in bondlength
$\Delta = 0.5\text{eV}$	1.704	3+	2.450	3+	-8% in bondlength
	1.824	3+	2.389	3+	$\text{O}_{6.5}$ geom.

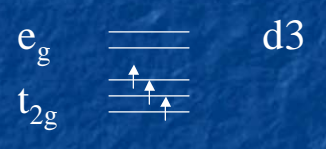
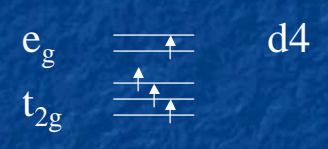
W.M. Temmerman, H. Winter, Z. Szotek and A. Svane, PRL 86 (2001) 2435

Manganites

- CaMnO_3
- Cubic
- Insulator
- AF2 (G type)
- Mn^{4+} ordering
- LaMnO_3
- Distorted cubic
- Insulator
- AF1 (A type)
- Mn^{3+} ordering

Colossal Magnetoresistance in $\text{La}_{(1-x)}\text{Ca}_x\text{MnO}_3$
for $0.1 \leq x \leq 0.4$

Manganites

CaMnO_3	LaMnO_3
e_g 	e_g 
t_{2g}	t_{2g}
$S=3/2$	$S=4/2$

Correlations in LaMnO_3

- structure
- spin
- charge
- orbitals

1 CaMnO_3

FM	
Structure	Relative Energy (mRy)
LSDA	+126.19
$1t_{2g}$	+87.51
$2t_{2g}$	+46.36
$3t_{2g}$	0
$3t_{2g} d_{x^2-y^2}$	+137.85
$3t_{2g} d_{3z^2-r^2}$	+117.49
$3t_{2g} 2e_g$	+319.67

	Relative Energy (mRy)		
	FM	AF1 (A type)	AF2 (G type)
LSDA	+135.911	+129.829	+120.249
Mn^{4+}	+9.722	+5.396	0
$\text{Mn}^{3+}d_{x^2-y^2}$	+147.568	+136.713	+157.315
$\text{Mn}^{3+}d_{3z^2-r^2}$	+127.212	+153.908	+146.234

- Obtain correct valency Mn^{4+} and correct magnetic structure G type (AF2).
- $\Delta E_{\text{valency}} \sim 50\text{mRy}$
- $\Delta E_{\text{magnetism}} \sim 5\text{mRy}$

Cubic LaMnO₃

Correct valency

	Relative Energy (mRy)		
	FM	A-type (AF1)	G-type (AF2)
LSD	+167.02	+174.89	+188.53
Mn ⁴⁺	+51.03	+58.54	+62.56
Mn ³⁺ d _{x²-y²}	+90.21	+40.12	+40.20
Mn ³⁺ d _{3z²-r²}	0	+36.77	+41.34

Distorted LaMnO₃

Phase	n(E)	Mn d moment	Total Energy	Difference
AF1	gap .0954 eV	3.4327	-78979.019861	0
FM	51.215088	3.46323925	-78979.015581	4.28
AF2	5.437455	3.242377	-78978.964188	55.673

Correct magnetic structure in LSD (and also for Mn d⁴)

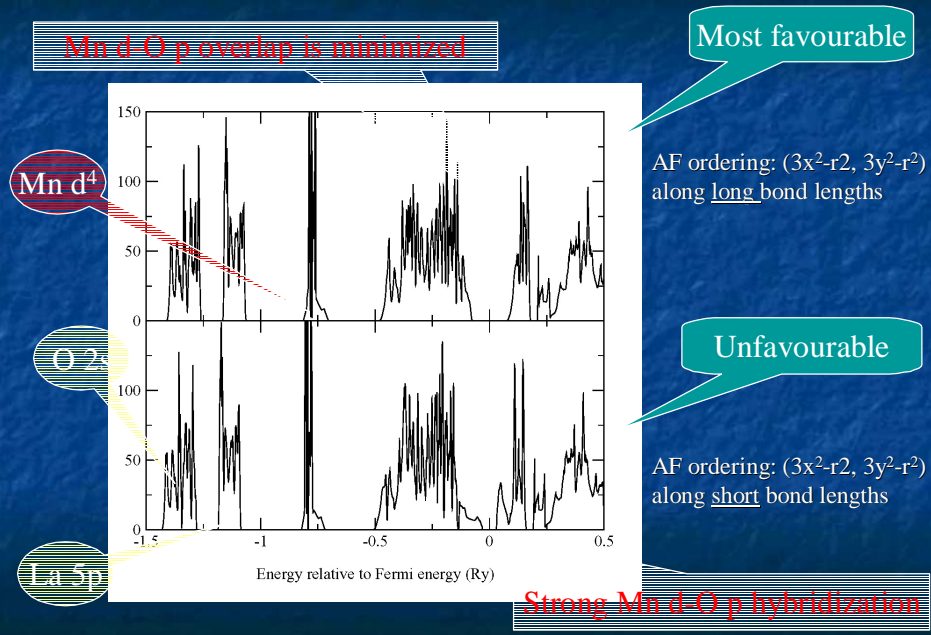
Orbital Ordering

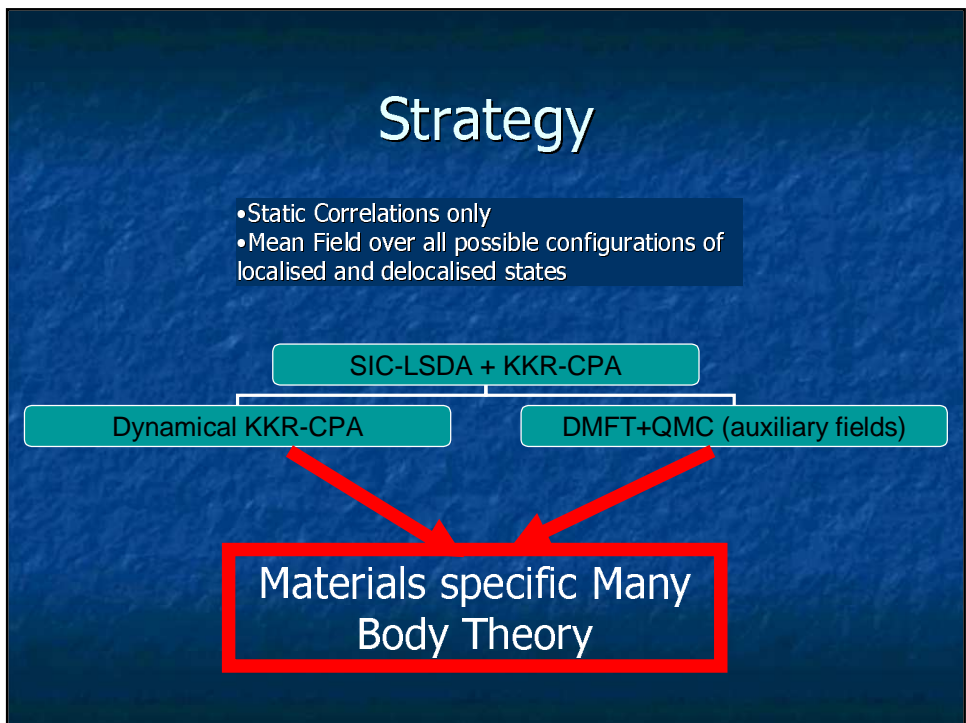
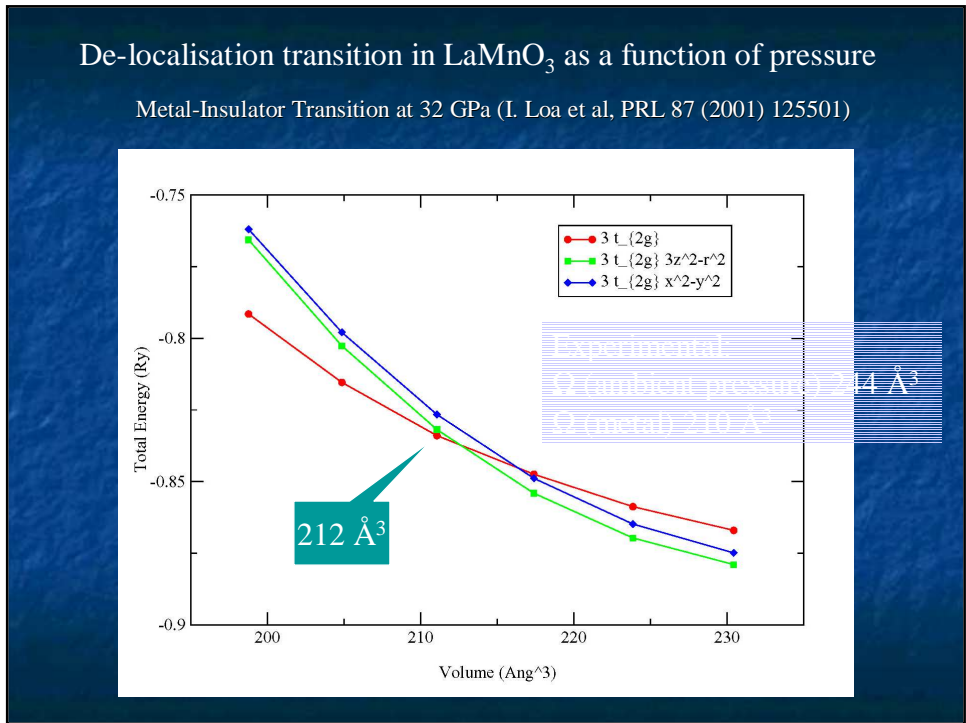
Distorted LaMnO₃

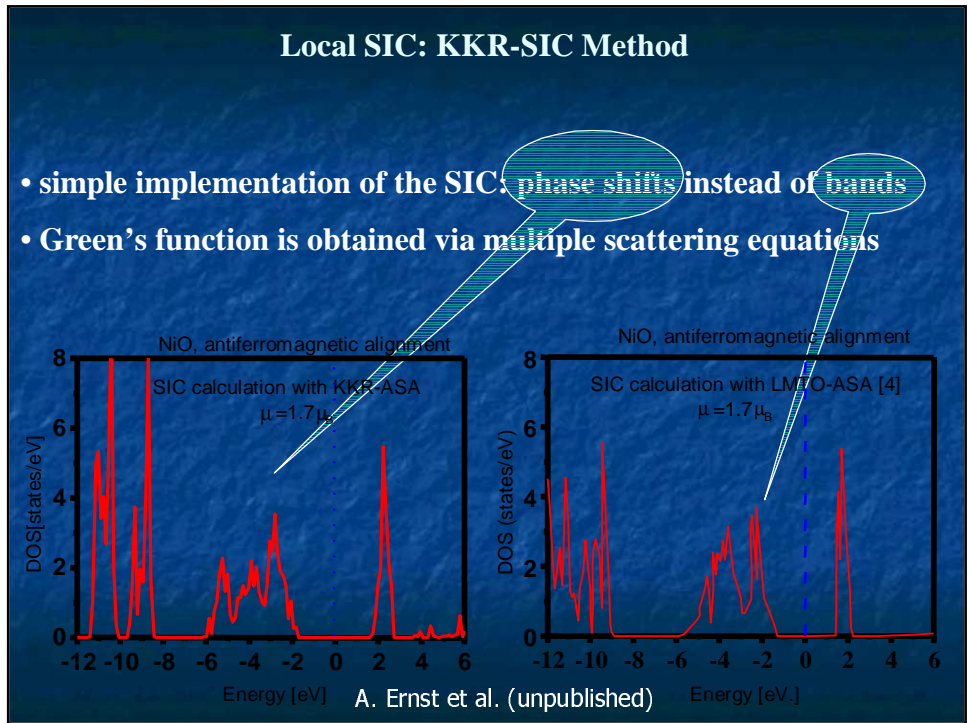
		AF 1			FM
	Mn(x)	Mn(y)	E_{SIC} (Ry)	Gap at E_f (eV)	Relative Energy (mRy)
FM OO	$d_{3x^2-r^2}$	$d_{3y^2-r^2}$	-45684	.3582	39.731
	$d_{3y^2-r^2}$	$d_{3x^2-r^2}$	-45526	.3660	40.475
	$d_{3z^2-r^2}$	$d_{3z^2-r^2}$	-43969	.6451	49.519
	d_{yz}	d_{yz}	-44452	.0692	57.320
	d_{xz}	d_{xz}	-44584	.0759	56.574
	d_{xy}	d_{xy}	-46042	1.1503	27.159
AF OO	$d_{3x^2-r^2}$	$d_{3y^2-r^2}$	-46395	2.0354	0
	$d_{3y^2-r^2}$	$d_{3x^2-r^2}$	-44667	.7887	65.164
	d_{yz}	d_{yz}	-43557	.5985	78.066
	d_{xz}	d_{xz}	-45343	1.8506	8.495

Assuming the experimental physical structure, the correct valency, magnetic and orbital ordering is obtained. Results readily explainable in terms of intuitive picture of minimising overlap between Mn eg orbitals and adjacent oxygen p orbitals.

Density of states in the Orbital Ordered State







Summary

- SIC: order parameters: $n(r)$, $m(r)$ and $n_\alpha(r)$
- SIC can determine if electron forms part of the valence band or not

Conclusion

The SIC describes the $\alpha \leftrightarrow \gamma$ transition in Ce, valency change in rare earths and TM oxides, M/I transition in YBCO as localisation/delocalisation transitions.

Collaborators

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