Skipped valence and ligand holes, or how to make magnetic gold?

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or
how to make magnetic gold?

(and nonmagnetic iron)

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[oxides vs peroxides]

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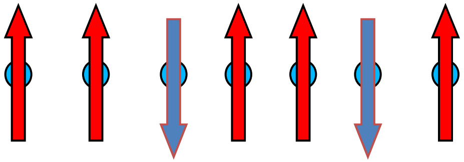
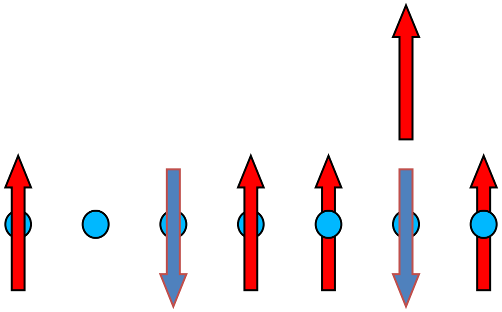
Outline

- Introduction. Small or negative charge-transfer gap systems and ligand holes
- Special properties of systems with negative charge-transfer gaps:
  strong covalency; magnetism; charge disproportionation
- Calaverite AuTe2 – special properties
- Magnetic gold?
- Pyrite FeO2: the system in between oxide and peroxide
- Negative charge transfer gaps: oxides vs peroxides
- Peroxides in batteries
- Conclusions

STRONGLY CORRELATED ELECTRONS

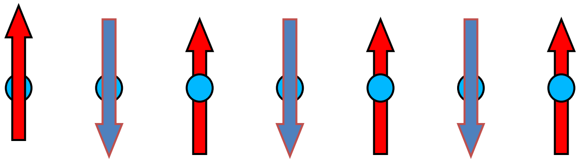


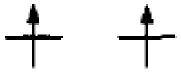


$$\mathcal{H} = -t \sum_{\langle ij\rangle,\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

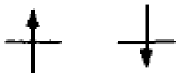
$n = N_{el}/N = 1$; $U/t >> 1$ - Mott insulators, localized electrons

$$H_{eff} = \frac{2t^2}{U} \sum_{\langle ij\rangle} \mathbf{S}_i \mathbf{S}_j .$$



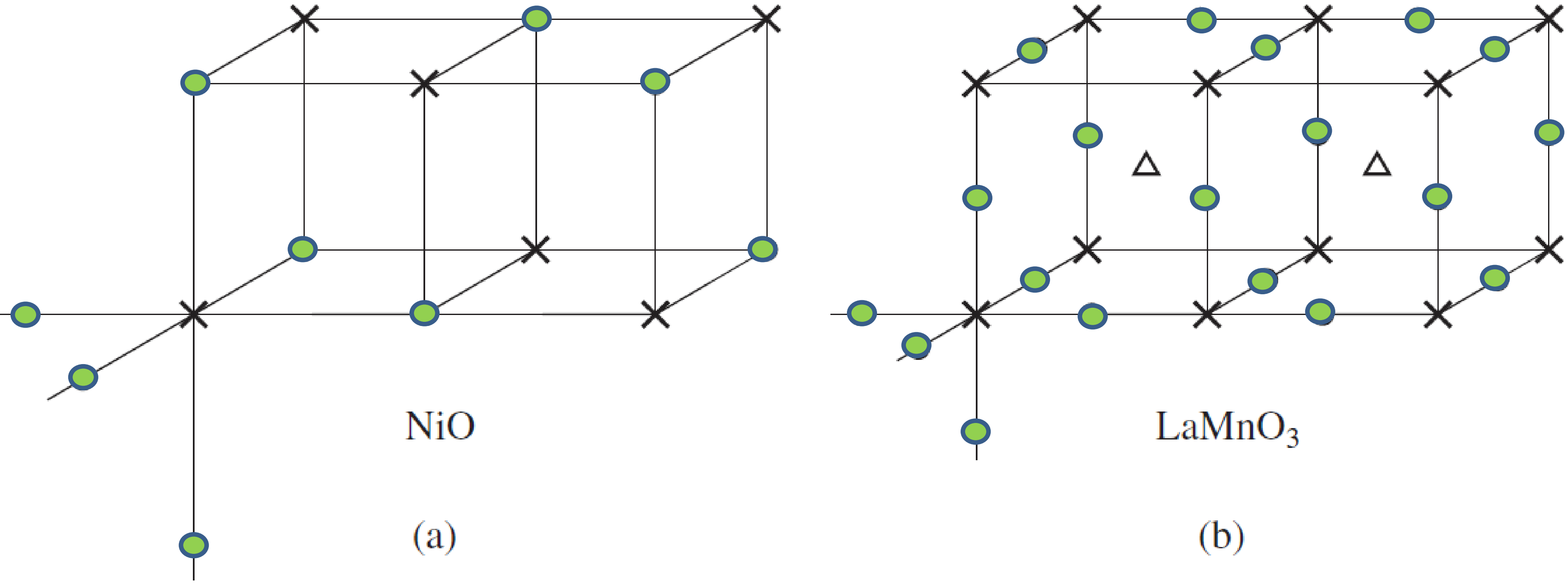


$\Delta E = 0$



$\Delta E = -\frac{2t^2}{U}$

Most often **oxygen ions** (cations, ligands) between transition metal ions



NiO

(a)

$\mathrm{LaMnO_3}$

(b)

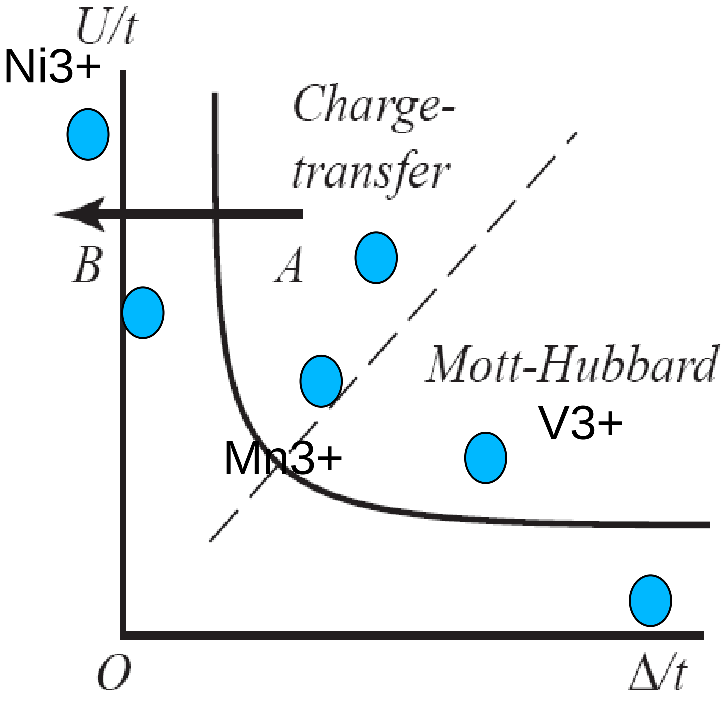
One has to include corresponding oxygen p-orbitals in an apparent way ---> three-band, or d-p model

$$\begin{aligned}\mathcal{H} = \varepsilon_d \sum d^{\dagger}_{i\sigma} d_{i\sigma} + \varepsilon_p \sum p^{\dagger}_{j\sigma} p_{j\sigma} \\ + \sum t_{pd,ij} (d^{\dagger}_{i\sigma} p_{j\sigma} + \mathrm{h.c.}) + U_{dd} \sum n_{di\uparrow} n_{di\downarrow} \\ \left(+ U_{pp} \sum n_{pj\uparrow} n_{pj\downarrow} + U_{pd} \sum n_{di\sigma} n_{pj\sigma'} \right) .\end{aligned}$$

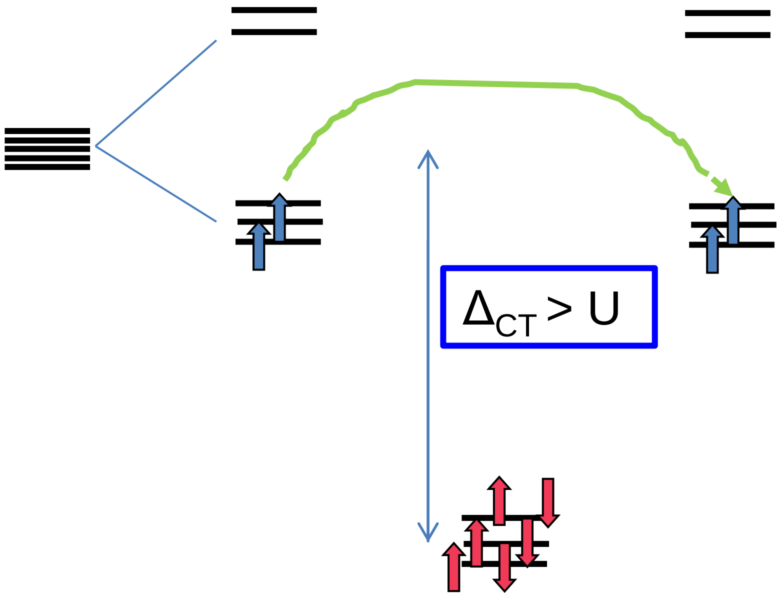
Zaanen-Sawatzky-Allen phase diagram

$$d^n d^n \longrightarrow d^{n-1} d^{n+1}\,, \qquad \Delta E = U = U_{dd}$$

$$d^n p^6 \longrightarrow d^{n+1} p^5\,, \qquad \Delta E = \Delta_{\mathrm{CT}}$$

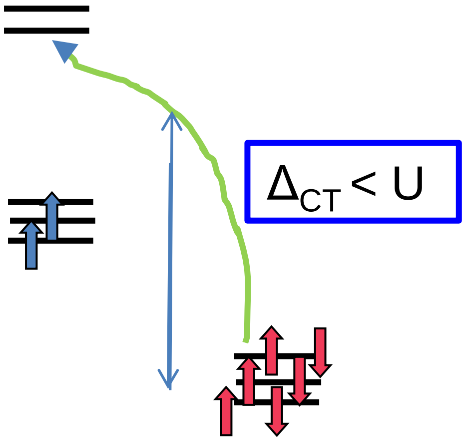


Mott-Hubbard insulator



$\Delta_{CT} > U$

Charge-transfer insulator



$\Delta_{CT} < U$

Small or negative charge transfer gaps, oxygen holes, self-doping

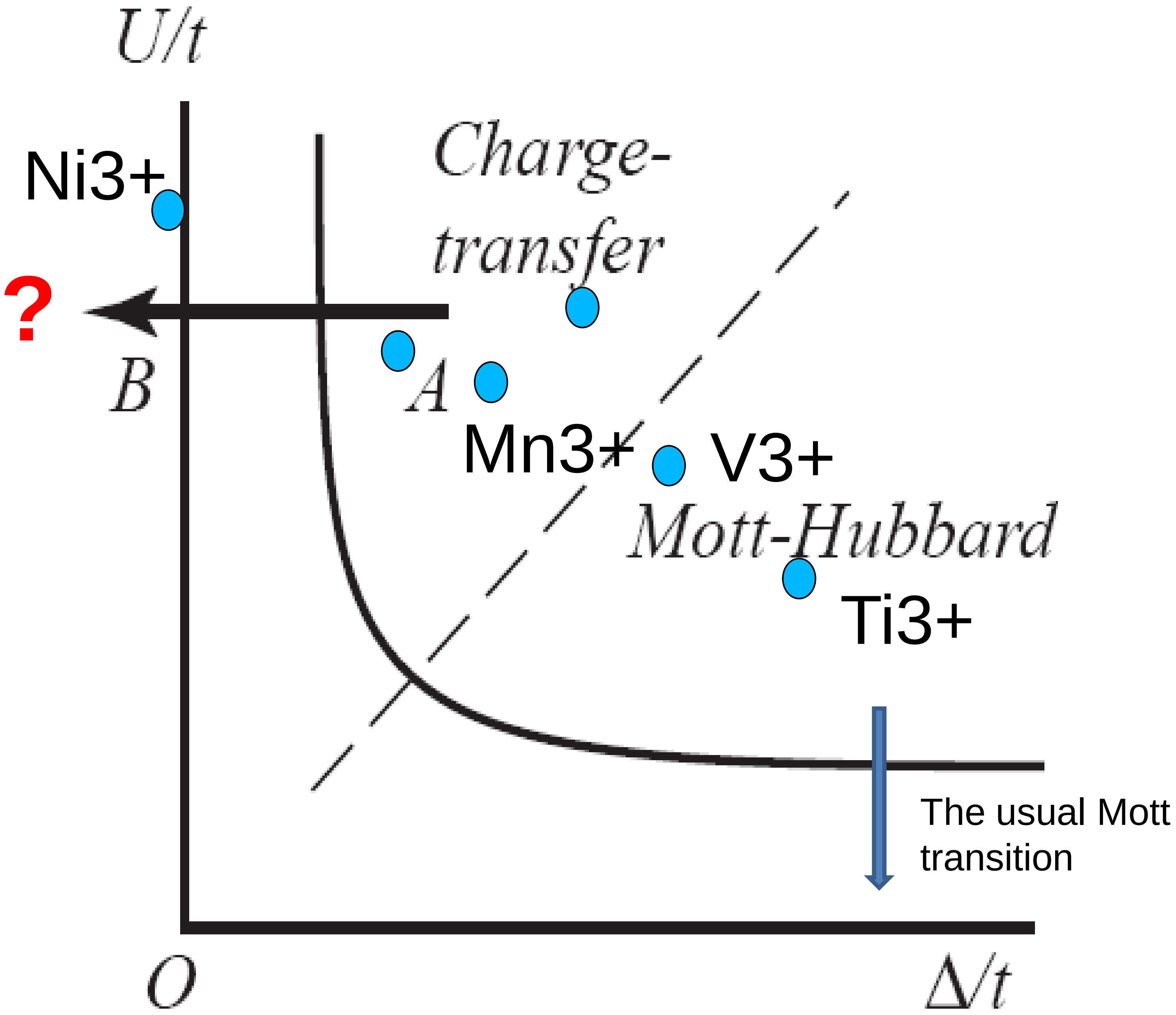
- Mostly in systems with high valence, or high (formal) oxidation state

- Can lead to the "reaction" $d^n\, p^6 \longrightarrow d^{n+1}\, p^5 = d^{n+1}\underline{L}$

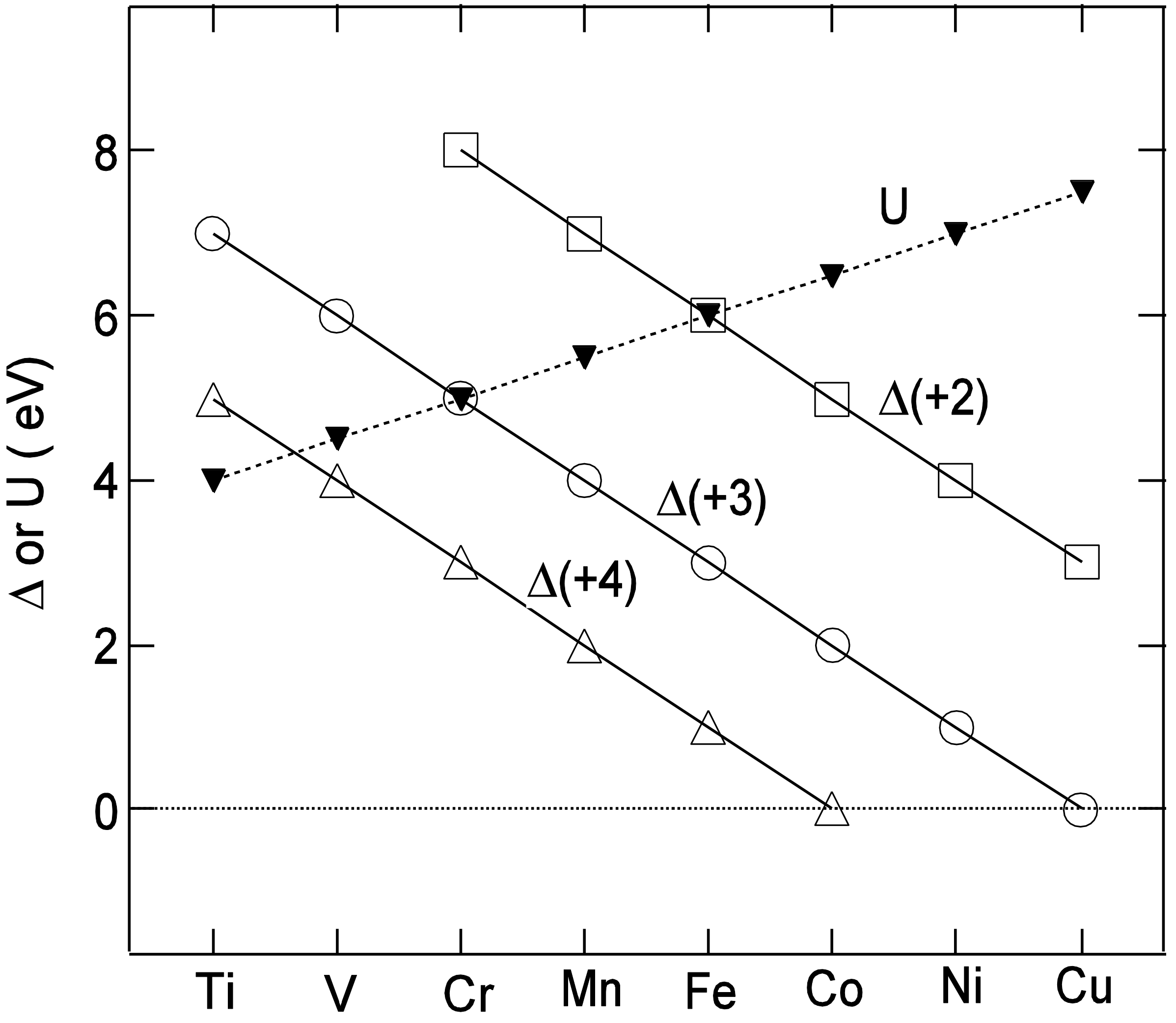
- As a result oxygen holes appear, even in undoped systems ("self-doping")

- The type of resulting state? Metal? Insulator? Magnetic properties?

- d-p covalency is always present. *Qualitative effects* due to negative CT gap?



The usual Mott transition



T. Mizokawa (see e.g. in **D. Khomskii, Transition Metal Compounds**, Cambridge University Press, 2014

● Novel properties in charge transfer systems

Different orbital ordering **{**M.Mostovoy and D.Khomskii, ``Orbital ordering in charge transfer insulators'', PRL **92**, 167201 (2004)}

(Ferro)magnetism

Charge disproportionation

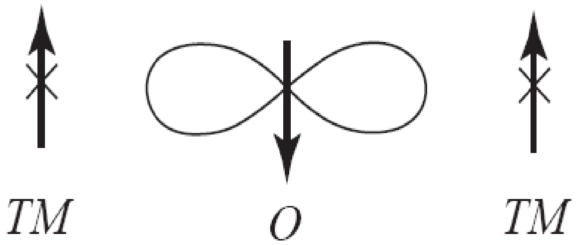
Contribution to (High-Tc) superconductivity?

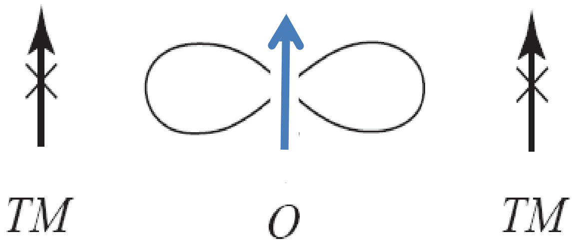
● (Ferro)magnetism of systems with oxygen holes

Oxygen holes can lead to the frustration of magnetic exchange

Possible result: ferromagnetism (a la double exchange)

Example: CrO2, self-doping (a lot of oxygen holes)
{Korotin et al ``CrO2: self-doped double-exchange ferromagnetic oxides'', Phys. Rev. Lett. 80, 4305 (1997)}





● Charge ordering

Usually – noninteger valence (Fe_3O_4, $La_{1/2}Ca_{1/2}MnO_3$, etc)

But sometimes – spontaneous charge ordering, or charge disproportionation

Examples: $BaBiO_3$

$$2Bi^{4+}(6s^1) \rightarrow Bi^{3+}(6s^2) + Bi^{5+}(6s^0)$$

Real charge redistribution may be small, but the quantum numbers are those of Bi^{3+} and Bi^{5+}

- # Charge disproportionation in transition metal compounds

Many compounds with (nominally) Fe^{4+}

$2Fe^{4+}(t_{2g}{}^{3}e_{g}{}^{1}) \rightarrow Fe^{3+}(t_{2g}{}^{3}e_{g}{}^{2}) + Fe^{5+}(t_{2g}{}^{3}e_{g}{}^{0})$

($CaFeO_3$; $Sr_3Fe_2O_7$; $Sr_{2/3}La_{1/3}FeO_3$)

Nickelates $RNiO_3$ (Low Spin); $AgNiO_2$ (R.Coldea)

$2Ni^{3+}(t_{2g}{}^{6}e_{g}{}^{1}) \rightarrow Ni^{2+}(t_{2g}{}^{6}e_{g}{}^{2}) + Ni^{4+}(t_{2g}{}^{6}e_{g}{}^{0})$

=> mostly happens for systems with negative CT gap and a lot of oxygen holes!

Bi perovskites: all different and interesting!

$BiMnO_3$: ferromagnetic insulator; Jahn-Teller distorted perovskite; ferroelectric?

$BiFeO_3$: rombohedral; good ferroelectric; spiral magnetic structure; classical type-I multiferroics

$BiCoO_3$: very strong tetragonal distortion! a la **$PbVO_3$** (pyroelectric). High spin – low spin transition under pressure

$BiNiO_3$: Ni^{2+}, Bi^{4+} → charge segregates into **Bi^{3+} + Bi^{5+}**

Under pressure: **$BiNiO_3$** goes back to **Ni^{3+}, Bi^{3+}** → charge segregates into **Ni^{2+} + Ni^{4+} !**

Something interesting with Pb3+?

Conditions for charge disproportionation

>>>> Need small energy loss for transferring (part of the) electron (reducing Coulomb energy cost)

Regime intermediate between localized and itinerant (close to Mott transition)

Oxygen holes !

Two oxygen holes “couple” to the same transition metal ion; charge ordering without moving the charges! (G.Sawatzky)

Strongly reduce Coulomb cost; gain in d-p covalency (plus lattice relaxation)

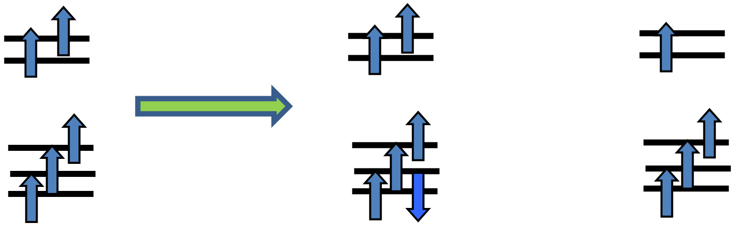
Need negative, or at least small U_{eff}

U_{eff} : $d^n + d^n \rightarrow d^{n+1} + d^{n-1}$

U_{eff} is determined by: $U_{on\text{-}site}$; J_{Hund} ; Δ charge transfer; t_{pd} –hybridization

Strongly depend on electronic configuratipon, i.e. on the type of the ion and on the valence

Fe^{3+} : $2Fe^{3+}(d^5) \rightarrow Fe^{2+}(d^6) + Fe^{4+}(d^4)$



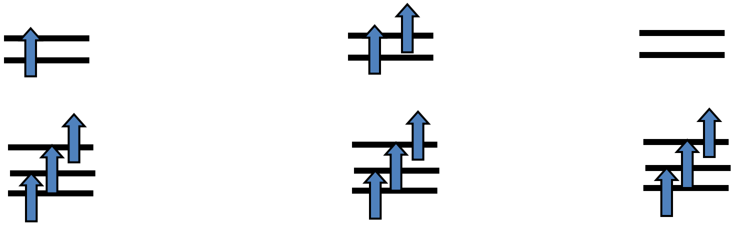
$2(-10J_H)$ vs $(-10J_H)$ + $(-6J_H)$

$(-20J_H)$ vs $(-16J_H)$

$$\boxed{U_{eff} = U + 4J_H}$$

U_{eff} is **large**, lose large Hund's energy (4 J_H) by making charge segregation

Fe^{4+}: $2Fe^{4+}(d^4) \rightarrow Fe^{3+}(d^5) + Fe^{5+}(d^3)$



$2(-6J_H)$ vs $(-10J_H) + (-3J_H)$

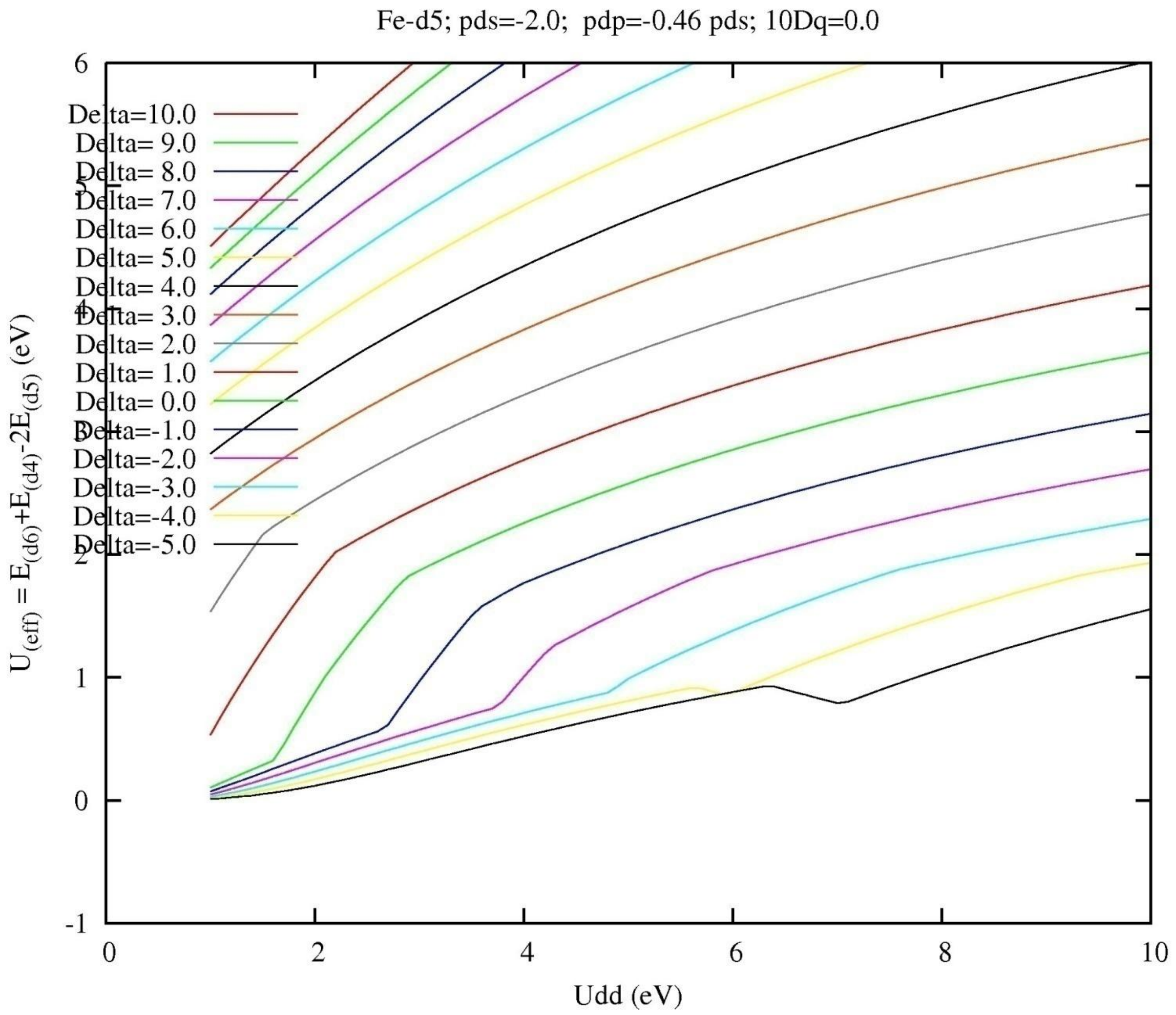
$(-12J_H)$ vs $(-13J_H)$

$U_{eff} = U - J_H$

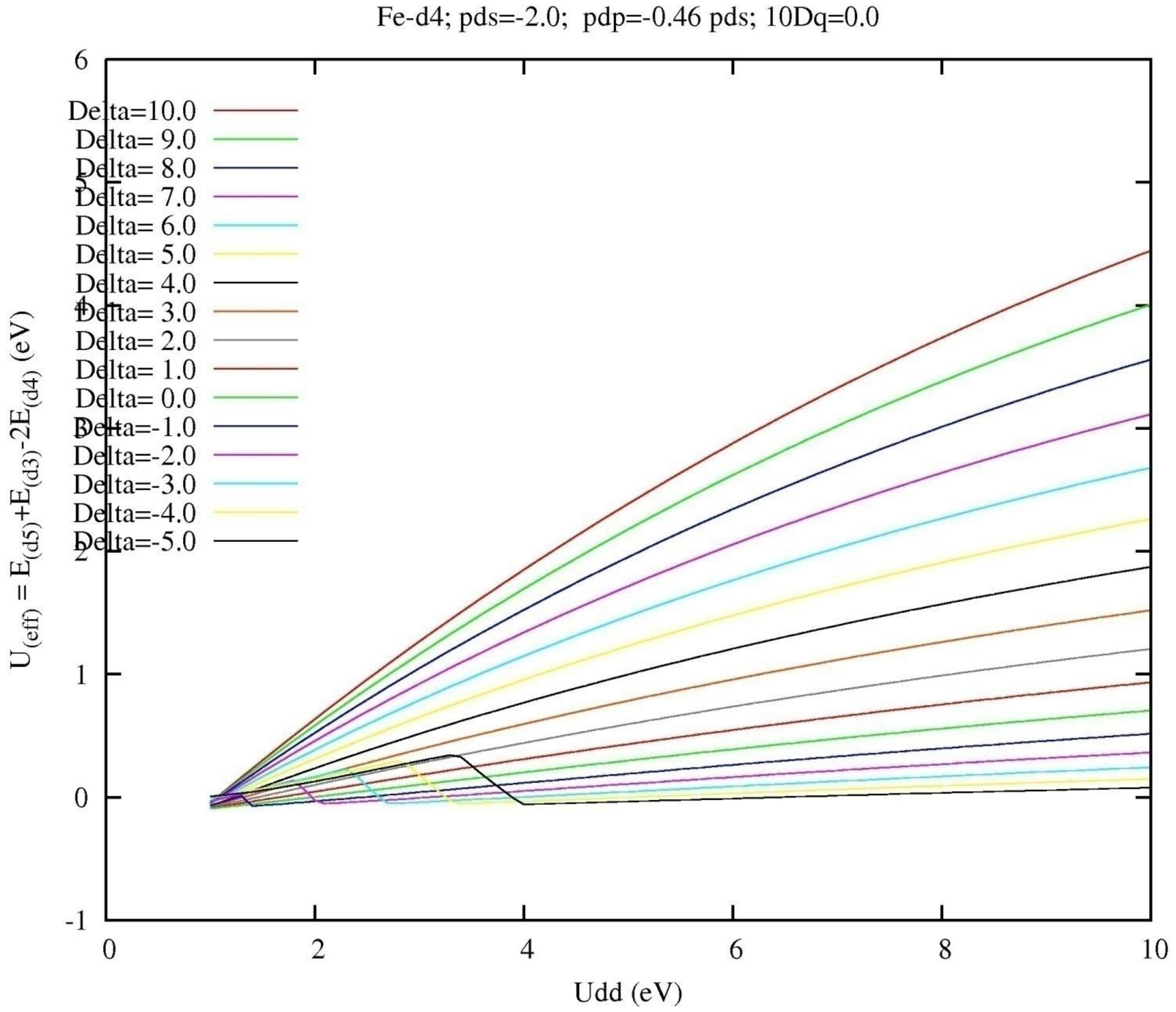
U_{eff} is **small**; gain Hund's energy ($-J_H$) by making charge segregation

Ni^{3+} - the same as **Fe^{4+}**

$Fe^{3+}(d^5)$

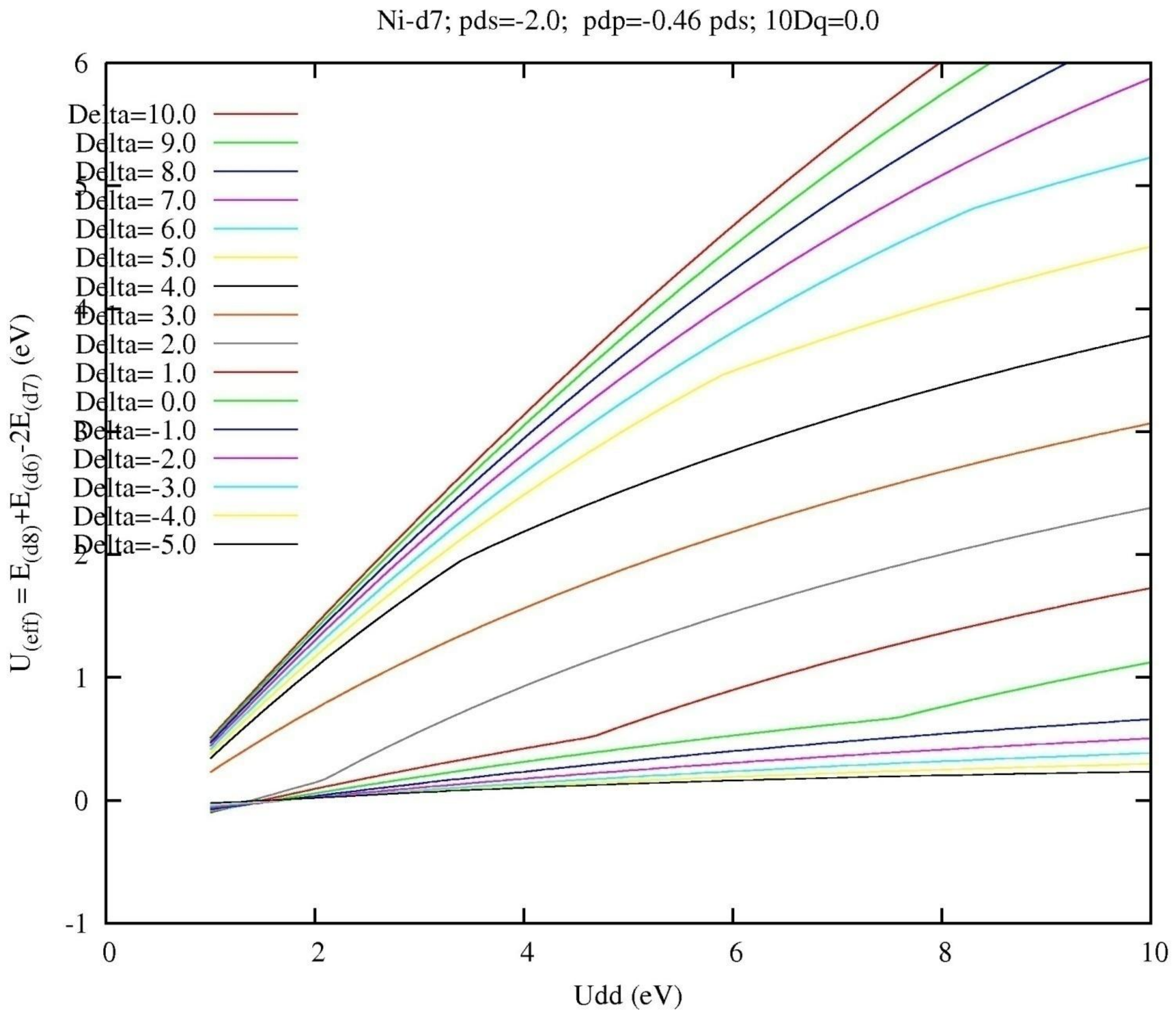

Fe-d5; pds=-2.0; pdp=-0.46 pds; 10Dq=0.0
Delta=10.0
Delta= 9.0
Delta= 8.0
Delta= 7.0
Delta= 6.0
Delta= 5.0
Delta= 4.0
Delta= 3.0
Delta= 2.0
Delta= 1.0
Delta= 0.0
Delta=-1.0
Delta=-2.0
Delta=-3.0
Delta=-4.0
Delta=-5.0
U(eff) = E(d6)+E(d4)-2E(d5) (eV)
Udd (eV)
-1
0
1
2
3
4
5
6
0
2
4
6
8
10

Fe^{4+}(d^4)



M.Haverkort, unpublished

Ni^{3+}(d^7)


Ni-d7; pds=-2.0; pdp=-0.46 pds; 10Dq=0.0
Delta=10.0
Delta= 9.0
Delta= 8.0
Delta= 7.0
Delta= 6.0
Delta= 5.0
Delta= 4.0
Delta= 3.0
Delta= 2.0
Delta= 1.0
Delta= 0.0
Delta=-1.0
Delta=-2.0
Delta=-3.0
Delta=-4.0
Delta=-5.0
U(eff) = E(d8)+E(d6)-2E(d7) (eV)
Udd (eV)
6
5
4
3
2
1
0
-1
0
2
4
6
8
10

Why gold?

1. Very inert, noble metal; very few compounds/minerals

2. Valence Au1+ (d10) and Au3+ (d8) are known; practically no Au2+ - “skipped valence” (C. Varma)

3. Definitely negative charge-transfer gap systems

4. Interesting superconducting compounds! (but no magnetic!)

Why not Au2+ ? → charge disproportionation!

$$2Au^{2+}(d^9) \rightarrow Au^{1+}(d^{10}) + Au^{3+}(d^8)$$

For example $CsAuCl_3 = Cs_2Au_2Cl_6 \rightarrow Cs_2Au^{1+}Au^{3+}Cl_6$

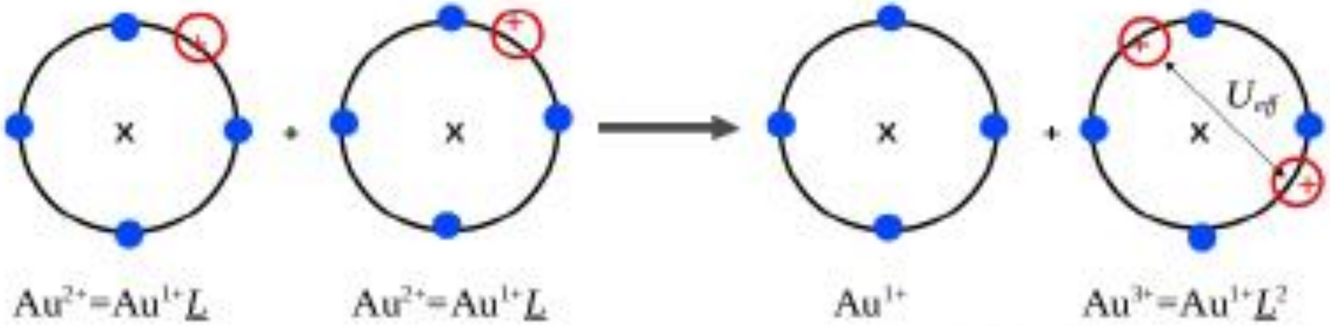
But in fact – action on ligands! Ligand holes

● $Cs_2Au_2Cl_6$

Check this idea on the example of CD: $Cs_2Au_2Cl_6$

the «reaction» $2Au^{2+}(d^9) \rightarrow Au^{1+}(d^{10}) + Au^{3+}(d^8)$

is in fact $2(Au^{1+}\underline{L}) \rightarrow Au^{1+} + (Au^{1+}\underline{L}^2)$



$\boxed{U_{eff}(L^2) << U_{dd}}$

Acta Cryst. (1979). A**35**, 360–365

The Influence of High Hydrostatic Pressure on the Crystal Structure of Cesium Gold Chloride ($Cs_2Au^IAu^{III}Cl_6$) in the Pressure Range up to 52×10^8 Pa

By W. Denner, Heinz Schulz and H. d'Amour

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(*Received 19 June 1978; accepted 31 October 1978*)

Abstract

Using a gasketed diamond-anvil high-pressure cell, which has been adapted to the automatic four-circle diffractometer, we have studied the structural changes of single crystals of the mixed-valence compound $Cs_2Au^IAu^{III}Cl_6$ under high hydrostatic pressure. Measurements with a modified measuring procedure at different pressures show a continuous decrease in the lattice constants. The changes in the relative volume are about 19% in the pressure range up to 52×10^8 Pa while the a/c ratio remains constant. The Cl atoms, which coordinate with the different gold atoms in the form of strongly distorted octahedra, move towards the symmetrical position between the Au^I and Au^{III} atoms as the pressure increases. At about 52×10^8 Pa the gold atoms become indistinguishable, this means only formal Au^{2+} atoms are present.

Introduction

The crystal structure of the mixed-valence compound $Cs_2Au^IAu^{III}Cl_6$ was first determined in 1938 by Elliott and Pauling from powder photographic data (Elliott & Pauling, 1938). The structure was redetermined using single-crystal data by Tindemans v. Eijndhoven & Verschoor (1974) and independently in 1975 by the authors. $Cs_2Au^IAu^{III}Cl_6$ crystallizes in the space group *I4/mmm* with lattice constants $a = 7{\cdot}495\ (1)$ and $c = 10{\cdot}880\ (2)$ Å. The two different gold atoms, valency +1 (Au^I) and +3 (Au^{III}), in this compound show typical coordination. The Au^I are linearly, the Au^{III} quadratic planar coordinated with the Cl atoms. In this way chains of strongly distorted $AuCl_6$ octahedra are produced, which are parallel to the c axis (Fig. 1). Within such a chain, there are alternately elongated octahedra with Au^{III} and compressed octahedra with Au^I in the centres. The different Au—Cl distances are given in Table 1. Neighbouring chains along [110] are translated by $c/2$ and connected by the Cl atoms of the planar Au^{III} coordination.

Table 1. Au—Cl *distances in the coordination octahedra at different pressures*

P (Pa × 10^{-8})	Au^I—Cl (1) (Å)	Au^I—Cl (2) (Å)	Au^{III}—Cl (1) (Å)	Au^{III}Cl (2) (Å)
10^{-3}	2·28 (003)	3·01 (003)	3·15 (003)	2·29 (003)
1·5	2·23 (09)	2·97 (03)	3·11 (09)	2·31 (03)
11·5	2·42 (09)	2·85 (03)	2·91 (09)	2·33 (03)
33·1	2·40 (10)	2·77 (03)	2·80 (10)	2·28 (03)
43·1	2·39 (17)	3·01 (12)	2·62 (17)	2·07 (12)
51·7	2·56 (13)	2·49 (11)	2·56 (13)	2·49 (11)

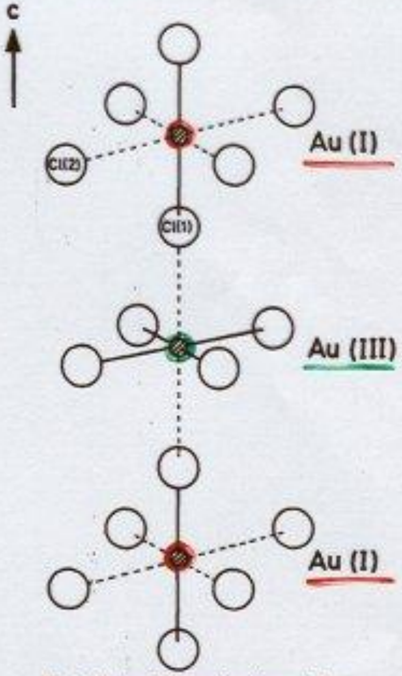
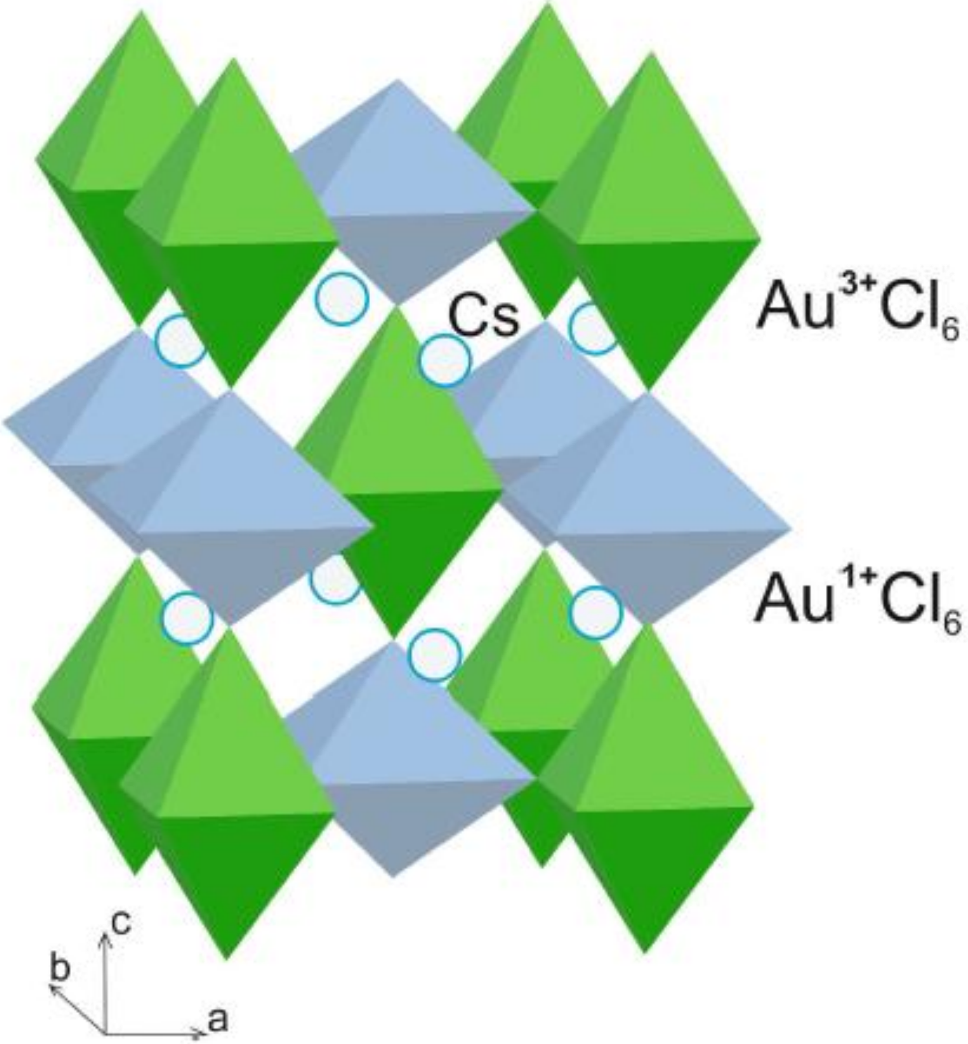
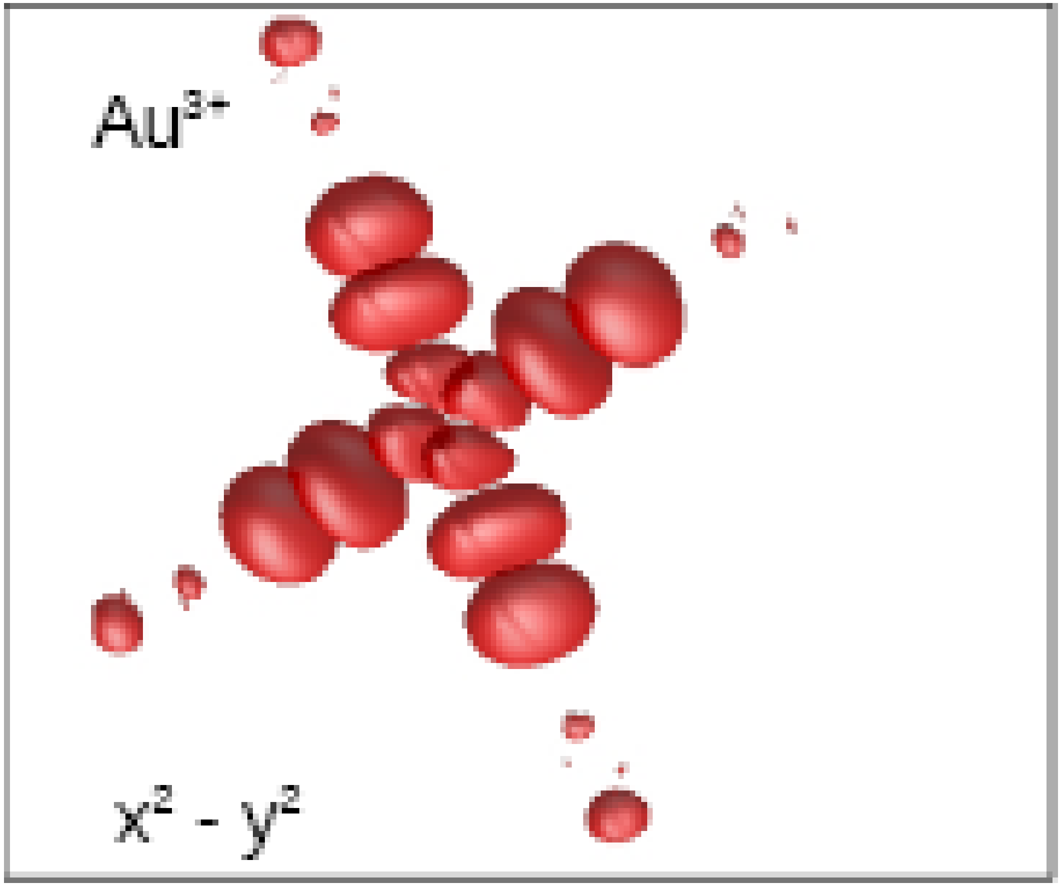


Fig. 1. Chain of distorted $AuCl_6$ octahedra.

0567-7394/79/030360-06$01.00



The crystal structure of $Cs_2Au_2Cl_6$.

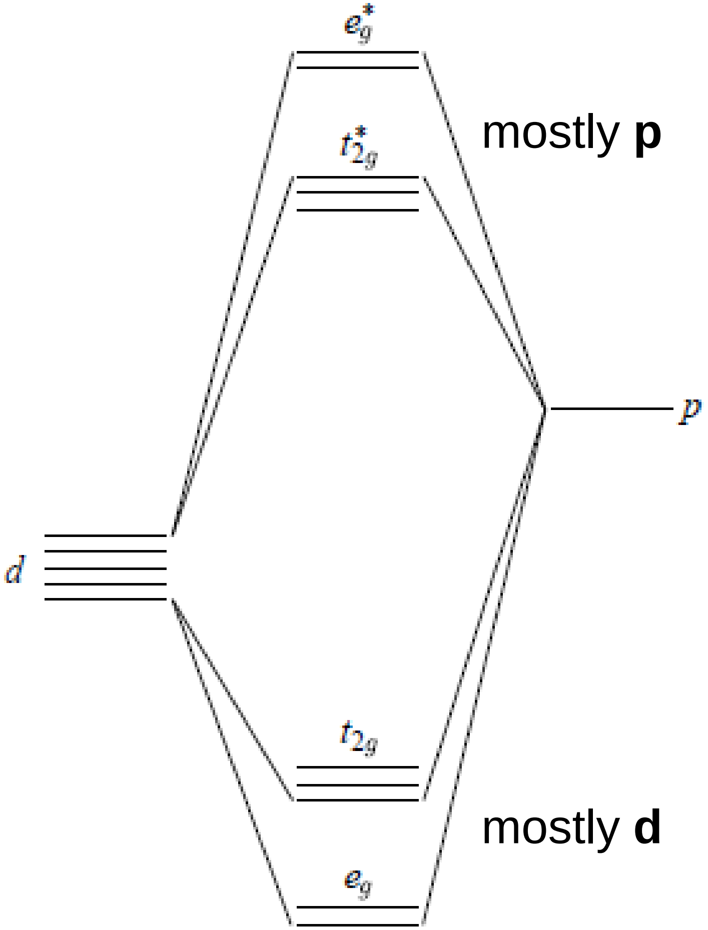


About 22% of holes on *d*-level of Au, and 78% on *p*-shells of ligands (Cl)

$Cs_2Au_2Cl_6$

A.Ushakov, S Steltsov and D.Khomskii,
J. Phys.: Condens. Matter **23**, 445601 (2011)

“Inverted” crystal field splitting for d-electrons:



mostly **p**

mostly **d**

A.Ushakov, S Steltsov and D.Khomskii,
J. Phys.: Condens. Matter **23**, 445601 (2011)

PHYSICAL REVIEW B VOLUME 61, NUMBER 1 1 JANUARY 2000-I

Photoinduced phase transition in a mixed-valence gold complex

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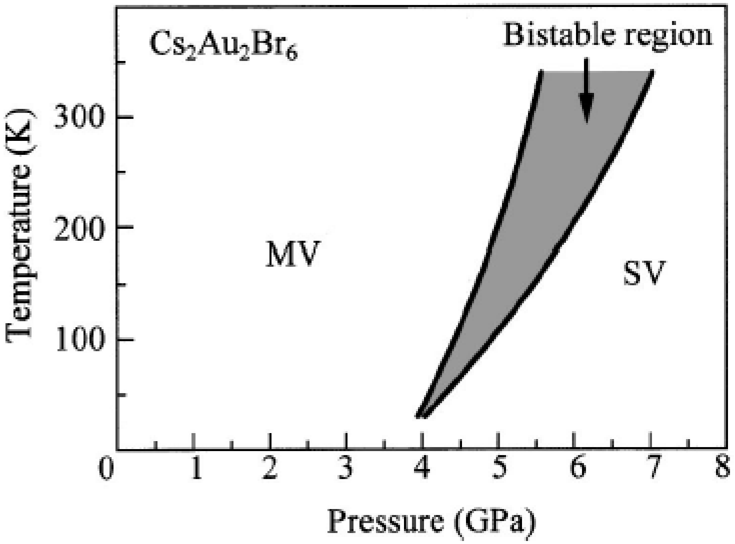
We have found a photoinduced phase transition (PIPT) in the mixed-valence (MV) gold complex $Cs_2Au_2Br_6$ from the MV state (ambient pressure phase) to the single-valence (SV) phase (high-pressure phase) in the pressure region from 6.4 to 6.8 GPa. We have observed an accumulation of the photoirradiation effect of each pulse shot, and have ascribed it to stabilization of the photogenerated SV clusters due to the cooperative Jahn-Teller instability of Au^{2+} ions. The PIPT shows a distinct threshold behavior against the photon density as well as the shots number, which has been interpreted in terms of the critical nucleation of the photoinjected SV clusters. We further found that the phototransformed SV phase is not stable below 5.5 GPa, and changes into the former MV phase after a long dead time of $\sim 10^4$ s.



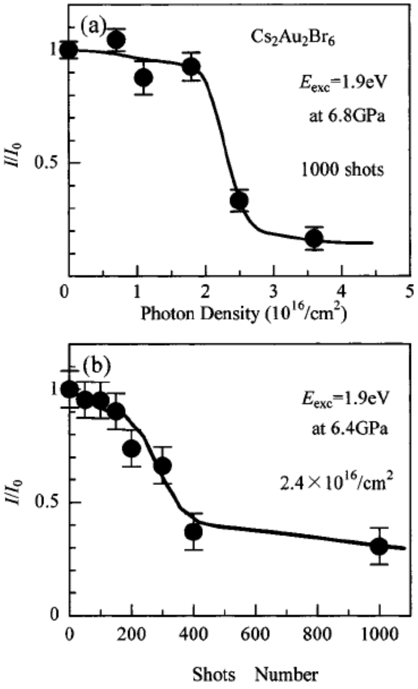
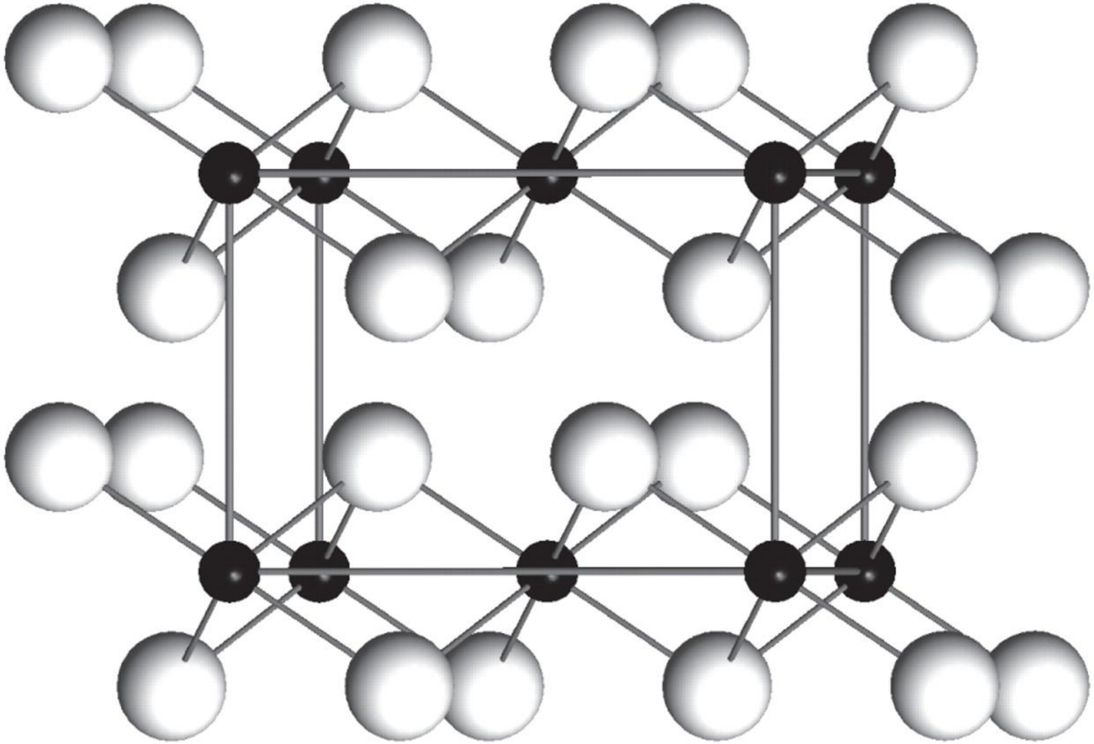


FIG. 4. (a) photon density and (b) shots number dependence of relative Raman intensity I/I_0 of the Au-Br stretching mode, where I_0 is the intensity before photoexcitation. The Raman mode is deactivated in the photogenerated SV phase.

- **Calaverite AuTe2**

(*the only mineral from which one can extract gold*!)



- **Gold telluride AuTe2** (mineral *calaverite*). Layered material with triangular **Au** layers, with distorted CdI2 structure. Similar mineral ***silvanite*** **AuAgTe4** – stripes of **Au3+** and **Ag1+**

Rare case of ***incommensurate crystal structure in natural minerals*****.**

Theoretically incommensurate structure and possibly superconductivity are due to charge disproportionation : in $\mathbf{Au^{2+}(Te_2)^{2-}}$ nominally $\mathbf{Au^{2+}}$ ions are unstable,

$\mathbf{2Au^{2+}}$--->$\mathbf{Au^{1+}}(d^{10})$ + $\mathbf{Au^{3+}}(d^8$ LS, S=0)),

but with practically all the holes on Te **(negative charge transfer gap situation),** i.e. the actual “reaction” is rather

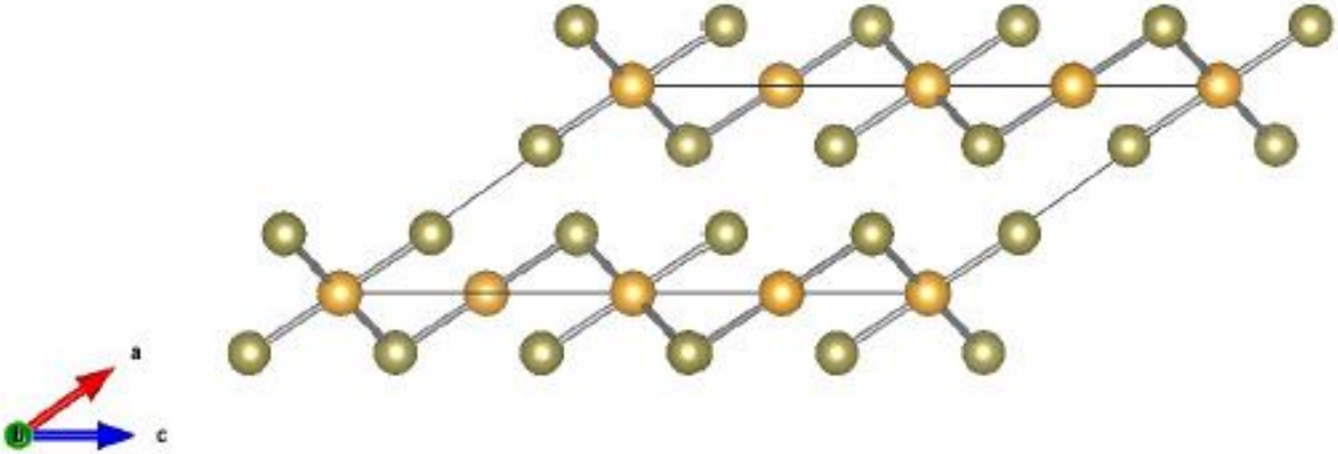
(L – ligand hole (hole on Te)

Why incommensurate? *– charge disproportionation in the frustrated (triangular) lattice*

Metal; becomes **superconducting** when doped by **Pt** and **Pd**, and under pressure.

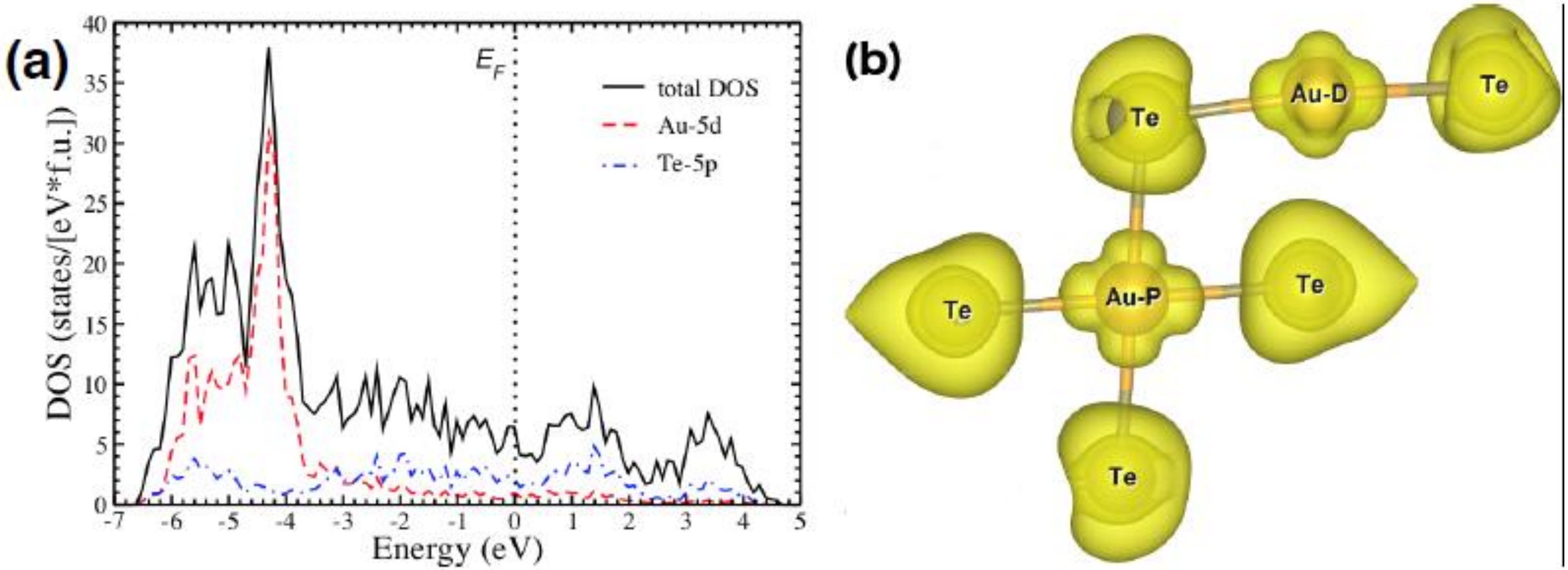
Both elements heavy; strong spin-orbit coupling. **Topological?**

*) Material with similar structure **IrTe2** – actively studied (several superstructures, etc). Also superconducting when doped by **Pt**

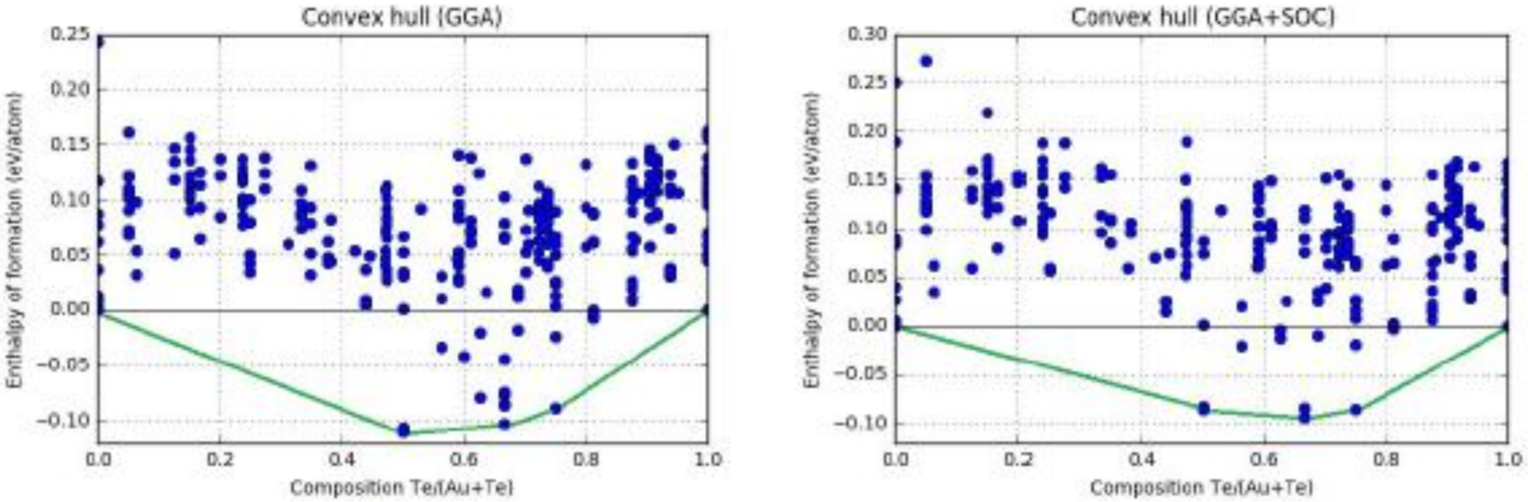

a
b
c

Calaverite $AuTe_2$: the system with spectacular properties due to negative charge transfer gap and self-doping

Sergey S. Streltsov[1,2*], Alexey V. Ushakov[1], and Daniel I. Khomskii[3]



New material predicted: **AuTe** (Roizen, Oganov)



(a) **(b)**

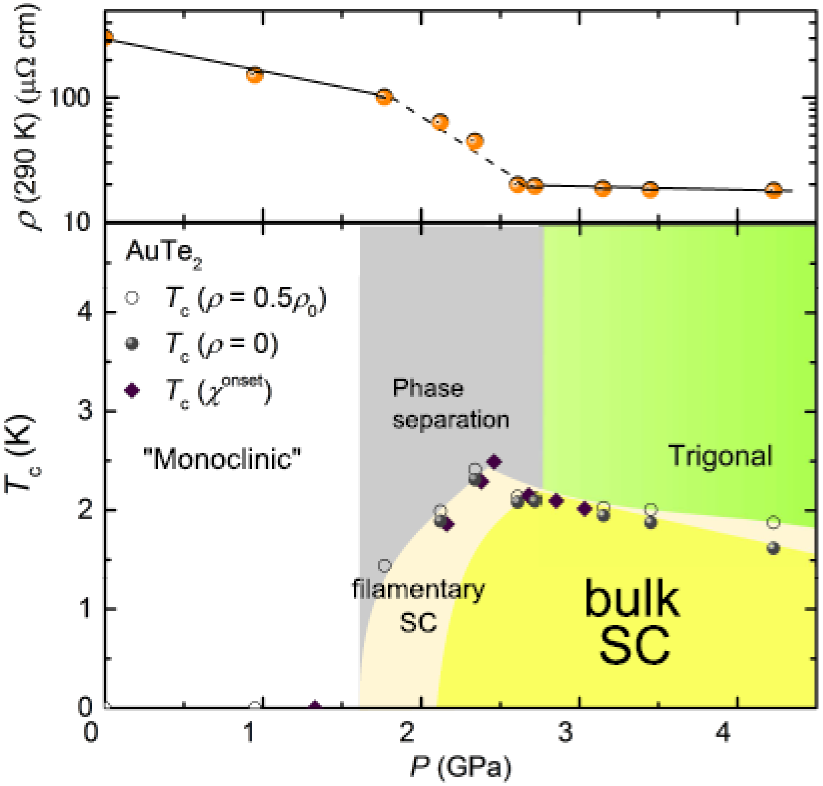
Figure 1. Convex hull diagrams of Au-Te system

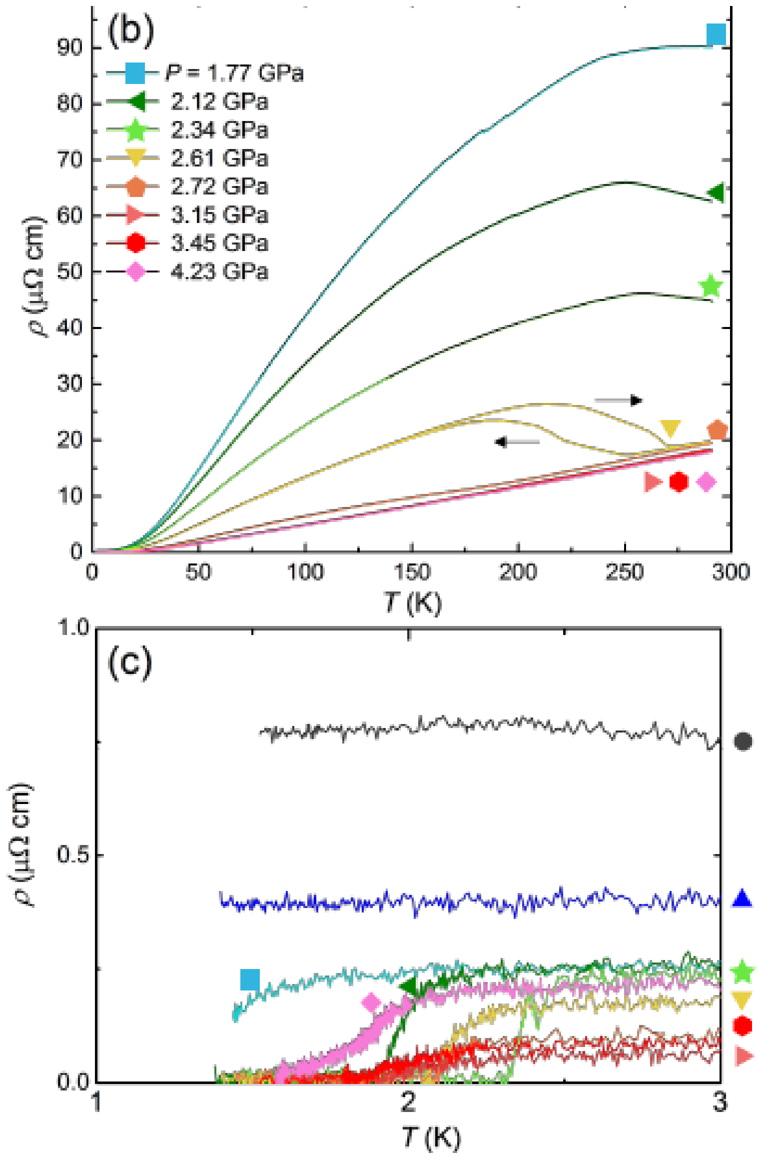
There exist a very rare mineral *muthmanite* **AuAgTe2 = $Au_{1/2}Ag_{1/2}Te$**

Pressure-Induced Superconductivity in Mineral Calaverite $AuTe_2$

Shunsaku Kitagawa[1], Hisashi Kotegawa[1], Hideki Tou[1], Hiroyuki Ishii[2], Kazutaka Kudo[2], Minoru Nohara[2], and Hisatomo Harima[1]

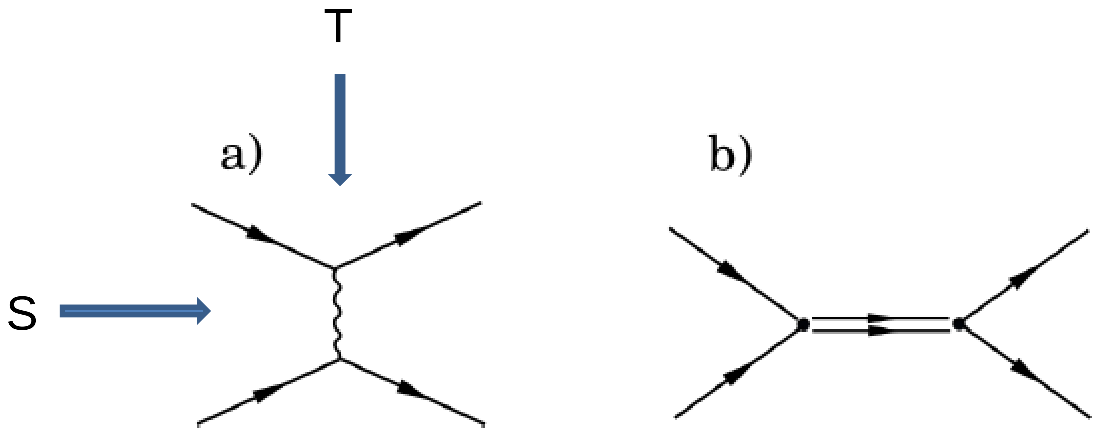
J. Phys. Soc. Jpn. 82, 113704 (2013)





Possible mechanism of superconductivity: effective negative-U (on-site electron attraction, formation of electron pairs (“bipolarons”)

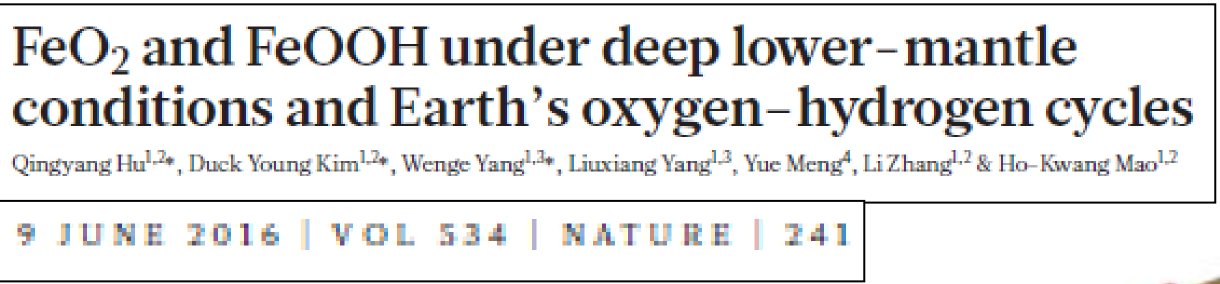
“S-channel” theory of superconduvitivty (Zvezdin-Khomskii; Freedberg-Lee)
(not to mix with s-wave!)



Diagrams illustrating (a) conventional BCS “t-”channel pairing and (b) “s-”channel pairing proposed for $AuTe_2$.

For **Ba(PbBi)O3** and **(BaK)BiO3** – first proposed by **Rice** @ **Sneddon** (1981)

● Nonmagnetic iron

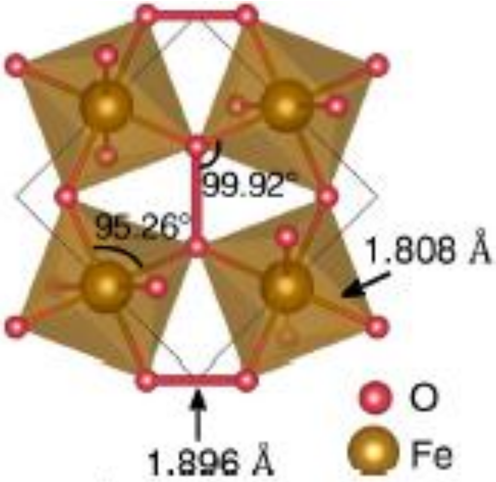


FeO$_2$ and FeOOH under deep lower-mantle conditions and Earth's oxygen–hydrogen cycles

Qingyang Hu[1,2*], Duck Young Kim[1,2*], Wenge Yang[1,3*], Liuxiang Yang[1,3], Yue Meng[4], Li Zhang[1,2] & Ho-Kwang Mao[1,2]

9 JUNE 2016 | VOL 534 | NATURE | 241

Pyrite structure, like **FeS2**



Extended Data Figure 1 | Bonding lengths and angles in pyrite-type FeO$_2$ at 76 GPa. The structure is viewed along the *x* axis of the experimental FeO$_2$ unit cell.

Peroxide/hyperoxides, contain O_2 molecular ions:

$(O_2)^-$ e.g. in **NaO_2**

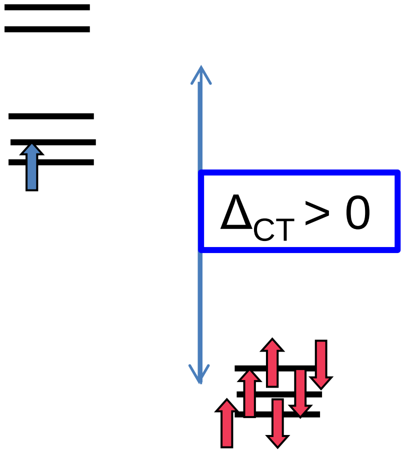
$(O_2)^{2-}$ e.g. in **MgO_2**

"Real" pyrite **FeS_2** (the "fool's gold"): **Fe^{2+} $(O_2)^{2-}$,** **Fe^{2+}** - nonmagnetic, low spin (S=0)

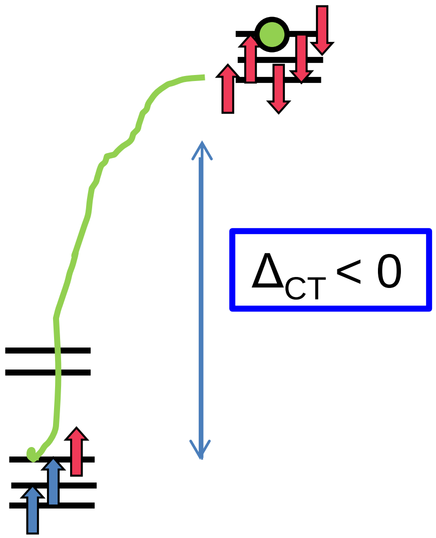
What about FeO_2?

Examples: **VO2** ($V^{4+}(d^1)O^{2-}_2$ $\Delta_{CT} > 0$)

CrO2 ($Cr^{4+}(d^2)O^{2-}_2$ $\Delta_{CT} < 0$)



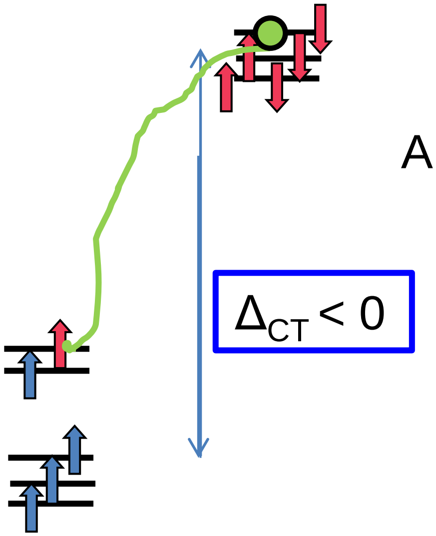
$\Delta_{CT} > 0$



$\Delta_{CT} < 0$

$Cr^{4+}(d^2)O^{2-}(p^6)$ --> $Cr^{3+}(d^3)O^{-}(p^5) = Cr^{3+}(d^3)\,\underline{L}$

Other examples: e.g. **CaFeO3**



$\Delta_{CT} < 0$

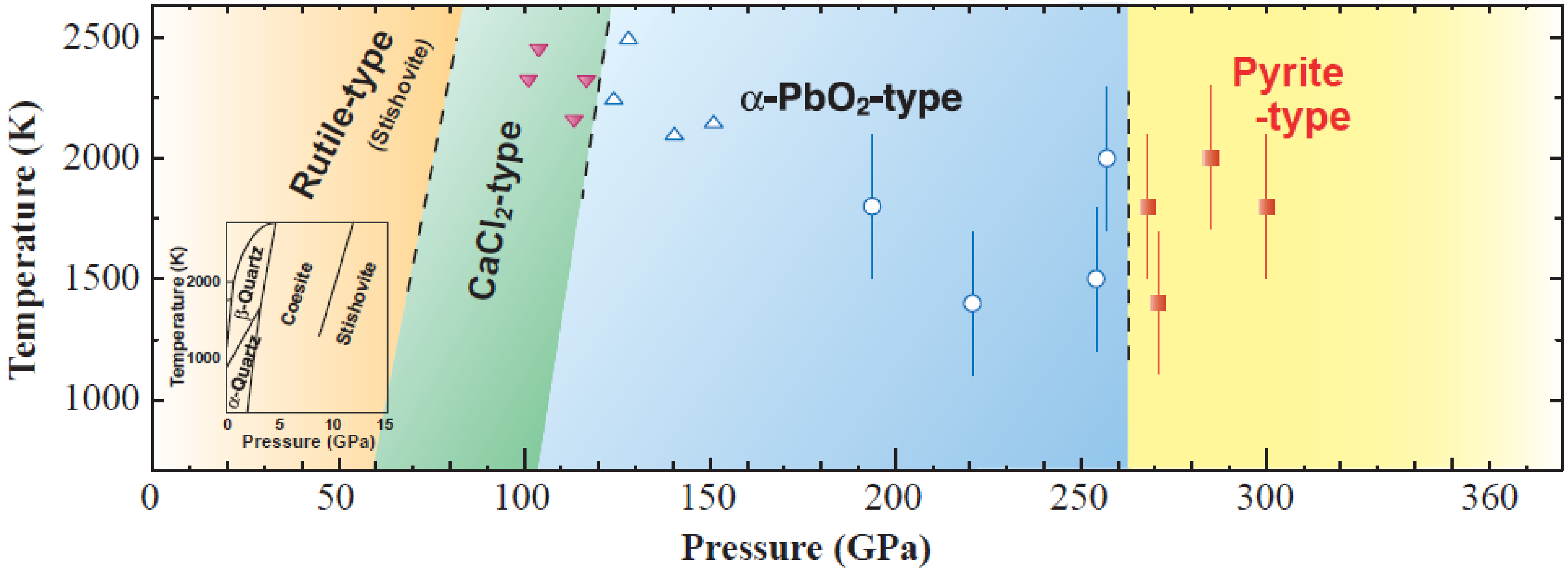
$Fe^{4+}(t_{2g}^{\,3}e_g^{\,1})O^{2-}(p^6) \rightarrow Fe^{3+}(t_{2g}^{\,3}e_g^{\,2})O^{-}(p^5) = Fe^{3+}(d^3)\,\underline{L}$

And then *charge disproportionation*

Spontaneous creation of ligand holes **(self-doping)**

M.A.Korotin, V.I.Anisimov, D.I.Khomskii and G.A.Sawatzky,``CrO2: self-doped double-exchange ferromagnetic oxides",Phys. Rev. Lett. 80, 4305 (1997)

SiO2: which is the high-pressure phases?



Geoscience: How much do we know about the Earth's interior?

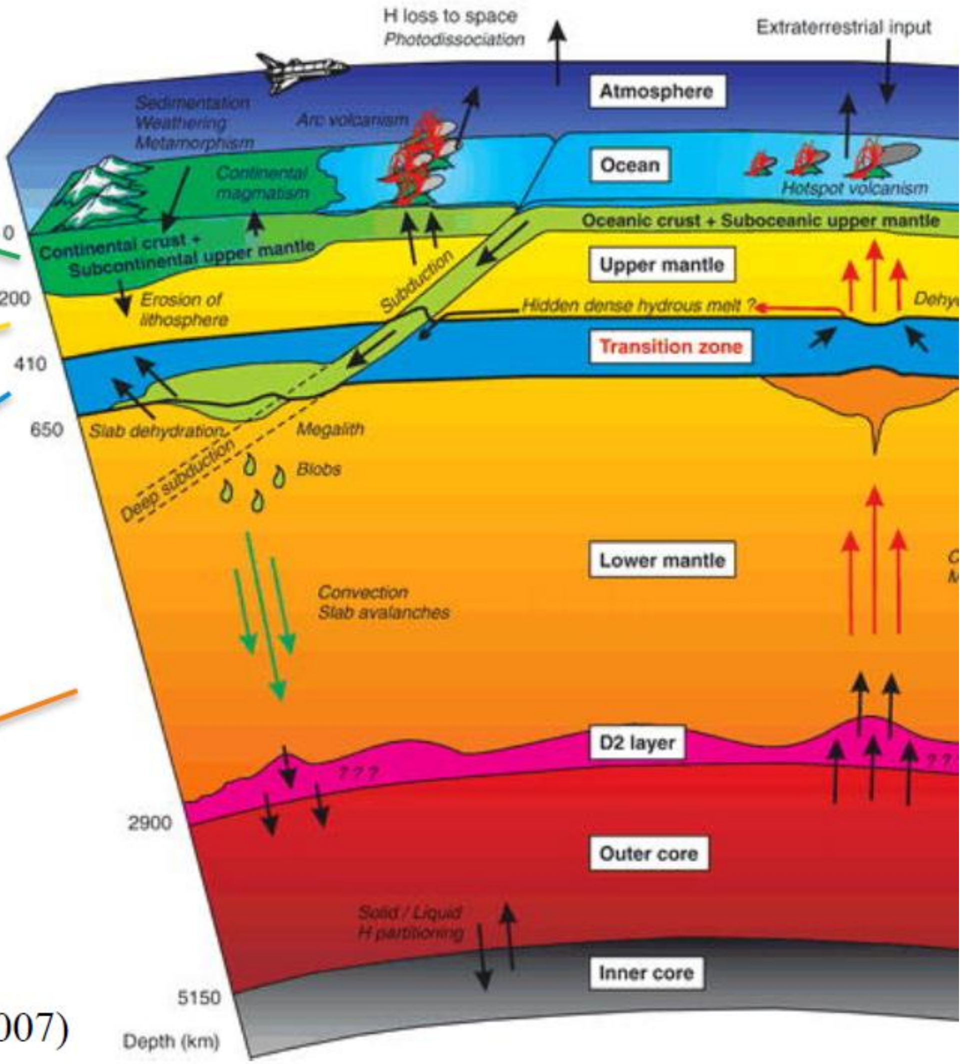
	vol. pct.
Plagioclase	30-40%
$Ca(Al_2Si_2)O_8$	
$Na(AlSi_3)O_8$	
Feldspar $K(AlSi_3)O_8$	10-20%
Quartz SiO_2	12-25%

Olivines: $(MgFe)_2SiO_4$
Pyroxenes: $(MgCa)SiO_3$
Garnets

$(MgFe)_2SiO_4$: structural transition from olivine to β-spinel

> A variety of chemical models can be made consistent with the geophysical data but the actual chemical composition of the lower mantle is unknown, except within very broad limits.

D. Anderson, the PREM developer
"New Theory of the Earth", p. 117 (2007)



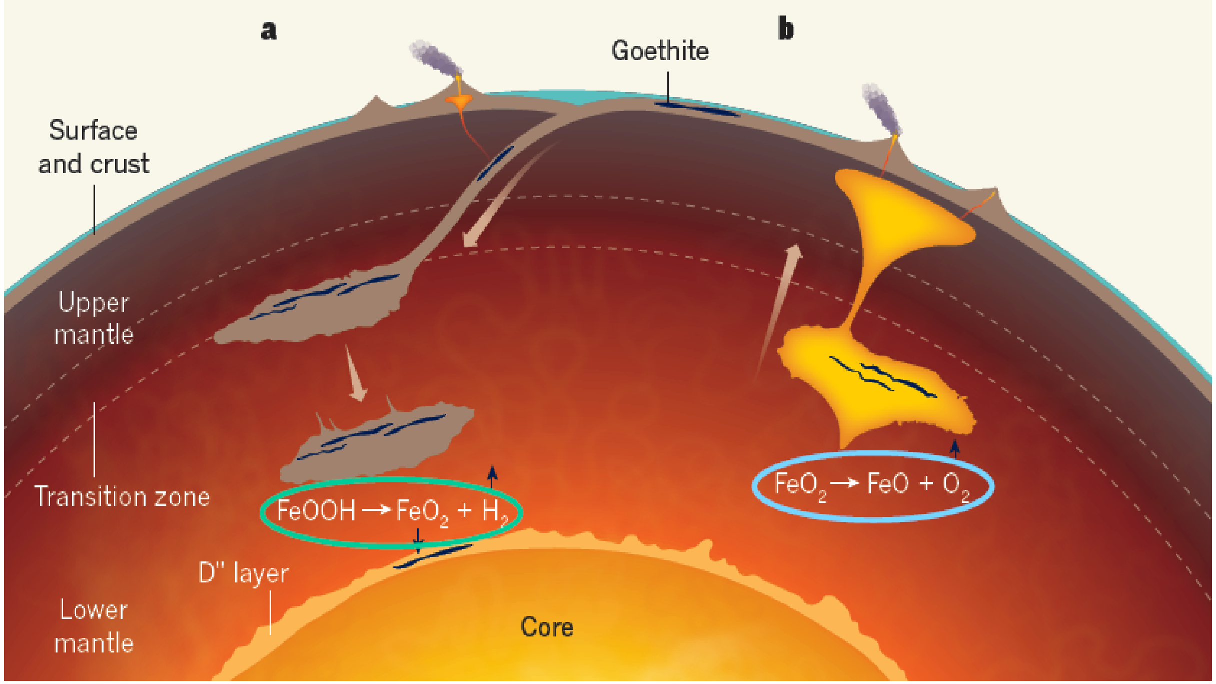
FeO_2: Additional source of oxygen?

$$2FeOOH = 2FeO_2 + H_2$$

$$Fe_2O_3 + \boxed{H_2O} = 2FeO_2 + H_2$$

$$2Fe_2O_3 \boxed{+ O_2} = 4FeO_2$$

←

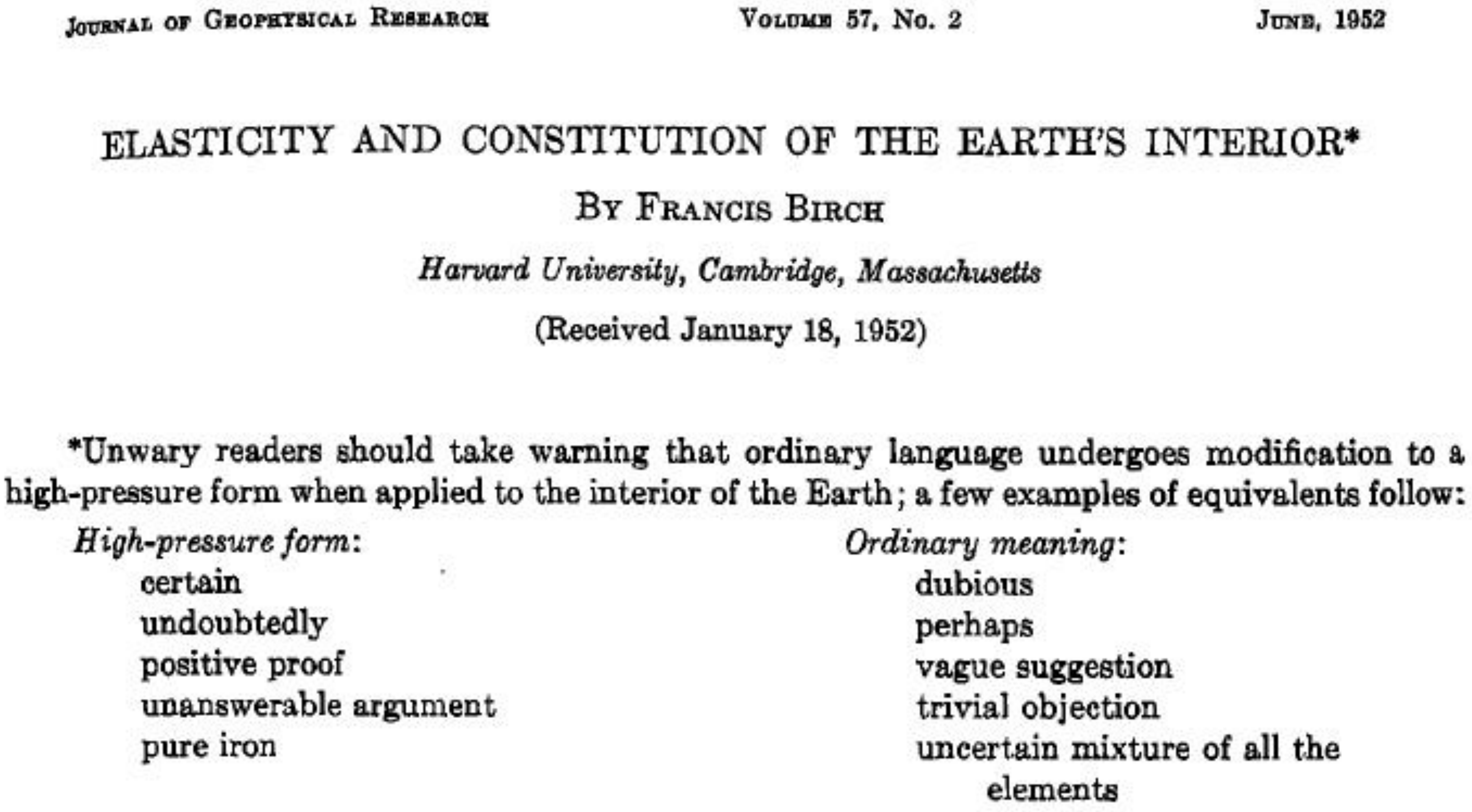


"… this process could have acted as an additional or <u>alternative oxygen source</u> for the Great Oxidation Events — the periods in Earth's history when the atmosphere became oxygenated. Until now, it was thought that the oxygen was supplied by biological activity alone."

Q. Hu et al. Nature 534, 241 (2016)

T. Yagi, Nature 534, 183 (2016)

Geoscience: How much do we know about the Earth's interior?



JOURNAL OF GEOPHYSICAL RESEARCH VOLUME 57, No. 2 JUNE, 1952

ELASTICITY AND CONSTITUTION OF THE EARTH'S INTERIOR*

BY FRANCIS BIRCH

Harvard University, Cambridge, Massachusetts

(Received January 18, 1952)

*Unwary readers should take warning that ordinary language undergoes modification to a high-pressure form when applied to the interior of the Earth; a few examples of equivalents follow:

High-pressure form:	*Ordinary meaning*:
certain	dubious
undoubtedly	perhaps
positive proof	vague suggestion
unanswerable argument	trivial objection
pure iron	uncertain mixture of all the elements

Unwary readers should take warning that **ordinary language undergoes modification to a high-pressure form** when applied to the interior of the Earth.
A few examples of equivalents follow: **(A.F.Birch, 1952)**

High Pressure Form	***Ordinary Meaning***
Certain	**Dubious**
Undoubtedly	**Perhaps**
Positive proof	**Vague suggestion**
Unanswerable argument	**Trivial objection**
Pure iron	**Uncertain mixture of all the elements**

● Peroxides/pyrites: negative charge transfer gap!

Rutile **$Ti^{4+}O2$, $V^{4+}O2$** – OK; **CrO2** – already negative CT gap, not **Cr^{4+}**, but rather **Cr^{3+} $\underline{L}$**

FeO2 could have been similar, ordinary (di)oxide, e.g. with rutile structure, but with negative CT gap. But instead it is similar to ***peroxide*** **FeO2**, like **MgO2**.

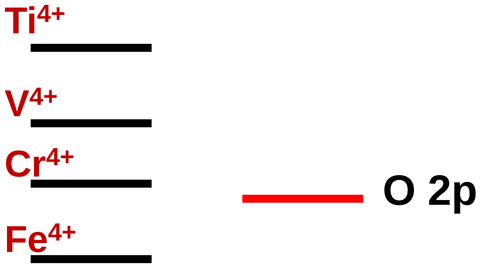
But not **Fe2+,** but **Fe3**+ - **in between oxide and peroxide!**

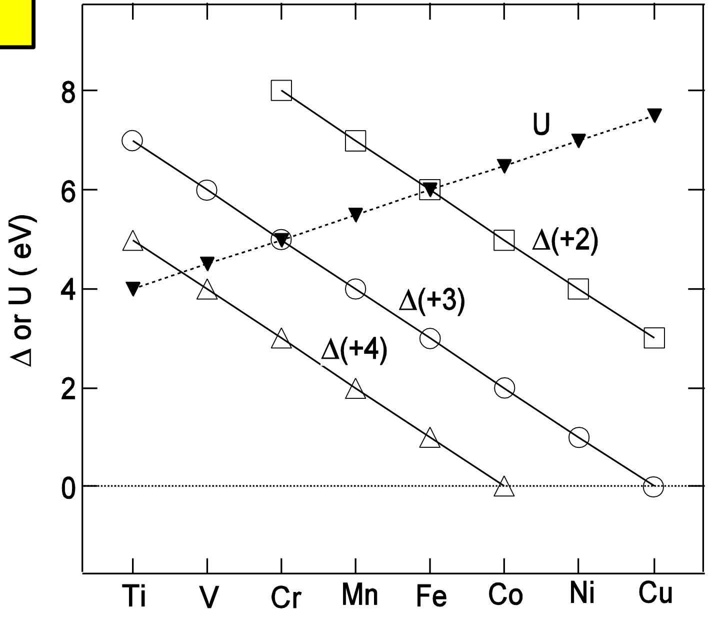
$Fe^{4+}(t_{2g}{}^{3}e_{g}{}^{1})O^{2-}(p^{6}) \rightarrow Fe^{3+}(t_{2g}{}^{3}e_{g}{}^{2})O^{-}(p^{5}) = Fe^{3+}(d^{3})$ L, not $Fe^{2+}(O2)^{2-}$!

FeO_2: possible novel magnetic constituent of Earth's lower mantle

Sergey S. Streltsov[1,2,*], Alexey O. Shorikov[1,2], Sergey L. Skornyakov[1,2], Alexander I. Poteryaev[1], and Daniel I. Khomskii[3]

Sci.Reports **7**, 13005 (2017)





Could have been **negative charge transfer gap**

Rutile **$Ti^{4+}O2$, $V^{4+}O2$** – OK;

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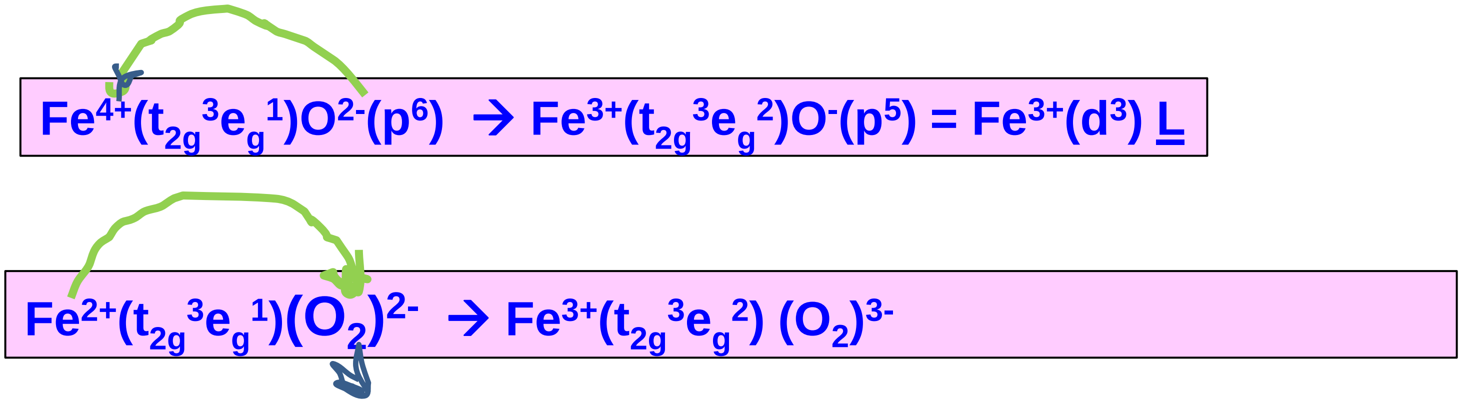

$$Fe^{4+}(t_{2g}^{3}e_{g}^{1})O^{2-}(p^{6}) \rightarrow Fe^{3+}(t_{2g}^{3}e_{g}^{2})O^{-}(p^{5}) = Fe^{3+}(d^{3})\ \underline{L}$$

$$Fe^{2+}(t_{2g}^{3}e_{g}^{1})(O_{2})^{2-} \rightarrow Fe^{3+}(t_{2g}^{3}e_{g}^{2})\ (O_{2})^{3-}$$

FeO_2: possible novel magnetic constituent of Earth's lower mantle

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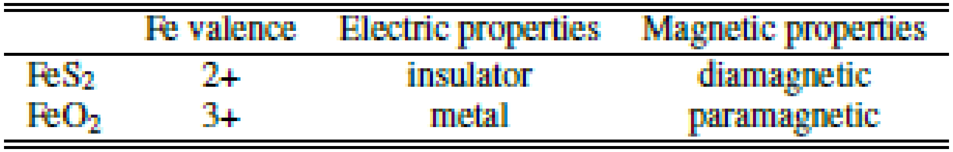
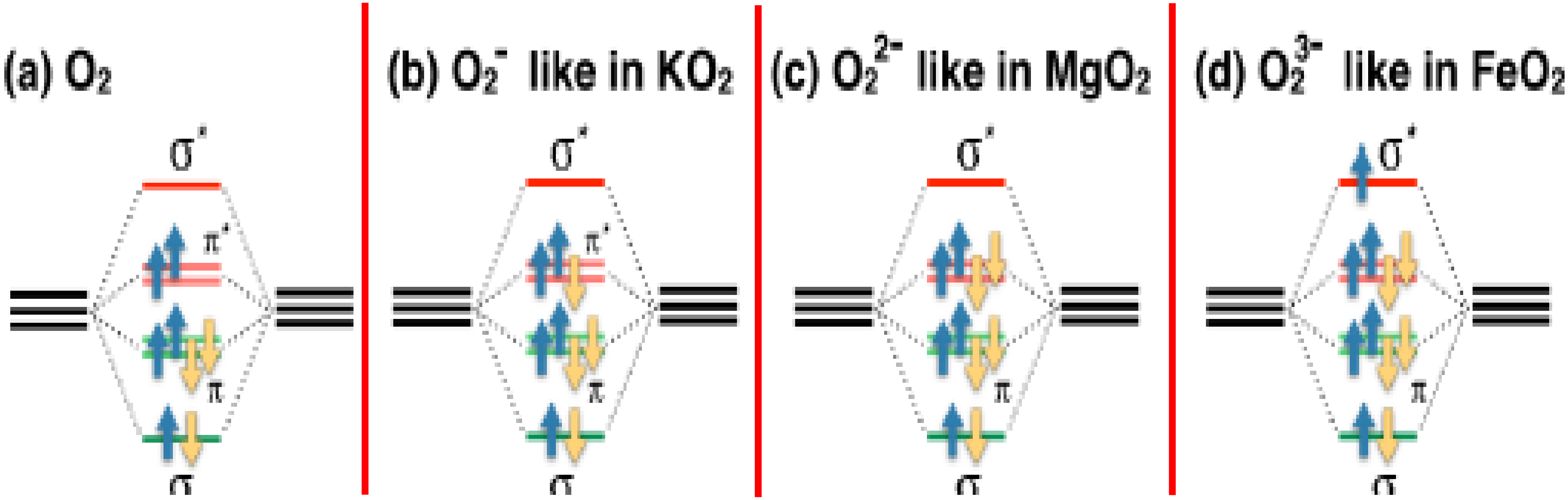
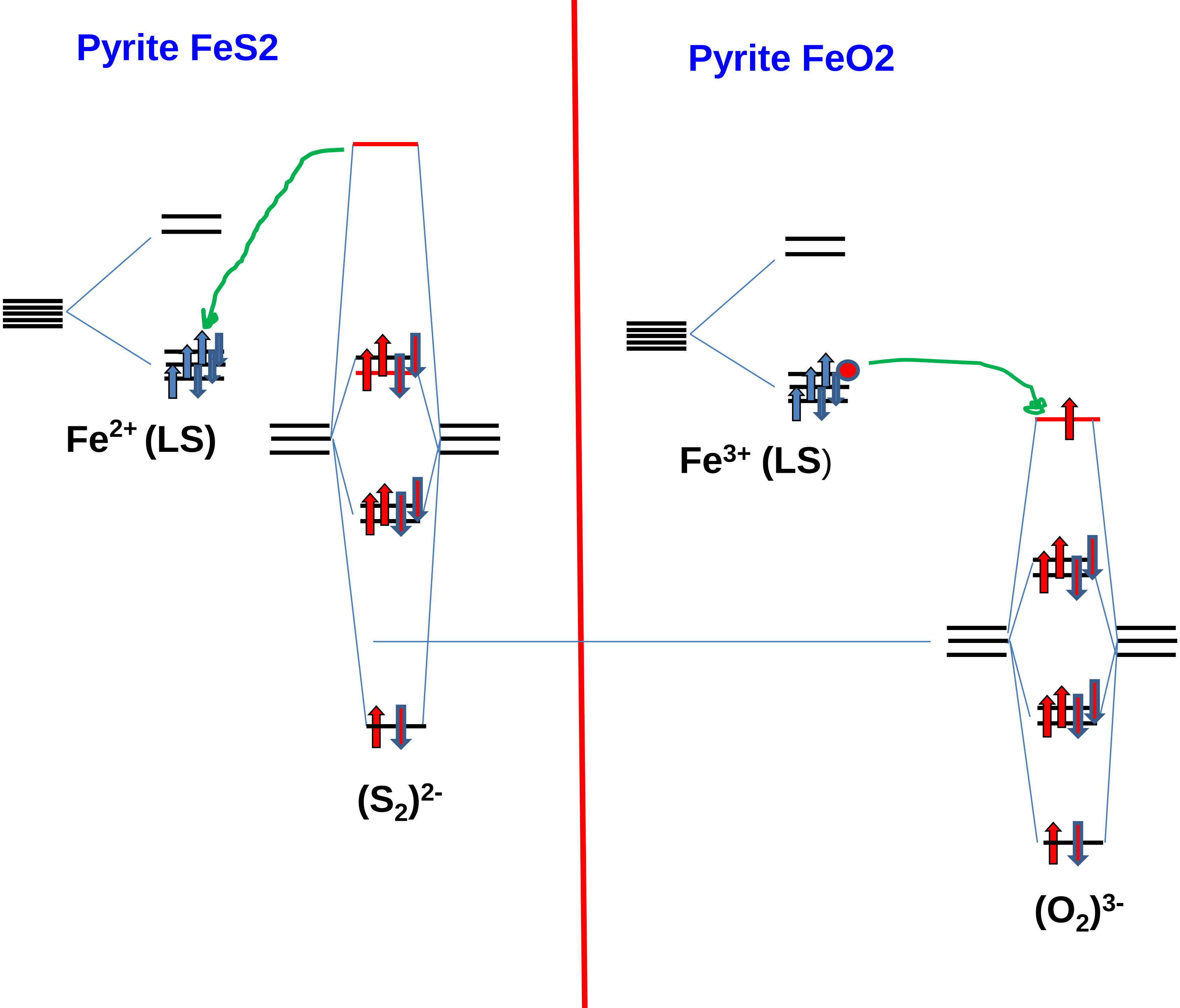
Sci.Reports **7**, 13005 (2017)



	Fe valence	Electric properties	Magnetic properties
FeS_2	2+	insulator	diamagnetic
FeO_2	3+	metal	paramagnetic



Why no pyrite CoO2, NiO2?


Pyrite FeS2
Fe^{2+} (LS)
$(S_2)^{2-}$
Pyrite FeO2
Fe^{3+} (LS)
$(O_2)^{3-}$

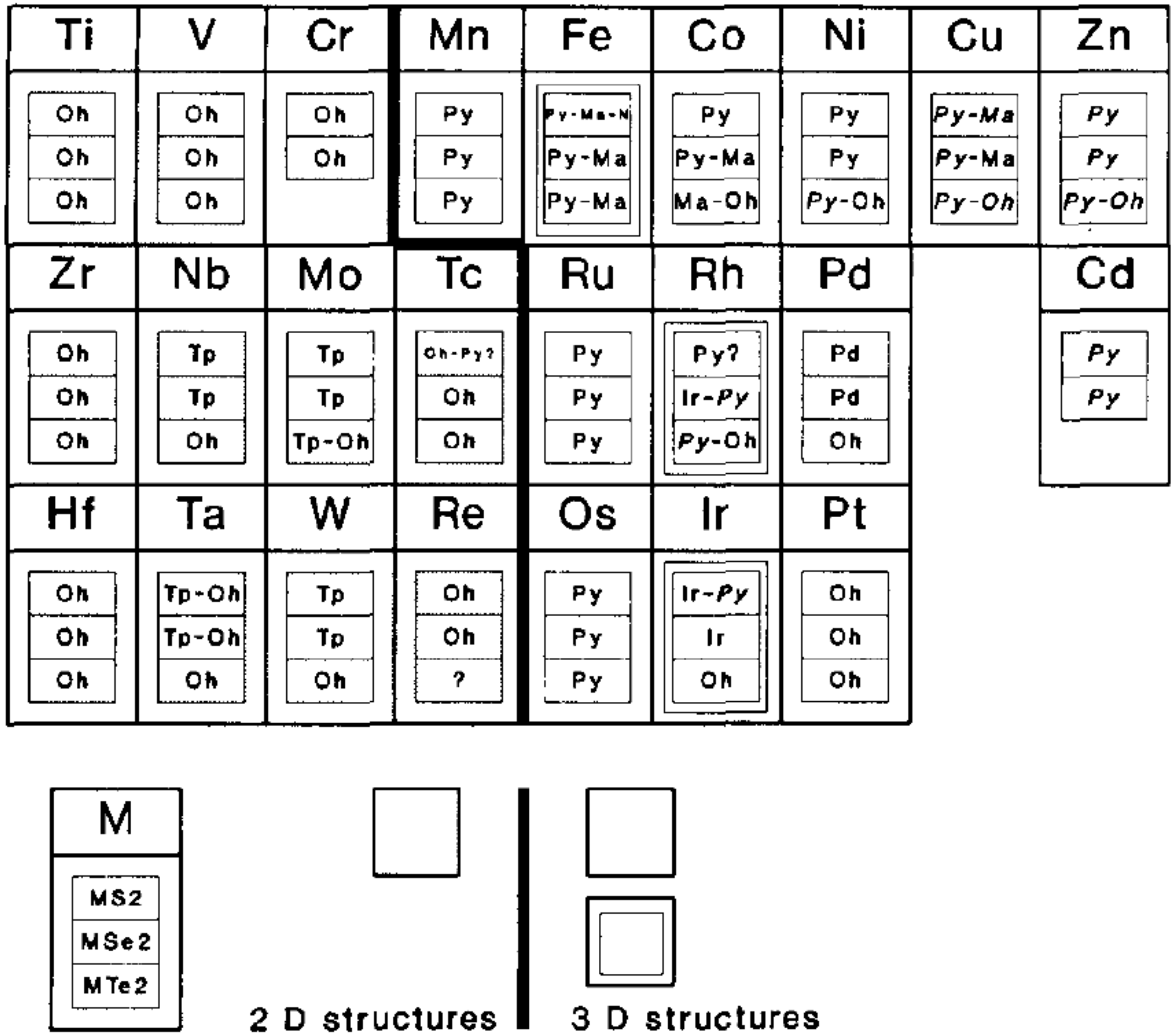
Phases MO_2, MS_2 , MSe_2 , MTe_2

Journal of Alloys and Compounds, *178* (1992) 253–283
JAL 5016

Occurrence and characterization of anionic bondings in transition metal dichalcogenides

S. Jobic, R. Brec and J. Rouxel

Rutile (**TiO2, VO2, CrO2**)
Layered (**TiS2, MoS2, IrTe2, AuTe2**)
Pyrite (**FeS2, OsSe2, PdSe2**)



Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Oh Oh Oh	Oh Oh Oh	Oh Oh	Py Py Py	Py-Ma-N Py-Ma Py-Ma	Py Py-Ma Ma-Oh	Py Py Py-Oh	Py-Ma Py-Ma Py-Oh	Py Py Py-Oh

Zr	Nb	Mo	Tc	Ru	Rh	Pd		Cd
Oh Oh Oh	Tp Tp Oh	Tp Tp Tp-Oh	Oh-Py? Oh Oh	Py Py Py	Py? Ir-Py Py-Oh	Pd Pd Oh		Py Py

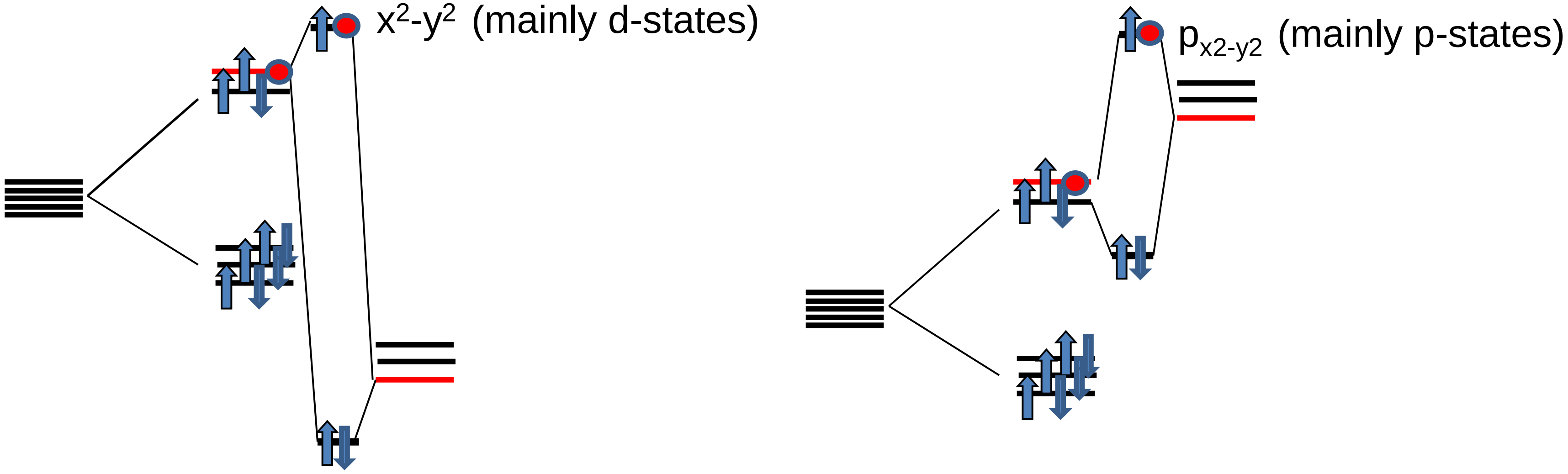
Hf	Ta	W	Re	Os	Ir	Pt
Oh Oh Oh	Tp-Oh Tp-Oh Oh	Tp Tp Oh	Oh Oh ?	Py Py Py	Ir-Py Ir Oh	Oh Oh Oh

M
MS2
MSe2
MTe2

2 D structures

3 D structures

Peroxides -- allows to have ligand holes on nonbonding orbitals



$\Delta_{CT} > 0$

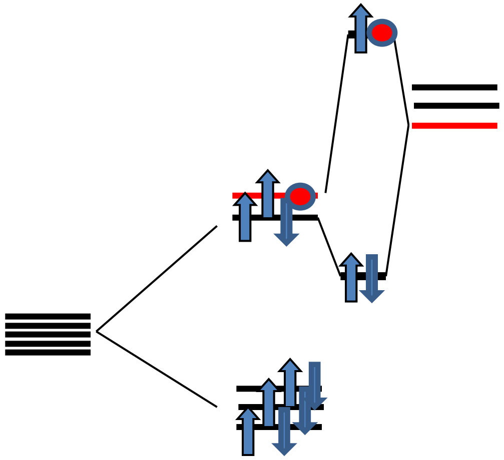
$$\Psi = \alpha|d\rangle + \beta|p\rangle$$

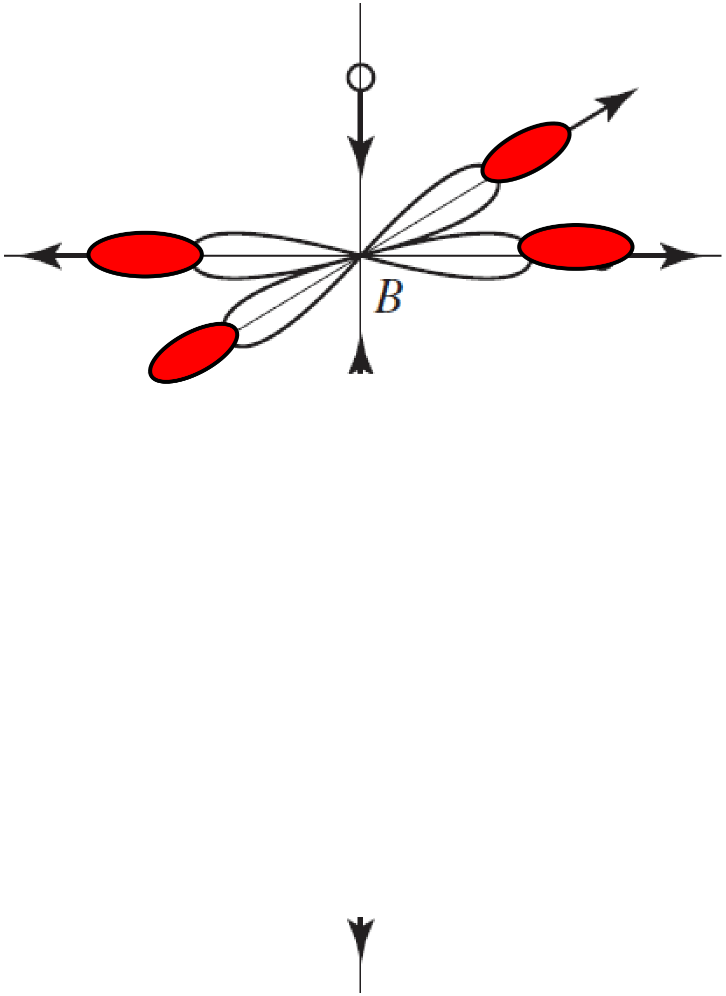
$\Delta_{CT} < 0$

The problem is that with d-electrons usually p-orbitals ***with the same symmetry*** are hybridised – e.g. **in Zhang-Rice singlets**. I.e. it looks as a quantitative effect, not qualitative.

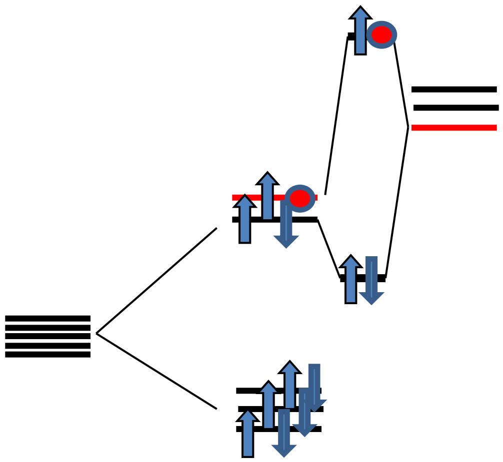
Can one have situations with holes ***on other*** p-orbitals?

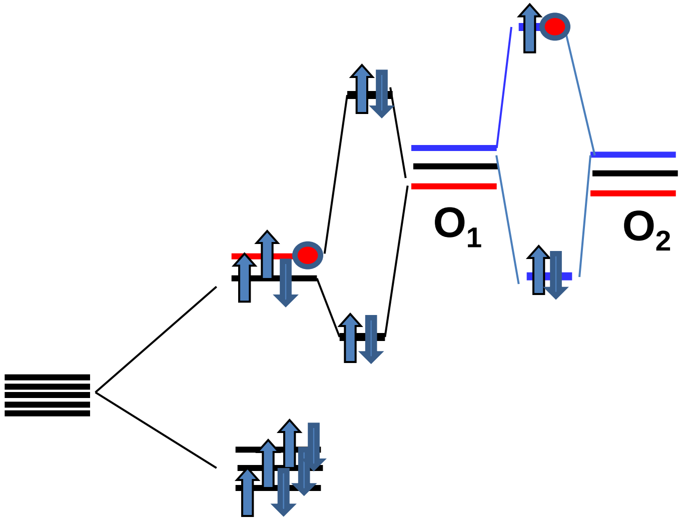
Bonding p-orbitals (gives Zhang-Rice singets)



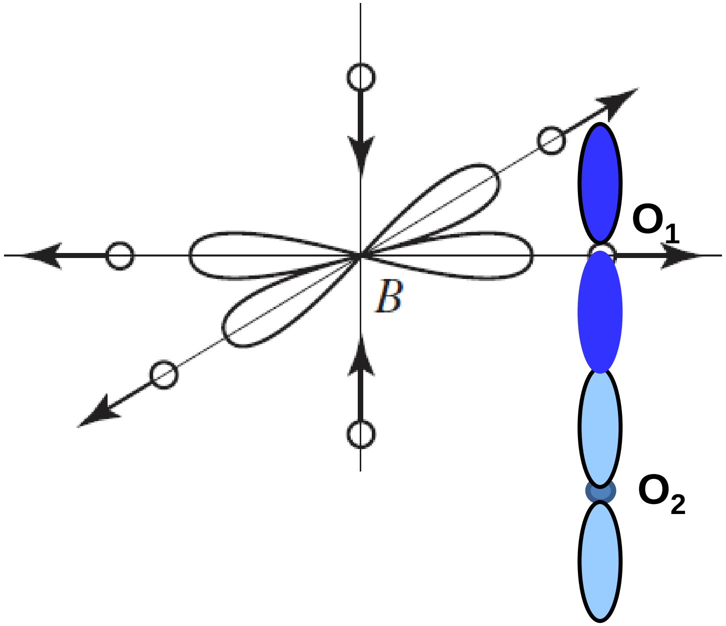


Peroxides

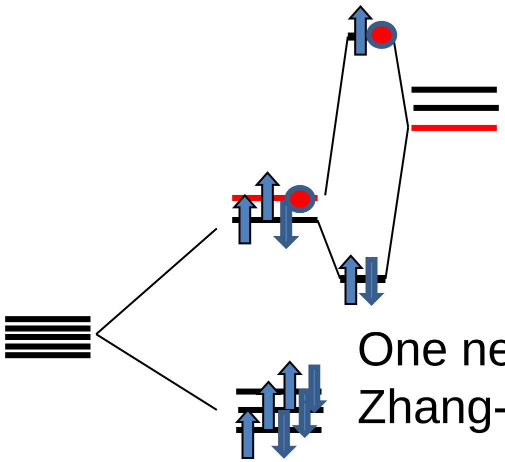




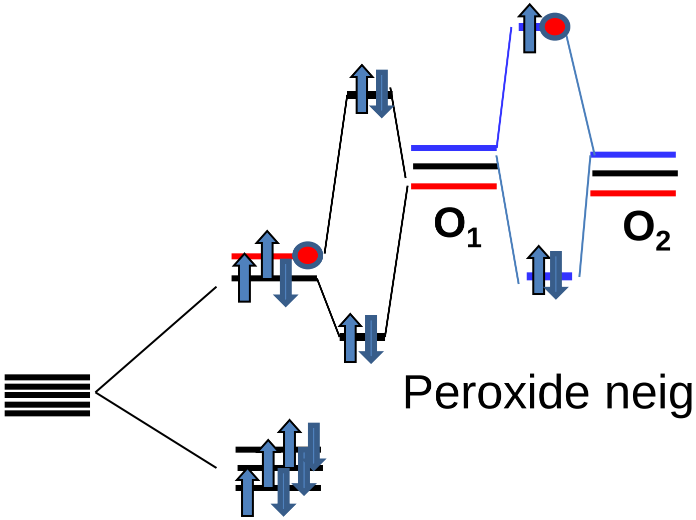
Peroxide ions allow to occupy **nonbonding** (for d-states) p-orbitals (bonding-antibonding for peroxide ions)



Peroxides

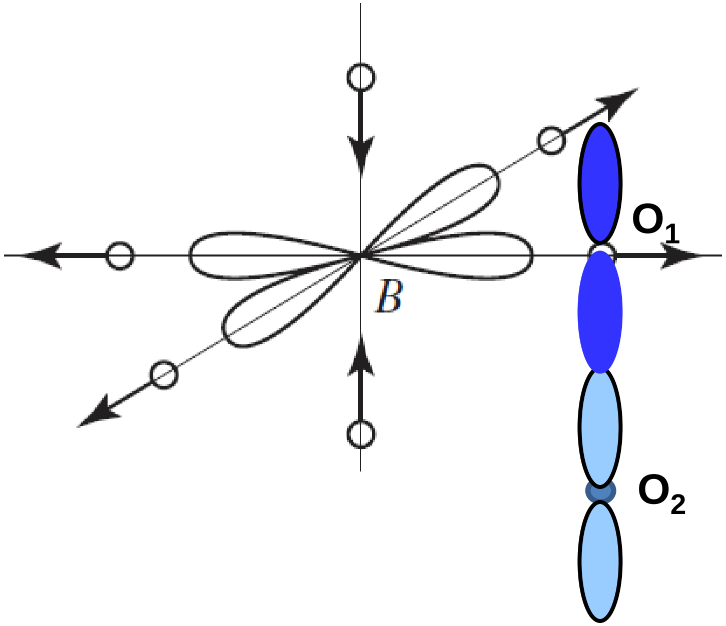


One neighbouring oxygen:
Zhang-Rice state



Peroxide neighbour

Peroxide ions allow to occupy **nonbonding** (for d-states) p-orbitals (bonding-antibonding for peroxide ions)

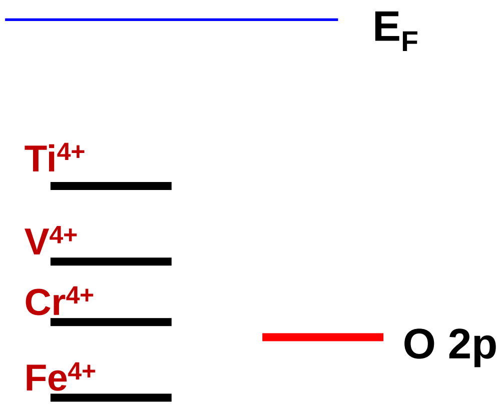


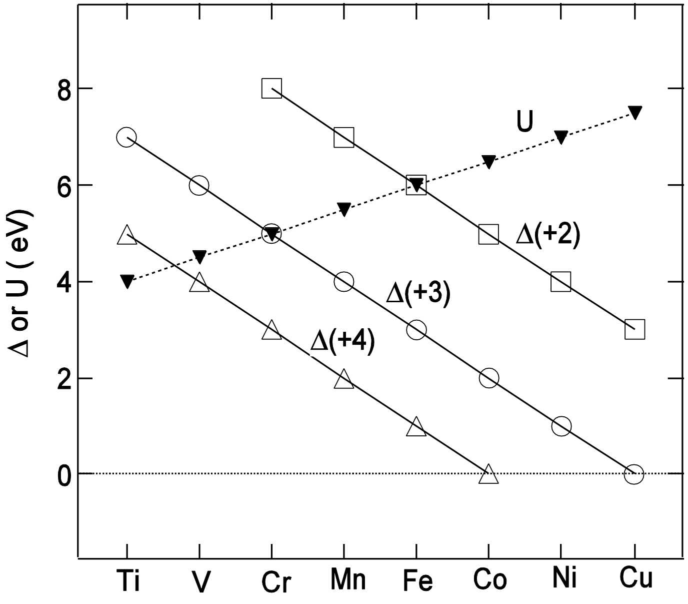
Peroxides and charge transfer gaps

$Ti^{4+}O_2$ $V^{4+}O_2$ $Cr^{4+}O_2 = Cr^{3+}\underline{L}$ $(O^{2-}O^{-})$ $Fe^{3+}\underline{L}$ $(O^{2-}O^{-})$ $Mn^{4+}O_2$ $\underline{Co/NiO_2?}$

When can one have peroxides? ---- Negative charge transfer gaps!

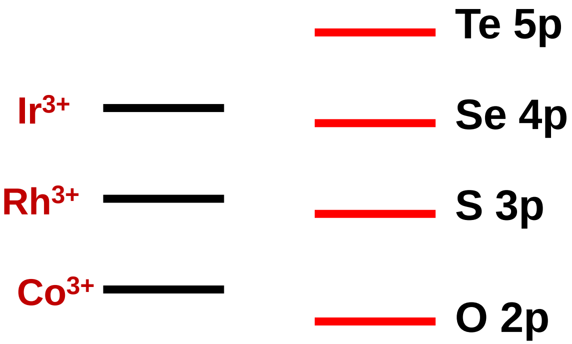
Tendencies in periodic table:

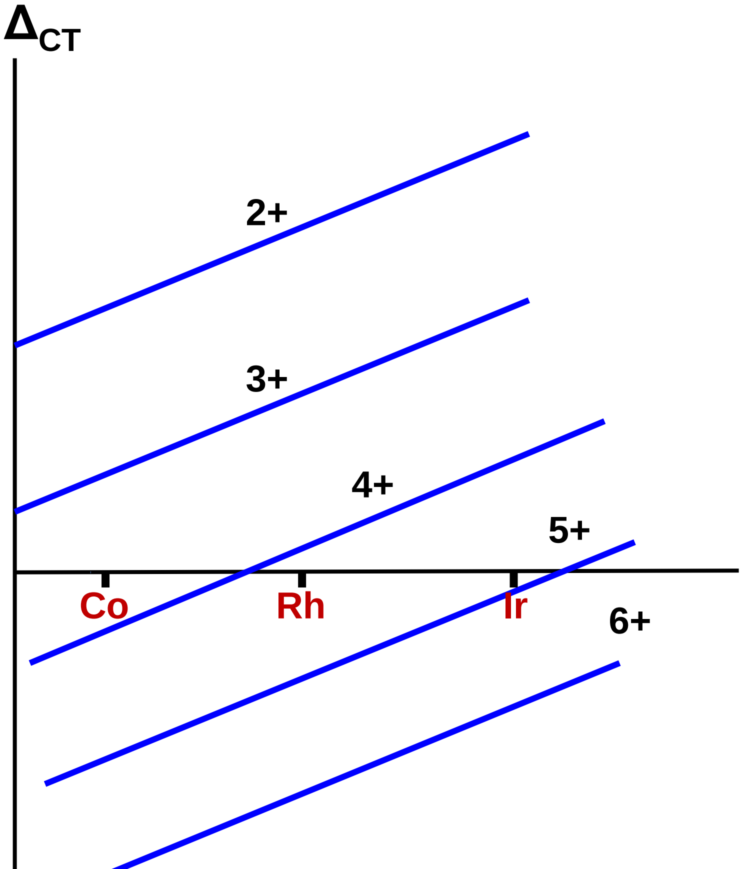


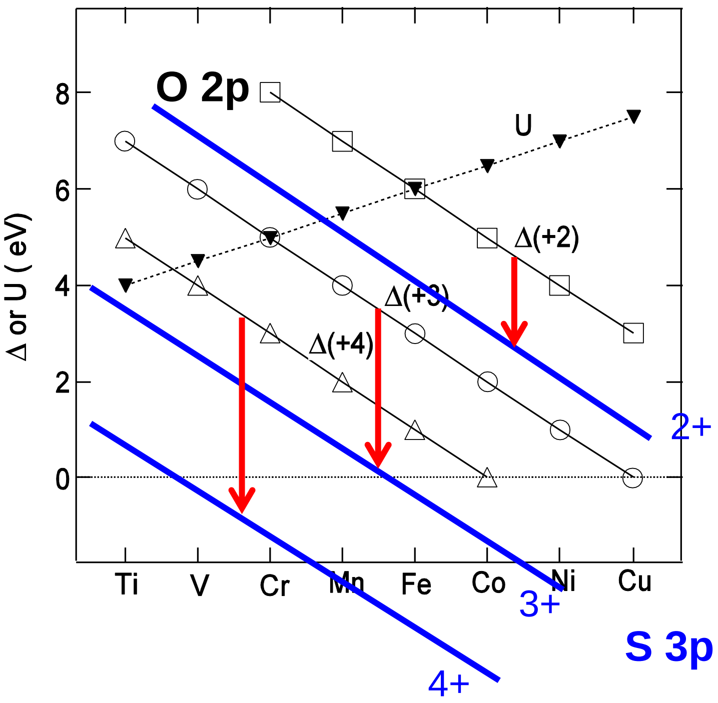


Why no pyrite CoO2, NiO2?

Going down in Periodic Table:

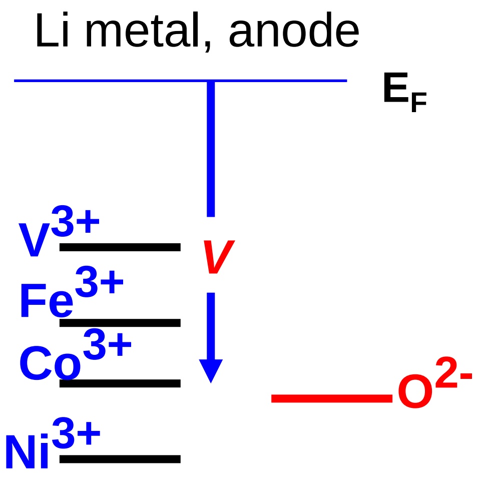






Negative charge transfer gaps and peroxides in batteries

Usual cathode materials: e.g. **LixCoO2**. Charging: **Li ↘ , Co3+ → Co4+**
But in fact ligand holes, $Co^{3+}\underline{L} = Co^{3+}O^{-}$



For large voltage *V* better to deal with metals with smaller charge transfer gaps! (e.g. not with V, but with Co)

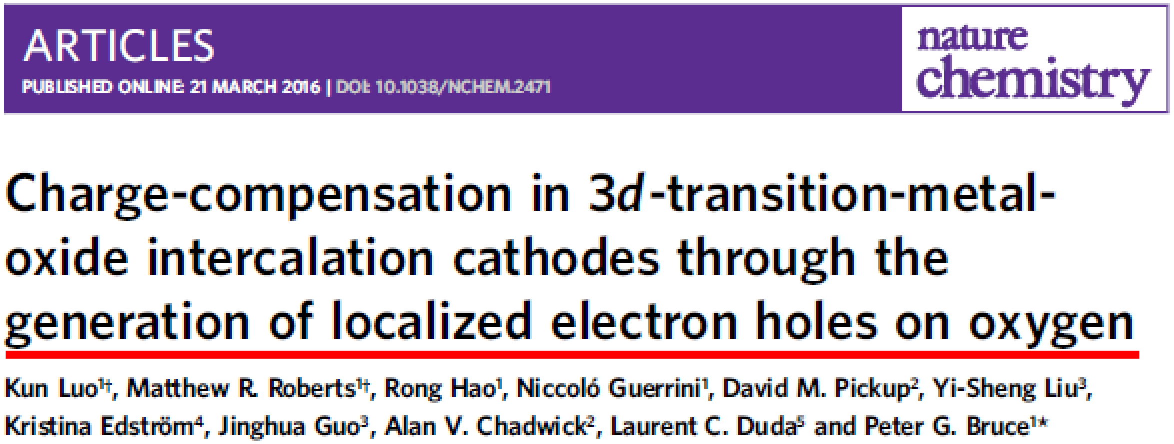
And one can change the valence not only of metal, but also of oxygen → extra capacity!

Li2IrO3 (and **β-Li2IrO3**)

$$Li_2Ir^{4+}O_3 \longrightarrow Li_1Ir^{5+}O_3 \longrightarrow Li_{0.5}Ir^{5+}(O_3)^{5.5-}$$

Negative charge transfer gaps and peroxides in batteries

NATURE CHEMISTRY | VOL 8 | JULY 2016 692 |
The structural and chemical origin of the **oxygen redox activity** in layered and cation-disordered Li-excess cathode materials
Dong-Hwa Seo1,2†, Jinhyuk Lee1,2†, Alexander Urban2, Rahul Malik1, ShinYoung Kang1 and Gerbrand Ceder1,2,3*

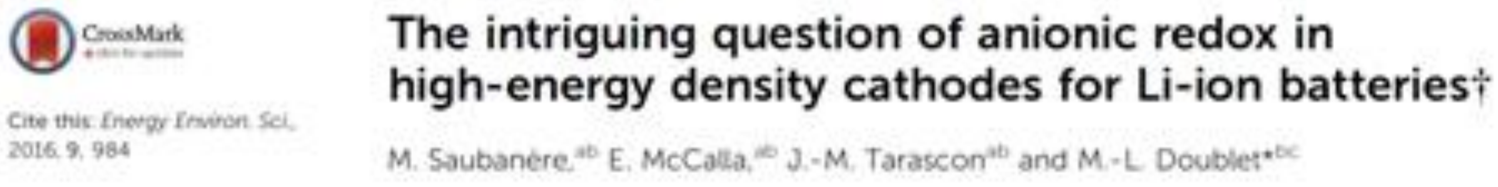


ARTICLES
PUBLISHED ONLINE: 21 MARCH 2016 | DOI: 10.1038/NCHEM.2471

nature chemistry

Charge-compensation in 3*d*-transition-metal-oxide intercalation cathodes through the generation of localized electron holes on oxygen

Kun Luo[1†], Matthew R. Roberts[1†], Rong Hao[1], Niccoló Guerrini[1], David M. Pickup[2], Yi-Sheng Liu[3], Kristina Edström[4], Jinghua Guo[3], Alan V. Chadwick[2], Laurent C. Duda[5] and Peter G. Bruce[1*]

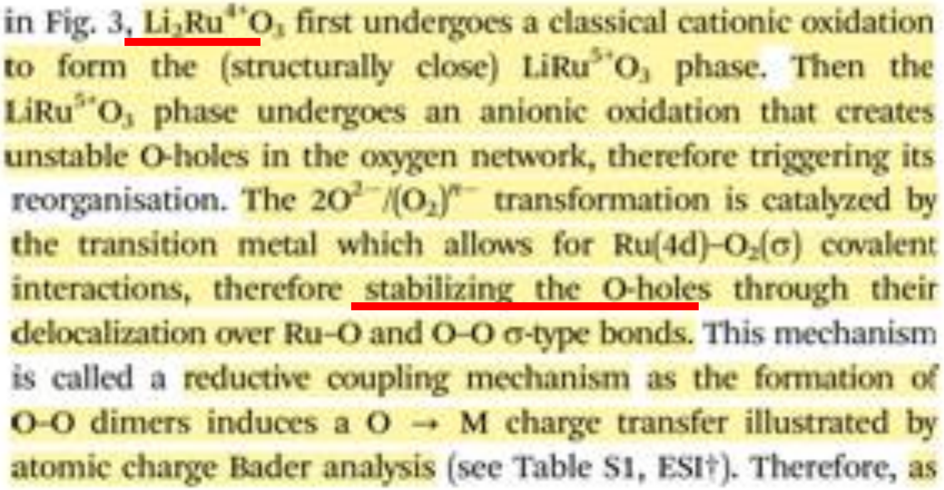


The intriguing question of anionic redox in high-energy density cathodes for Li-ion batteries†

Cite this: *Energy Environ. Sci.*, 2016, 9, 984

M. Saubanère,[ab] E. McCalla,[ab] J.-M. Tarascon[ab] and M.-L. Doublet*[bc]

E. McCalla, J-M. Tarascon, "Visualization of O-O peroxo-like dimers in high-capacity layered oxides for Li-ion batteries", *Science* 2015 (350), 1516



in Fig. 3, $Li_2Ru^{4+}O_3$ first undergoes a classical cationic oxidation to form the (structurally close) $LiRu^{5+}O_3$ phase. Then the $LiRu^{5+}O_3$ phase undergoes an anionic oxidation that creates unstable O-holes in the oxygen network, therefore triggering its reorganisation. The $2O^{2-}/(O_2)^{n-}$ transformation is catalyzed by the transition metal which allows for Ru(4d)–$O_2(\sigma)$ covalent interactions, therefore stabilizing the O-holes through their delocalization over Ru–O and O–O σ-type bonds. This mechanism is called a reductive coupling mechanism as the formation of O–O dimers induces a O → M charge transfer illustrated by atomic charge Bader analysis (see Table S1, ESI†). Therefore, as

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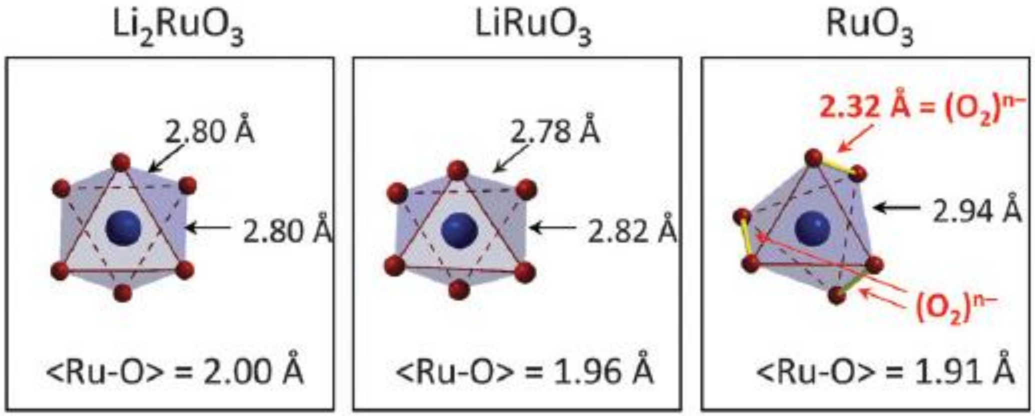
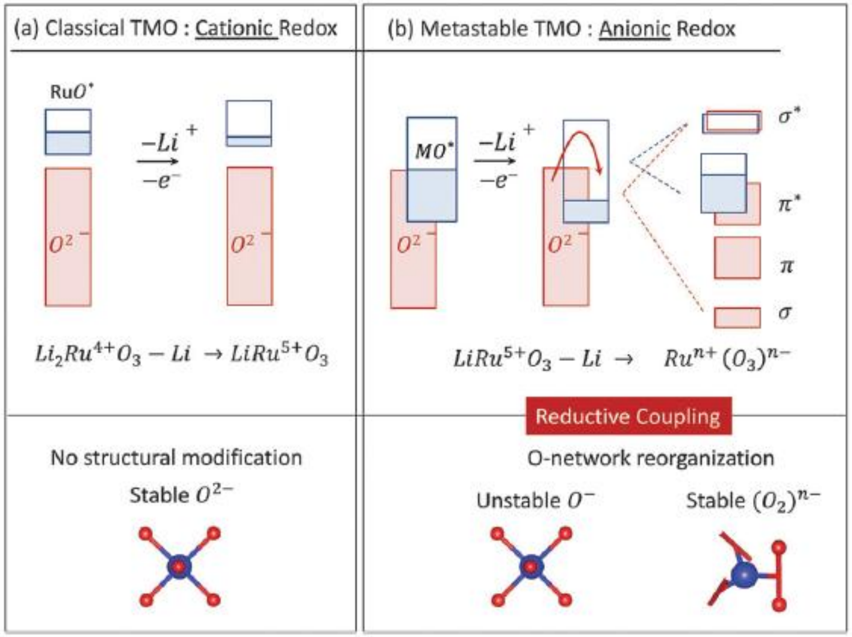
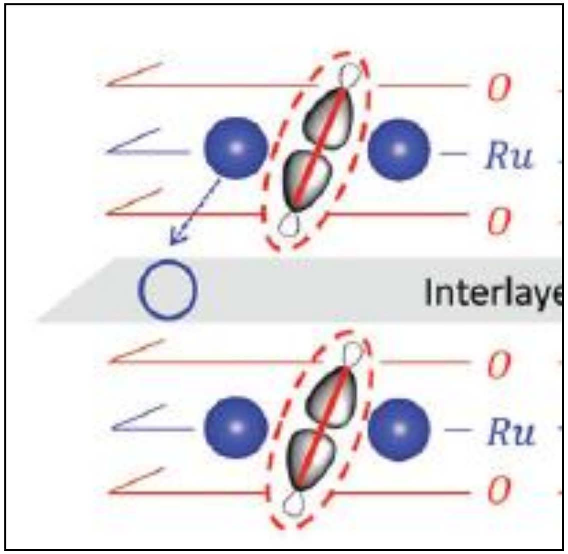
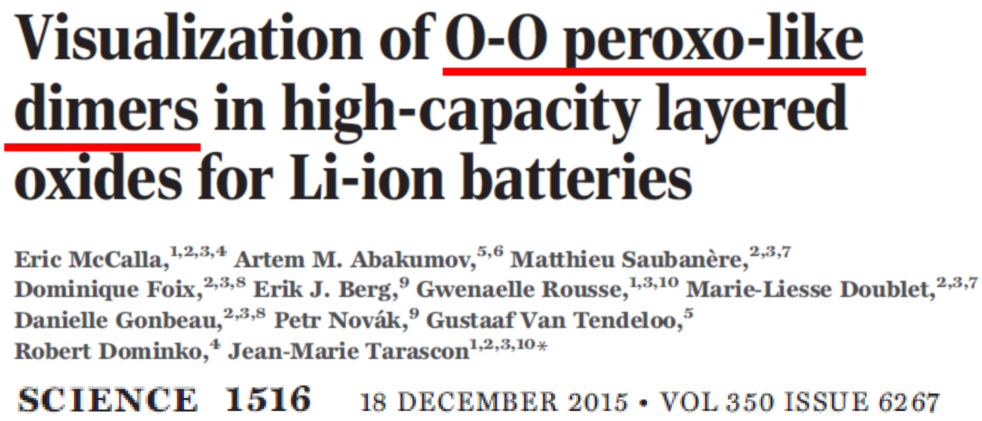




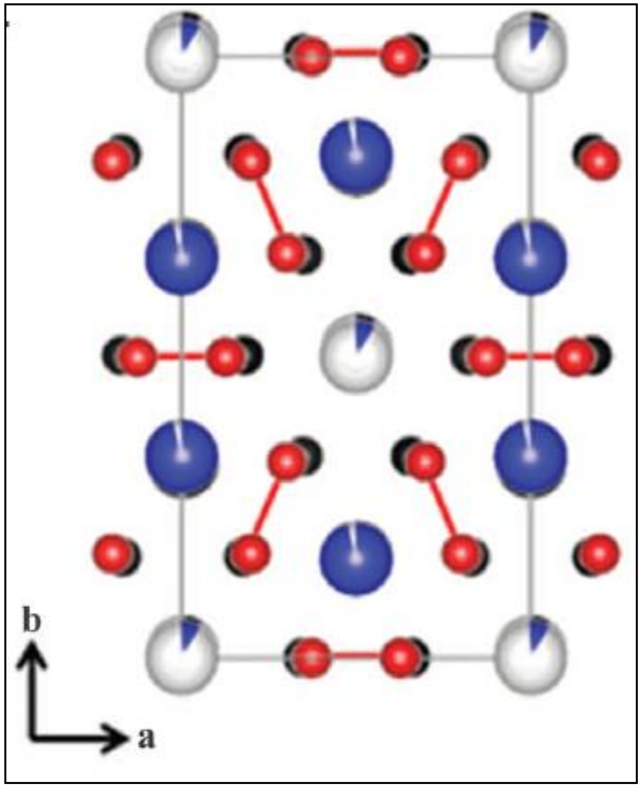




Visualization of O-O peroxo-like dimers in high-capacity layered oxides for Li-ion batteries

Eric McCalla,[1,2,3,4] Artem M. Abakumov,[5,6] Matthieu Saubanère,[2,3,7]
Dominique Foix,[2,3,8] Erik J. Berg,[9] Gwenaelle Rousse,[1,3,10] Marie-Liesse Doublet,[2,3,7]
Danielle Gonbeau,[2,3,8] Petr Novák,[9] Gustaaf Van Tendeloo,[5]
Robert Dominko,[4] Jean-Marie Tarascon[1,2,3,10]*

SCIENCE 1516 18 DECEMBER 2015 • VOL 350 ISSUE 6267



Li2IrO3 (and β-Li2IrO3)

$Li_2Ir^{4+}O_3 \longrightarrow Li_1Ir^{5+}O_3 \longrightarrow Li_{0.5}Ir^{5+}(O_3)^{5.5-}$

I.e. further charging (removal of Li) leads to creation of oxygen holes, and eventually – peroxide ions $(O_2)^{2-}$

It occurs in a situation with small/negative CT gaps. Ligand holes – **an extra charging, OK!**

But peroxide ions $(O_2)^{2-}$ might be unstable: $2\,(O_2)^{2-} \longrightarrow 2O^{2-} + O_2$,
and oxygen can escape cathode – **bad!**

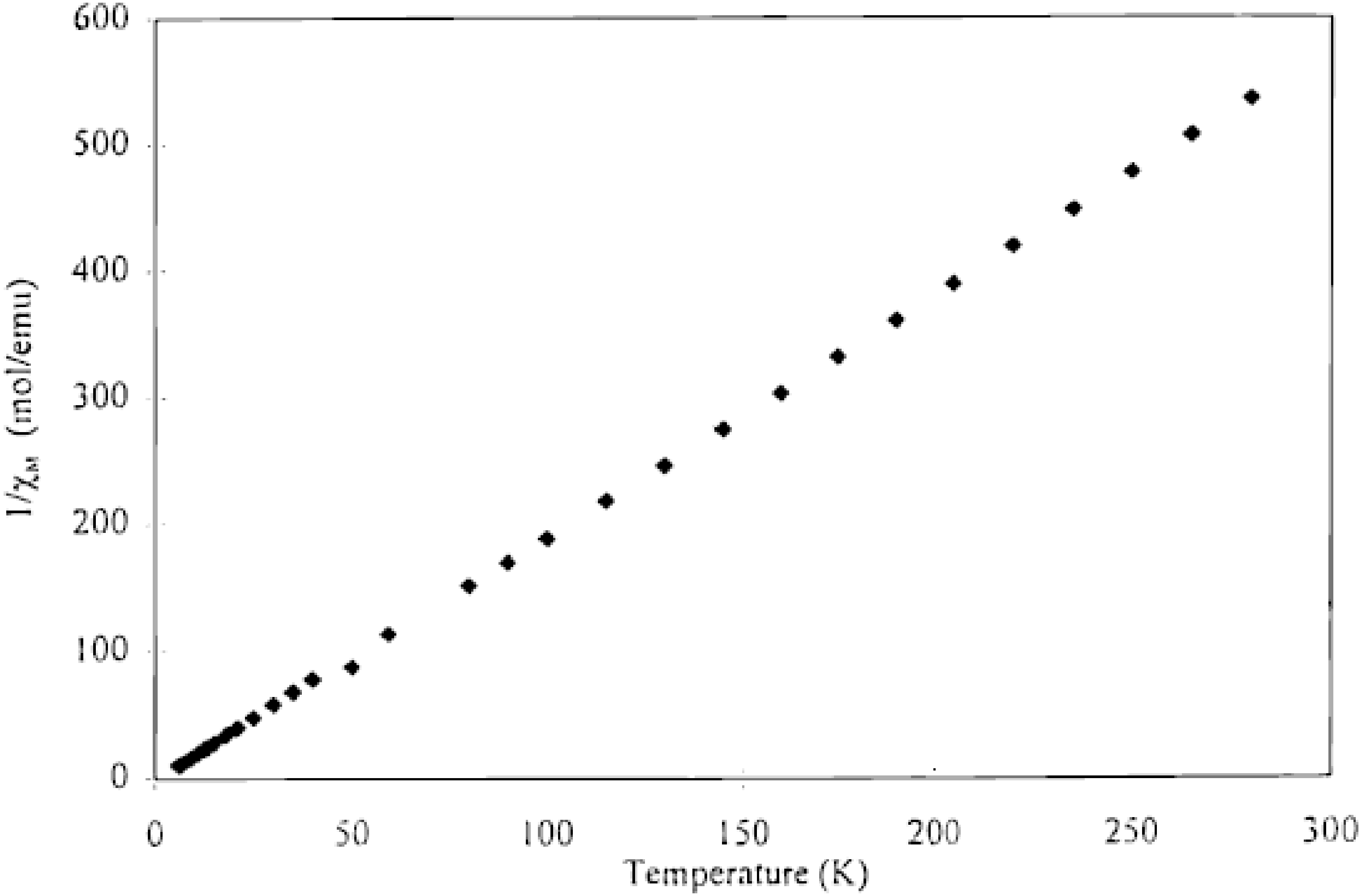
Competition between formation of peroxide ions and Zhang-Rice singlets!

- # Magnetic gold ?

Cu: Cu^{1+} (d^{10}), S=0 –- OK
Cu^{2+} (d^{9}), S=1/2 –- OK (magnetic)
Cu^{3+} (d^{8}) = Cu^{2+} (d^{9}) $\underline{L}$, S=0 (Zhang-Rice singlets)

Ag: Ag^{1+} (d^{10}), S=0 –- OK
Ag^{2+} (d^{9}), S=1/2 –- possible but very difficult to stabilize; rare (not in oxides)
Ag^{3+} (d^{8}) (= Ag^{2+} (d^{9}) $\underline{L}$), S=0 – OK

Au: Au^{1+} (d^{10}), S=0 – OK
Au^{2+} (d^{9}), S=1/2 – **never** **(?)**
Au^{3+} (d^{8}) (= Au^{2+} (d^{9}) $\underline{L}$, or rather Au^{1+} (d^{10}) $\underline{L}^2$), S=0 -- OK



600
500
400
300
200
100
0
0
50
100
150
200
250
300
$1/\chi_M$ (mol/emu)
Temperature (K)

● Magnetic gold !

J. Am. Chem. Soc. **1997,** *119,* 1020−1026

Au_3F_8

Synthesis of Au(II) Fluoro Complexes and Their Structural and Magnetic Properties

Scott H. Elder, George M. Lucier, Frederick J. Hollander, and Neil Bartlett*

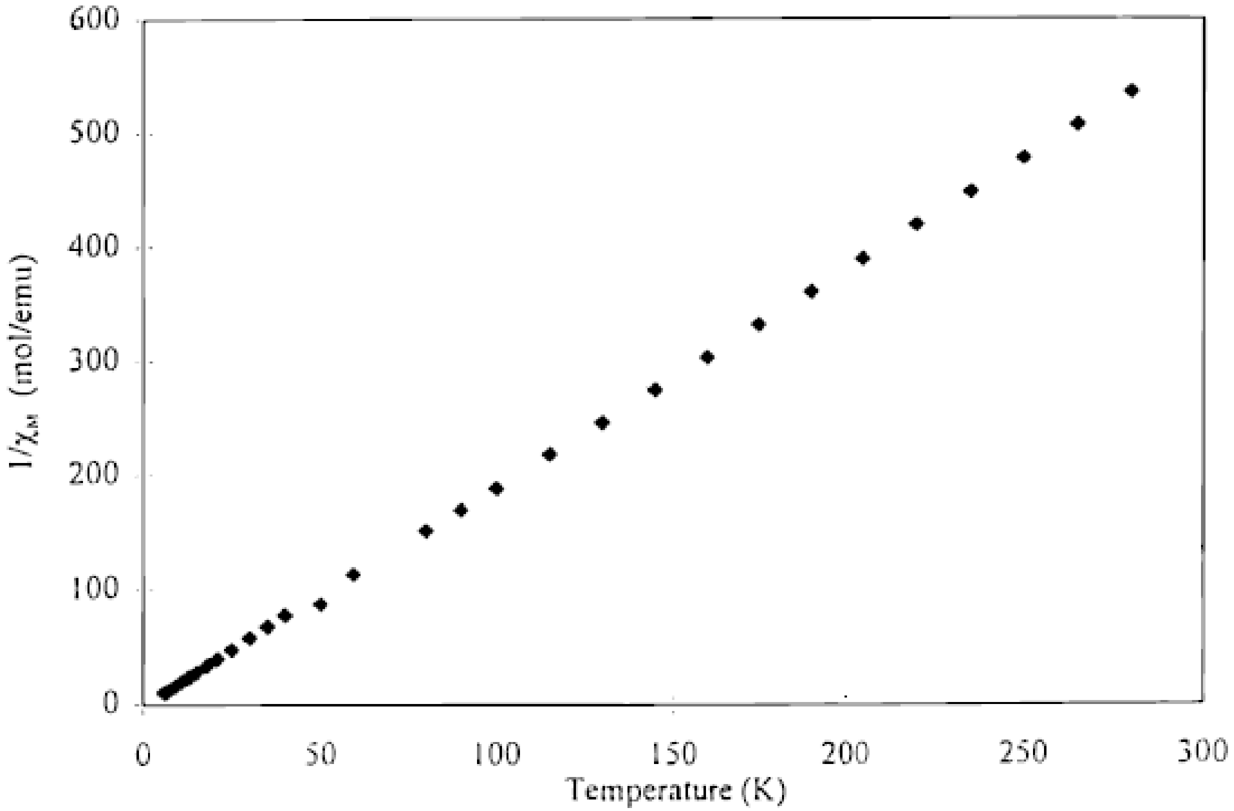


Figure 3. Reciprocal of molar susceptibility (at 5 kG) versus temperature for $Au(AuF_4)_2$; $\mu_{eff} = 2.05\ \mu_B$.

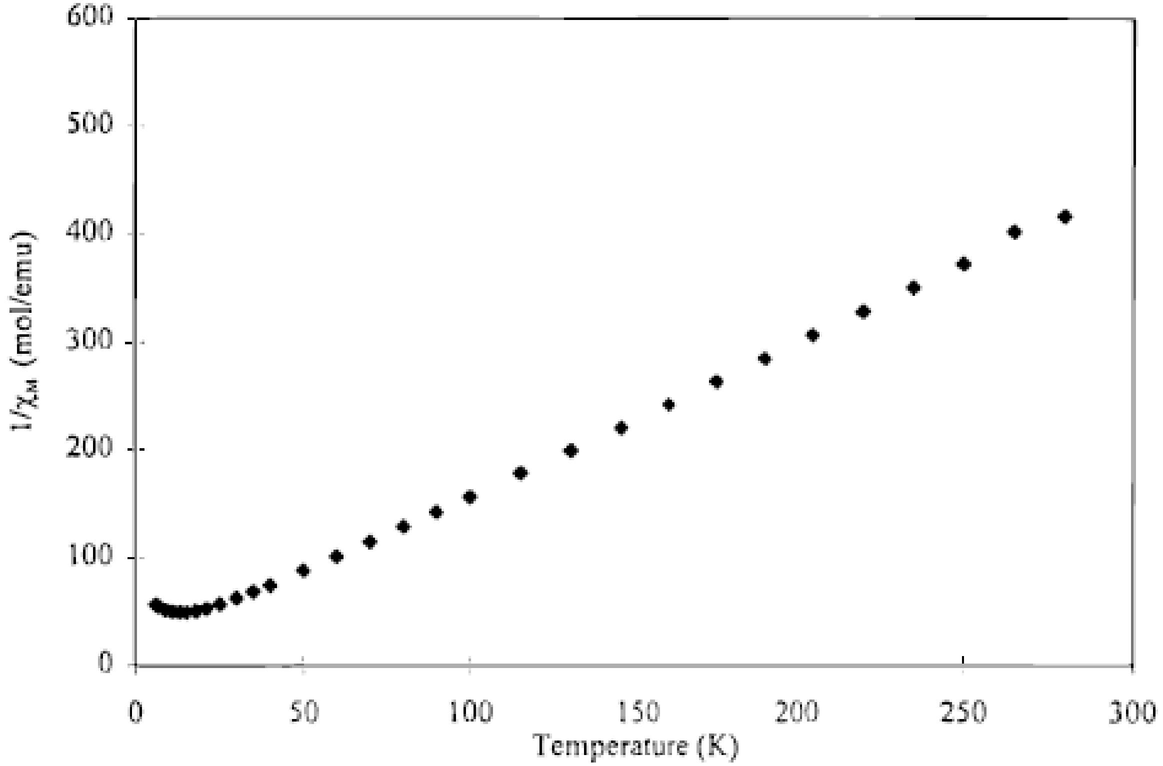


Figure 1. Reciprocal of molar susceptibility (at 5 kG) versus temperature for $Au(SbF_6)_2$; μ_{eff} (for 50−280 K) = $2.37\mu_B$.

Why **Fluorine** ?

- Much smaller covalency $\mathbf{t_{pd}}$
- Larger charge transfer gap $\mathbf{\Delta_{CT}}$
- Smaller crystal field splitting $\mathbf{\Delta_{CF} \sim t_{pd}^2 / \Delta_{CT}}$ (weak ligand)
- Weaker electron-lattice coupling, weaker Jahn-Teller effect

In effect one can suppress in fluorides the charge disproportionation *(much less ligand holes!)* and stabilize unusual valence states such as **Au**$^{\mathbf{2}+}$

One can (hope) to stabilize the **high-spin states** of ions such as **Pd$^{\mathbf{2+}}$, Pt$^{\mathbf{2+}}$** and may be **"Cu$^{\mathbf{3+}}$"** (d^8)

Conclusions

One can get magnetic gold !
(and superconducting)

And one can also have nonmagnetic iron (e.g. in pyrite FeS_2; but “more magnetic” in pyrite FeO_2 stabilized at high pressures and temperatures; important for Earth’s lower mantle!)

For negative CT gap one can get peroxide ions, instead of Zhang-Rice singlets.

Oxygen holes and peroxides can be important for the performance of batteries

● Intermezzo:
Everything you always knew about spin-orbit coupling, but forgot (to ask)

Why SOC is especially strong in 4d and 5d systems?

SOC ~ $Z^?$ **Usual answer SOC ~ Z^4.**

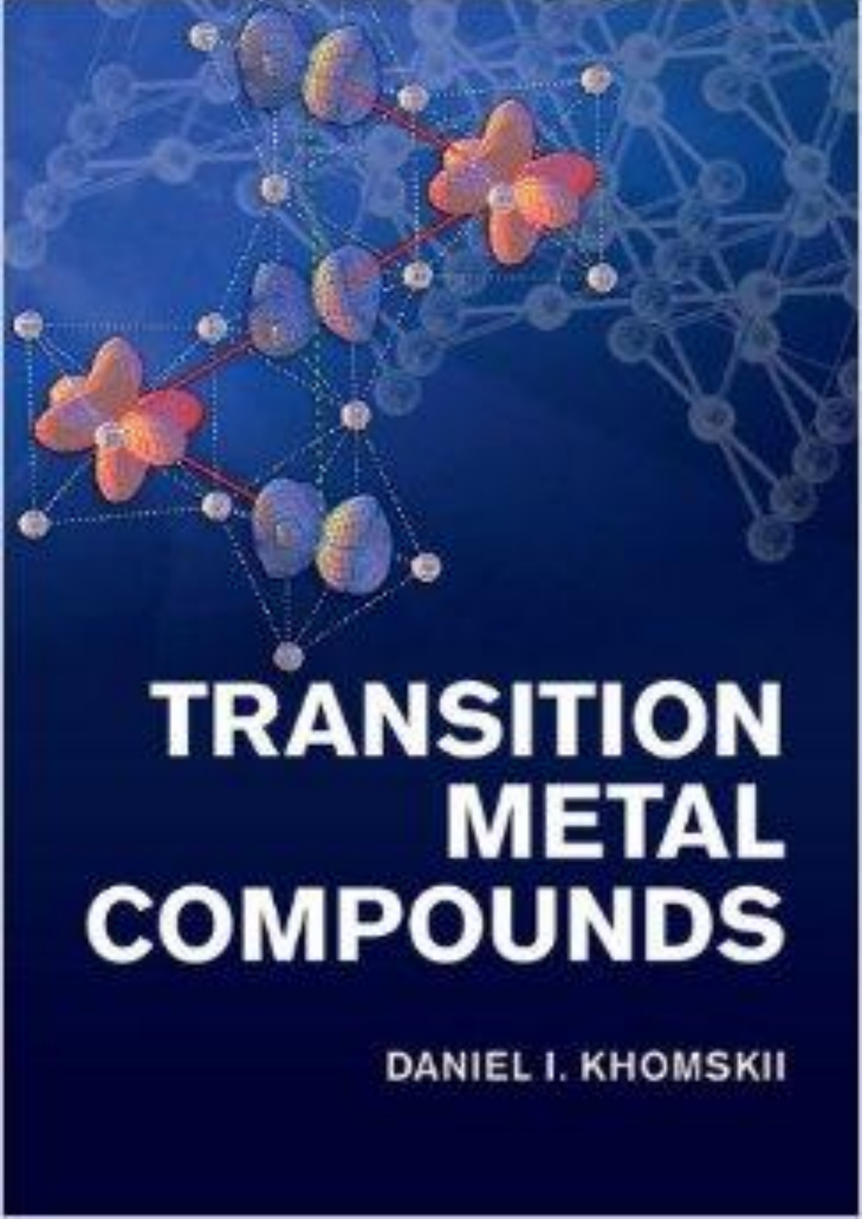
First, one often forgets about difference between SOC for the multiplet λ **LS**, and SOC for individual electrons $\zeta\, l_i s_i$

$$\boxed{\lambda = \zeta/2S}$$

I.e. for example for Ir4+(d^5, S=1/2) **$\lambda = \zeta = 0.4$ eV**.
But for Ir5+(d^4, S=1) **$\lambda = \zeta/2 = 0.2$ eV** !

And it is *not* λ , *but* ζ which depends in a regular way on **Z.**

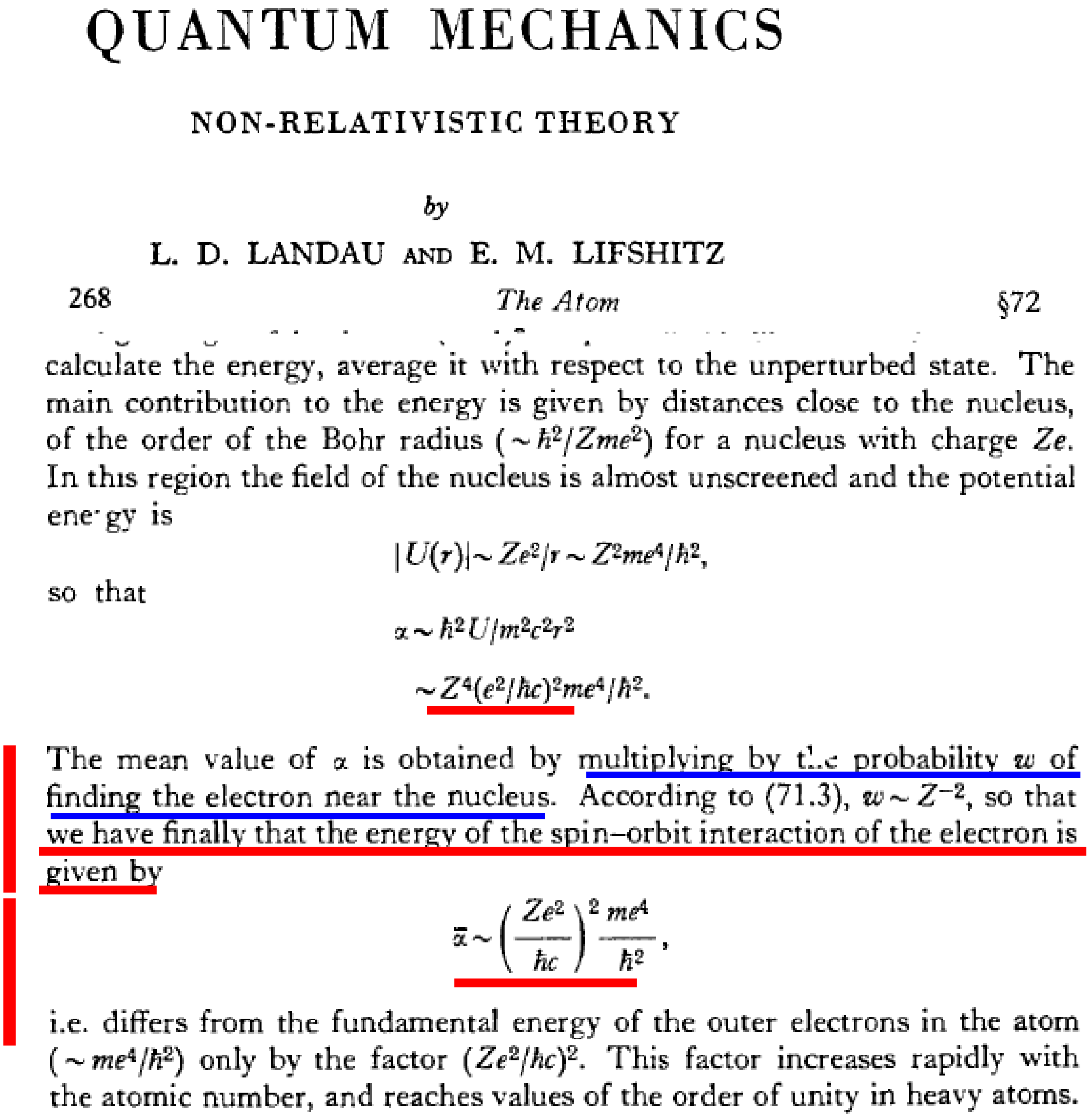
But how?



Transition Metal Compounds Hardcover
by Daniel I. Khomskii
Cambridge University Press, 2014

Describing all aspects of the physics of transition metal compounds, this book provides a comprehensive overview of this unique and diverse class of solids. Beginning with the basic concepts of the physics of strongly correlated electron systems, the structure of transition metal ions, and the behaviours of transition metal ions in crystals, it goes on to cover more advanced topics such as metal-insulator transitions, orbital ordering, and novel phenomena such as multiferroics, systems with oxygen holes, and high-Tc superconductivity. Each chapter concludes with a summary of key facts and concepts, presenting all the most important information in a consistent and concise manner. Set within a modern conceptual framework, and providing a complete treatment of the fundamental factors and mechanisms that determine the properties of transition metal compounds, this is an invaluable resource for graduate students, researchers and industrial practitioners in solid state physics and chemistry, materials science, and inorganic chemistry.

SOC ~ $Z^{?}$



QUANTUM MECHANICS

NON-RELATIVISTIC THEORY

by

L. D. LANDAU AND E. M. LIFSHITZ

268 *The Atom* §72

calculate the energy, average it with respect to the unperturbed state. The main contribution to the energy is given by distances close to the nucleus, of the order of the Bohr radius ($\sim \hbar^2/Zme^2$) for a nucleus with charge Ze. In this region the field of the nucleus is almost unscreened and the potential energy is

$$|U(r)| \sim Ze^2/r \sim Z^2me^4/\hbar^2,$$

so that

$$\alpha \sim \hbar^2 U/m^2c^2r^2$$

$$\sim Z^4(e^2/\hbar c)^2 me^4/\hbar^2.$$

The mean value of α is obtained by multiplying by the probability w of finding the electron near the nucleus. According to (71.3), $w \sim Z^{-2}$, so that we have finally that the energy of the spin–orbit interaction of the electron is given by

$$\bar{\alpha} \sim \left(\frac{Ze^2}{\hbar c}\right)^2 \frac{me^4}{\hbar^2},$$

i.e. differs from the fundamental energy of the outer electrons in the atom ($\sim me^4/\hbar^2$) only by the factor $(Ze^2/\hbar c)^2$. This factor increases rapidly with the atomic number, and reaches values of the order of unity in heavy atoms.

A quick estimate:

Ir: atomic number **Z=77;   λ = 400 meV**

V: atomic number **Z=23;   λ = 30 meV**

λ(Ir)/ λ (V) = 13.3

[Z(Ir)/Z(V)]^2 **= 11.2**

[Z(Ir)/Z(V)]^4 **= 125   -- way off !**

→ **Landau seems to be right!**

● LS (Russel-Saunders) vs jj-coupling

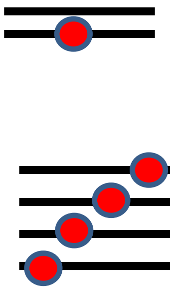
LS coupling scheme (light elements, relatively week SOC): first form state of maximum spin S and maximum orbital moment L possible, and then use spin-orbit coupling to form multiplets with **J**=**L**+**S**

jj-coupling scheme: heavy elements, e.g. rare earths**:**
every electron forms **j**=**s**+**l,** then form total **J**=Σ **j**$_i$

Actually one-electron schemes (e.g. all band-structure calculations) in fact use **jj**-scheme! (without mentioning, or even realising it)

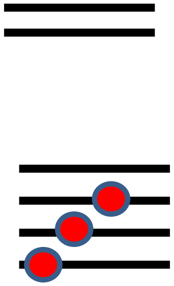
Often it is OK. E.g. **Ir4+**(t_{2g}^5): S=1/2, l_{eff}=1, J=1/2 ; 3/2 by LS –scheme.
Ground state J=1/2 doublet, excited state J=3/2 quartet.

In **jj** scheme it would be



lowest j=3/2 quartet in **jj**-scheme filled, upper j=1/2 doublet half-filled. The same for d^4 configurations with J=0 (**Ru4+**, **Ir5+**)

But for example the result is very different for d^3 (t_{2g}^3) configuration, **like Cr3+**, **Os5+** etc:
here in LS scheme **S=3/2, but L=0 !   no SOC at all !**
But in **jj**-scheme it would be also a 4-fold degenerate state, as for S=3/2, but with strong orbital admixture!

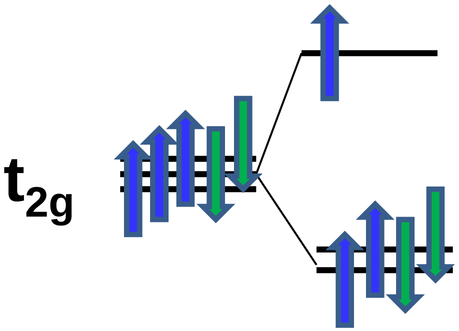


3d systems are definitely in LS regime, 4d – also. But what about 5d? (Rare earths are already **jj**)

Spin-obit coupling vs Jahn-Teller distortions

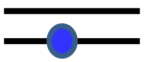
d5 (e.g. Ir4+)

No SOC

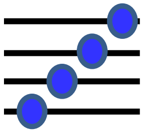


JT, c/a >1

Strong SOC



J=1/2 Kramers doublet,
no JT !

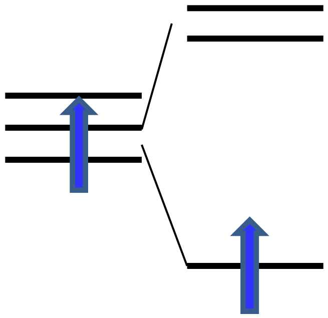


J=3/2 quartet

Strong SOC for J=1/2 _suppresses_ JT !

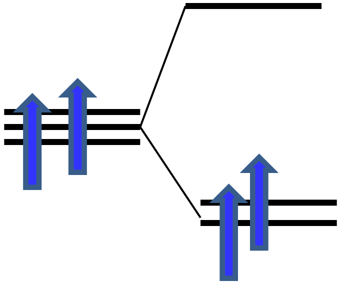
Spin-obit coupling vs Jahn-Teller distortions

No SOC



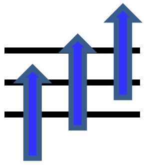
JT, c/a<1

d1



JT, c/a>1

d2

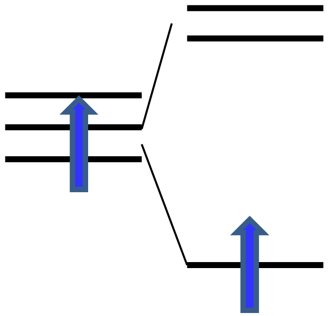


No JT !

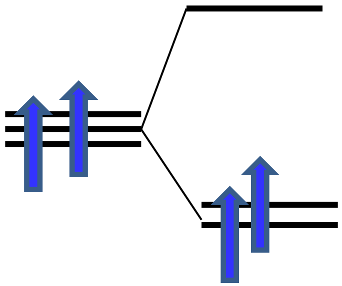
d3

Spin-obit coupling vs Jahn-Teller distortions

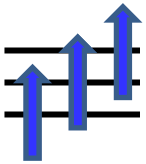
No SOC



JT, c/a<1



JT, c/a>1



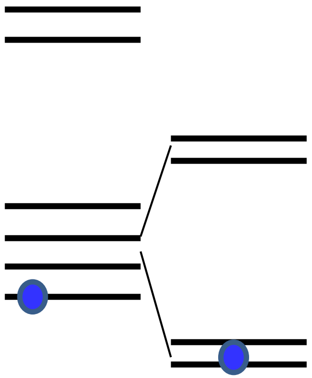
No JT !

d1

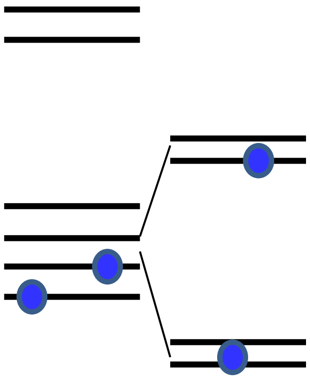
d2

d3

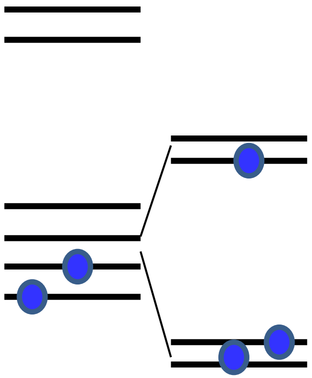
Strong SOC



J=3/2 quartet – two
Kramers doublets, **JT!**
most probably c/1<1



d2 – no JT !



d3 – also JT !!!

For d3 configuration SOC *activates* JT !

TABLE I. A list of ordered double perovskites. Note the discrepancy in Curie-Weiss temperature and μ_{eff} may originate from the experimental fitting of data at different temperature range.

Compound	B' config.	Crystal structure	Θ_{CW} (K)	μ_{eff} (μ_B)	Magnetic transition	Frustration para. f	Ref
$\mathrm{Ba_2}Y\mathrm{MoO_6}$	$\mathrm{Mo}^{5+}(4d^1)$	Cubic	−91	1.34	PM down to 2 K	$f \gtrsim 45$	11
$\mathrm{Ba_2}Y\mathrm{MoO_6}$	$\mathrm{Mo}^{5+}(4d^1)$	Cubic	−160	1.40	PM down to 2 K	$f \gtrsim 80$	12
$\mathrm{Ba_2}Y\mathrm{MoO_6}$	$\mathrm{Mo}^{5+}(4d^1)$	Cubic	−219	1.72	PM down to 2 K	$f \gtrsim 100$	13
$\mathrm{La_2LiMoO_6}$	$\mathrm{Mo}^{5+}(4d^1)$	Monoclinic	−45	1.42	Short-range AFM $T_N \sim 20$ K	$f \gtrsim 2$	13
$\mathrm{Sr_2Mg}Re\mathrm{O_6}$	$Re^{6+}(5d^1)$	Tetragonal	−426	1.72	Spin glass, $T_G \sim 50$ K	$f \gtrsim 8$	14
$\mathrm{Sr_2Ca}Re\mathrm{O_6}$	$Re^{6+}(5d^1)$	Monoclinic	−443	1.659	Spin glass, $T_G \sim 14$ K	$f \gtrsim 30$	15
$\mathrm{Ba_2Ca}Re\mathrm{O_6}$	$Re^{6+}(5d^1)$	Cubic to tetragonal (at $T \sim 120$ K)	−38.8	0.744	AFM $T_N = 15.4$ K	$f \sim 2$	16
$\mathrm{Ba_2LiOsO_6}$	$\mathrm{Os}^{7+}(5d^1)$	Cubic	−40.48	0.733	AFM $T_N \sim 8$ K	$f \gtrsim 5$	17
$\mathrm{Ba_2NaOsO_6}$	$\mathrm{Os}^{7+}(5d^1)$	Cubic	−32.45	0.677	FM $T_N \sim 8$ K	$f \gtrsim 4$	17
$\mathrm{Ba_2NaOsO_6}$	$\mathrm{Os}^{7+}(5d^1)$	Cubic	~ -10	~ 0.6	FM $T_N = 6.8$ K	$f \gtrsim 4$	18