The Explicit Role of Anion States in High-Valence Metal Oxides

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• Mona Berciu UBC
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• Steve Johnson
Content

• Introduction
• Importance of the anion states
• Hole doped states in divalent Cu and Ni Oxides
• Undoped negative charge transfer gap systems
• General Classification of transition metal and rare earth compounds Mott Hubbard, Charge transfer, Mixed valent and negative charge transfer
• Negative charge transfer gap systems Nickelates, Bismuthtates
• Mixed valent rare earths SmB6
If we cannot solve a problem exactly
The starting point really matters

Start the thinking with the most likely oxidation state or valence of the cations before switching on the cation - anion hybridization in models

Standard rules for formal cation valence:
1. Anions are closed shell O(2-), Cl(1-) etc
2. Fixed valence cations La(3+), Ca(2+) etc
3. Valence of omivalent cation – composition
4. This puts low energy charge degrees of freedom on the cations
There are many examples where this formal definition is not what happens in reality.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Formal Valence</th>
<th>Actual Valence</th>
<th>Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrO₂</td>
<td>Cr⁴⁺</td>
<td>Mixed close to 3⁺</td>
<td>Holes in O 2p band Half met. ferromag</td>
</tr>
<tr>
<td>FeS₂</td>
<td>Fe⁴⁺</td>
<td>Fe²⁺ S=0</td>
<td>S₂ pairs forming S₂(2-)</td>
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<tr>
<td>BaO₂</td>
<td>Ba⁴⁺</td>
<td>Ba²⁺</td>
<td>(O₂)²⁻ Pairs</td>
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<tr>
<td>KO₂</td>
<td>K⁴⁺</td>
<td>K¹⁺</td>
<td>(O₂)¹-pairs S=1/2 Ferron=magnet</td>
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<tr>
<td>La(1-x)SrxCuO₄</td>
<td>Cu mixed valent 2/3⁺</td>
<td>Cu²⁺</td>
<td>Holes in O2p metal/high Tc</td>
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<tr>
<td>(Li/Na)NiO₂</td>
<td>Ni³⁺</td>
<td>Ni²⁺</td>
<td>Holes in O₂p</td>
</tr>
<tr>
<td>ReNiO₃</td>
<td>Ni³⁺</td>
<td>Ni²⁺</td>
<td>Holes in O₂p</td>
</tr>
</tbody>
</table>
In the doped cuprates should Cu or O be at the center of attention for low energy scale charge degrees of freedom? (not withstanding the importance of Cu)
Correlated Electrons in a Solid

\[ U : d^n d^n \rightarrow d^{n-1} d^{n+1} \]

\[ \Delta : p^6 d^n \rightarrow p^5 d^n \]

\[ U = E_{I}^{TM} - E_{A}^{TM} - E_{pol} \]

\[ \Delta = E_{I}^{O} - E_{A}^{TM} - E_{pol} + \delta E_{M} \]

If \( \Delta < (W+w)/2 \) \( \rightarrow \) Self doped metal (mixed valent!!)

- ZSA, PRL 55, 418 (1985)
Note that in CuS the Cu is 1+ with holes in O 2p. Also in CuCr2S4 and Se4.

For divalent cations:

Note that CT energy decreases as we move down in the periodic table for the anion, i.e., F-Cl-Br-I or O-S-Se-Te.
On hole doping the O1s to 2p first peak rises strongly indicating the doped holes are mainly on O 2p.
Three early papers all in 1988 with O playing a central role
Anderson Impurity calculation for ARPES starting from Cu(d10) full O 2p band, full d-d multiplet interaction using respectively the one (d9 ground state and optical spectrum) and two particle Greens function for ARPES


Note the large Energy scale Covered by each Irreducible representations Of two d holes in the D4h point group

Local spin compensated State LIKE Zhang Rice singlet

Dashed lines are the Multiplets Of FREE Cu d8
Example Cu$^{2+}$ as in LaCuO$_4$ (d$^9$ s=1/2).

For the N-1 electron states we need $d^8$, $d^9L$, $d^{10}L^2$ where $L$ denotes a hole in O 2p band. The $d^8$ states exhibit multiplets

$$3d(x^2 - y^2, 3z^2 - r^2, xy, xz, yz)$$

$$b_{1g}, a_{1g}, b_{2g}, e_g$$

Given here are the various representations spanned by 2 $d$ holes in D$_{4h}$ symmetry and the Coulomb matrix elements in terms of the A,B,C Racah parameters. H. Eskes et al PRL 61, 1415 (1988).

D$^8$ with 2 holes in $x^2-y^2$
As in most Hubbard theories
Is part of a 4X4 Matrix in D$_{4h}$

Doped Holes mainly on O but O has TWO Cu nn so equally shared between them leading to a 3 SPIN POLARON


Doped holes mainly on O but form a molecular orbital about a selected Cu with x2-y2 symmetry
Is single band Hubbard justified for Cuprates?

The localized states of (3) are, however, not orthogonal because the neighboring squares share a common O site. Thus,

$$\langle P_{i\sigma}^{(S)} | P_{j\sigma'}^{(S)*} \rangle = \delta_{\sigma\sigma'} \delta_{i,j} - \frac{1}{4} \delta_{(ij),0}$$

(6)

where $\delta_{(ij),0} = 1$ if $i,j$ are nearest neighbors. In analogy to the treatment of Anderson for the isolated spin quasiparticle, we construct a set of Wannier functions ($N_5 = \text{num.}

Strong argument for $tJ$ or single band Hubbard

FIG. 1. Schematic diagram of the hybridization of the O hole ($2p^5$) and Cu hole ($3d^9$). The signs + and − represent the phase of the wave functions.
More recent Large scale exact diagonalization of 3 band like model Bayo Lau Thesis UBC 2011

PhysRevLett.106.036401, (2011)
PhysRevB.84.165102 (2011)

\[ H_{3B} = T_{pd} + T_{pp} + \Delta_{pd} \sum n_{l+\epsilon,\sigma} + U_{pp} \sum n_{l+\epsilon,\uparrow} n_{l+\epsilon,\downarrow} + U_{dd} \sum n_{l,\uparrow} n_{l,\downarrow} \]  

(1)

\[ H_{\text{eff}} = T_{pp} + T_{\text{swap}} + H_{J_{pd}} + H_{J_{dd}} \]  

(2)

\[ T_{\text{swap}} = -t_{sw} \sum s_{\eta} P_{l+\epsilon+\eta,\sigma} P_{l+\epsilon,\sigma'} |\sigma'_{l+\eta,\eta} \rangle \langle \sigma_{l+\epsilon,\eta} | \]
The dispersion and the quasi particle spectral weight periodic cluster 32Cu 64 O

Bayo Lau et al PRB 81, 172401
PhysRevLett.106.036401, (2011)
PhysRevB.84.165102 (2011)
Bayo Lau Thesis UBC 2012

FIG. 2. a) Energy and b) quasiparticle weight (bottom) for the lowest eigenstates with $S_T = \frac{1}{2}$ and $\frac{3}{2}$ vs. momentum. Different sets are shifted so as to have the same GS energy.
Note a quantum spin $\frac{1}{2}$ antiferromagnet has a nn spin correlation of -.33, singlet -.75, a Neel antiferromagnet =-.25, and a ferromagnet =+.25.

Exact diagonalization studies of 32Cu 64O

FIG. 3. $\langle C_x(\delta, a) \rangle$ for the lowest energy state at (a) $(\frac{\pi}{2}, \frac{\pi}{2})$ with $S_T = \frac{1}{2}$, and (b) at $(\pi, \pi)$ with $S_T = \frac{3}{2}$. The darkly-shaded bullet denotes the oxygen position at $l + e_x$. Each

Shows strong ferro correlations close to the doped hole. This does not look like a ZR singlet but actually

The spatial O hole has $x^2-y^2$ symmetry at $\pi/2 \pi/2$
Antiferro CuO$_2$ lattice

hole notation

Eigenstate of N-1 electron system is a linear combination of these three states and has a strong phonon component

HOLE ON O$_2$P STRONGLY DRESSED BY A PHONON PLUS TWO MAGNONS
What would this isolated 3 spin SPIN ½ polaron look like

\[
\begin{align*}
|\uparrow\rangle &= \sqrt{\frac{1}{3}} p_\uparrow^\dagger \frac{|\uparrow\uparrow\rangle + |\uparrow\downarrow\rangle}{\sqrt{2}} - p_\downarrow^\dagger \sqrt{\frac{2}{3}} |\uparrow\rangle \\
|\downarrow\rangle &= \sqrt{\frac{1}{3}} p_\uparrow^\dagger \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}} - p_\downarrow^\dagger \sqrt{\frac{2}{3}} |\downarrow\rangle \\
|0+\rangle &= \sqrt{\frac{1}{3}} p_\uparrow^\dagger \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}} \\
|0-\rangle &= \sqrt{\frac{1}{3}} p_\downarrow^\dagger \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}} \\
|\frac{3}{2}, \frac{3}{2}\rangle &= p_\uparrow^\dagger |\uparrow\rangle \\
|\frac{3}{2}, \frac{1}{2}\rangle &= \sqrt{\frac{2}{3}} p_\uparrow^\dagger \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}} + \sqrt{\frac{1}{3}} p_\downarrow^\dagger |\uparrow\rangle \\
|\frac{3}{2}, -\frac{1}{2}\rangle &= \sqrt{\frac{2}{3}} p_\uparrow^\dagger \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}} + \sqrt{\frac{1}{3}} p_\downarrow^\dagger |\downarrow\rangle \\
|\frac{3}{2}, -\frac{3}{2}\rangle &= p_\downarrow^\dagger |\downarrow\rangle \\
\end{align*}
\]

<table>
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<th>Wavefunction</th>
<th>Total Spin</th>
<th>$\frac{\langle H J_{pd} \rangle}{J_{pd}}$</th>
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</tr>
<tr>
<td>$</td>
<td>\downarrow\rangle$</td>
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<tr>
<td>$</td>
<td>0+\rangle$</td>
<td>$\frac{1}{2}$</td>
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<tr>
<td>$</td>
<td>0-\rangle$</td>
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<td>\frac{3}{2}, \frac{3}{2}\rangle$</td>
<td>$\frac{3}{2}$</td>
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<td>\frac{3}{2}, \frac{1}{2}\rangle$</td>
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<td>$</td>
<td>\frac{3}{2}, -\frac{1}{2}\rangle$</td>
<td>$\frac{3}{2}$</td>
</tr>
<tr>
<td>$</td>
<td>\frac{3}{2}, -\frac{3}{2}\rangle$</td>
<td>$\frac{3}{2}$</td>
</tr>
</tbody>
</table>
THE main hole dressing is “A PHONON PLUS TWO MAGNONS”

This is an important contributor to the MIR optical spectrum
Jose Lorenzana, Thilo Kopp, Markus Grueninger, Dirk van der Marel,

Experiment Optical absorption
J. Lorenzana and GAS PRL, 74, 1867 (1995)
Ibid PRB 52 9576 (1995) THEORY
Phonon plus two magnon virtual bound State in Cuprates / Nickelates


Taken from Grueninger Thesis Groningen 1999
Note that the valence of Cu in say LaSrCuO$_4$ (formally 3+) would likely be 2+ with one hole per 2 O in the CuO$_2$ plane i.e. Negative charge transfer
Note the high “pre-Edge feature and the Spectral weight Transfer from high To low energy scales

Just as in the cuprates doped holes mainly on O NOT Ni3+

**Ni(1-x)Li(x)O**

**FIG. 1.** Oxygen K-edge absorption spectra of MgO (Ref. 26), NiO, Li₃Ni₁₋ₓO for indicated values of x, and Li₂O.
LaNiO$_3$ thin film on LSAT  Sutarto, Wadati, Stemmer UCSB

O $K$ XAS

Note the huge O 1s -2p prepeak just as in the cuprates Holes ON O
Before going on an example of how crystal field splitting and Hunds rule coupling determine the ground state ionic configuration Ni$^{3+}$ (d$^7$) in Oh symmetry.

**Fig. 1:** (a) The Hund’s rule and crystal field energetics are introduced for a Ni$^{3+}$ (d$^7$) system.
Results of a Configuration interaction calculation

Fig. 2: Results of a full configuration interaction calculation. (a) The low spin phase space is
You can understand that for large hybridization low spin can also occur for positive charge transfer energy.

Physical picture for high spin to low spin transition:

- **d7 Ni3+**
  - $E(HS) = -11J - 8DQ$
  - $E(LS) = -9J - 18DQ$
  - HS to LS for $10DQ > 2J$

- **d5; Fe3+, Co4+**
  - $E(HS) = -10J$
  - $E(LS) = -4J - 20DQ$
  - HS to LS for $10DQ > 3J$
Three cases: Charge transfer, Mixed valent, and Negative charge transfer

![Diagram](image)

Recall the O band (18 electrons / unit cell) in 3d perovskite (RENiO3)
For negative CT there would be 1 hole per 3 oxygens and NI (2+) 3d8
Moving from MH to CT to Mixed valent to Negative CT (holes on anions)

Increasing formal Cation valence

Mott-Hubbard
\[ |\psi_0\rangle = |d^n\rangle \]

Positive Charge Transfer
\[ |\psi_0\rangle = |d^n\rangle \]

Mixed Valence
\[ |\psi_0\rangle = ? \]

Negative Charge Transfer
\[ |\psi_0\rangle = |d^{n+1} L\rangle \]

Kondo Lattice/ Kondo Insulator
The mixed valent state wave function or ground state has been a mystery for as long as I can remember

- Could be charge ordered Verwey transition in Fe₃O₄
- Could be a charge density wave.
- We will describe later that it could also form a coherent state where the mixed valence is in momentum SmB₆
- Excitonic insulator?
- Could be a simple metal if U and the multiplet splittings are much less than the d-d intercice hopping
- Perhaps you have other ideas
Nickelates $\text{RENiO}_3$: formally Ni would be $3^+ \text{ d}^7$ (low spin) However Ni$^{3+}$ is a strong Jahn Teller Ion but there is no Evidence for distortions resulting from this.
Aside from the XAS of O Recent RIXS point to negative charge transfer gap system (results obtained by)

Valentina Bisogni and Thorsten Schmitt from PSI

Sara Catalano, Marta Gibert, Raoul Scherwitzl Jean-Marc Triscone, and Pavlo Zubko From Geneva

Valentina Bisogni et all Nature communications in press
Ni 2p XAS energy region: Up to now the peaks A and B were considered to be multiplet structure in the final 2p5 3d8 local states.

RIXS demonstrates that a local d-d like description is OK for peak A with photon energy independent peak positions in RIXS.

Near linear dependence of the “Loss” energy with photon energy show that this is not RIXS but more like x-ray fluorescence.

So peak A in XAS involves the excited d electron and Ni 2p core hole intimately bound while peak B must involve an excitation into a delocalized continuum band state. The continuum starts at most 1 eV above the bound state. This has implications for the ground state and low energy excitations and the properties.
RIXS map of NdNiO$_3$ – 300 K Metallic Phase

Here the continuum states merge with the “bound states or resonances” extending to zero loss energy i.e., A METALLIC STATE.

Strong $T$ dependence of the XAS.
High oxidation states

• In general we expect the charge transfer energy to strongly decrease for higher oxidation states.

• This would mean a different starting point i.e.

  \[
  \begin{align*}
  \text{Cu}^3+ & \quad \rightarrow \quad \text{Cu}^2+ \quad \text{Ni}^3+ \quad \rightarrow \quad \text{Ni}^2+
  \\
  \text{Co}^4+ & \quad \rightarrow \quad \text{Co}^3+ \quad \text{Fe}^4+ \quad \rightarrow \quad \text{Fe}^3+ \quad \text{Mn}^4+
  \end{align*}
  \]

  The charge degrees of freedom are mainly on Oxygen.
BASIC STARTING POINT FOR NEGATIVE CHARGE TRANSFER GAP

- high density of large U Ni2+(d8) states with strong hybridization and exchange with the holes on O.
- THIS IS An ANDERSON LATTICE PROBLEM BUT WITH Vkd TOO LARGE FOR A Schrieffer Wolff transformation to KONDO.
- Also for KONDO we have a Nozieres exhaustion principle at work i.e. only enough holes to screen the spins of $\frac{1}{2}$ of the Ni’s
- Would likely remain metallic as in LaNiO3 (BAD METAL) UNLESS
- We include strong electron phonon interaction in Tpd
Negative charge transfer yields
Charge disproportionation without moving charge


Consider ReNiO3 as Ni2+L (1 O 2p hole per 3 O)
Then each Ni is surrounded by on average 2 L holes in an octahedron of O.

\[ \text{d8}_\text{L} + \text{d8}_\text{L} \rightarrow \text{d8} + \text{d8}_\text{L2} \]

Each second Ni2+ has a STRONGLY COMPRESSED octahedron of O with two holes of Eg symmetry in bonding orbital's I.e. d8 L2 (S=0)

= No Jahn Teller problem anymore
BOND DISPROPORTIONATION
Charge disproportionation without charge transfer


Crystalized Bipolarons (electron phonon) in 1/2,1/2,1/2, superstructure

In the insulating phase NOTE THAT THE SYMMETRY OF THE SHORT BOND LENGTH STATE IS EXACTLY THE SAME AS NI4+ LOW SPIN. There is no phase transition between the bond disproportionated and Charge disproportionated states but rather a crossover.
Total energy, charge density, magnetic moment, and density of states vs. checkerboard O octahedron compression/expansion.

Note the gap forming for displacements of > .09Å.
Nickelates in the magnetic phase have a 1/4,1/4,1/4 magnetic superstructure due to anti ferromagnetic ordering which has been assumed to be up up:down down in all three directions.

The Johnson calculation predicts Up zero; down zero.

Let's look at resonant magnetic x-ray diffraction.
Bond disproportionation and dynamical charge fluctuations in the perovskite rare earth nickelates

R. J. Green,1,2,3,* M. W. Haverkort,3 and G. A. Sawatzky1,2

Note the short bond length has virtually no Magnetic diffraction intensity i.e. $S \sim 0$ Long bond $S \sim 1$
Recent experiments by Mathias Hepting MPI Stuttgart and coworkers on NdNiO3 thin epitaxial films show magnetic diffraction energy dependence in almost too perfect agreement with the theory
To Be Published
Fig. 5: Energy dependence of magnetic scattering and tuning of magnetic moments due to external rotation of $\psi$. (a) 45°, (b) 145°, (c) 130°, (d) 10°.
How are systems like Ba or SrBiO3 different?

- Weak correlation if any
- Band theory should work
- Is there charge disproportionation? $2\text{Bi}^{4+} - \text{Bi}^{3+} + \text{Bi}^{5+}$ or $\text{Bi}^{3+}$ and one hole per Bi in the O 2p band
- How about electron phonon coupling?
- Is this in the end similar to Nickelates? Also $(1/2,1/2,1/2)$ superstructure

Kateryna Foyevstova et al
Projection of O 2p molecular orbitals onto the O 2p band structure in a perovskite structure

- A1g symmetry combination of O2p states in an octahedron
  Mix with s states i.e. Bi 6s states

- Eg symmetry combination of O2p states in an octahedron
  Mix with eg d states i.e. Ni3d eg
GAS and Robert Green Julich Lectures sept 2016

Before hybridization
Nid7 Bi6s1 below O

After hybridization
Note the “bound “state
Of Eg or A1g symmetry

The Bi6s-O 2p hybridization
\is extremely large from DFT
Hybridization – bond disproportionation effects in bismuth perovskites

In bond-disproportionated state, holes condense onto $A_{1g}$ O 2p +Bi6s molecular orbital states of the collapsed octahedra

Kateryna Foyevstova et al
Fig. 8: Projected densities of states for the compressed (upper) and expanded (lower) octahedra in the low temperature, breathing distorted phase of SrBiO$_3$. 
Bulk SmB6 a mixed valent, “in momentum space,” ground state

Alfred Cheung, Robert Green, Mona Berciu, Ilya Elfimov and George Sawatzky
Physics department and Max Plank/UBC center for quantum materials
From extensive studies in 60’s and 90’s
Very low work function
Very unstable and complicated surfaces
Great thermionic emitters

VERY recent (Piers) potential topological Insulators.

Sm has 24 B NN
SmB6 is strongly mixed valent from numerous studies; spectroscopy XPS, XAS, EELS, ME and optics and magnetic susceptibility close to 50/50; $2^+ (f6)/3^+ (f5)$ charge is compensated with 5d/Bp band occupation changes
VanderMarel et al. PRB 37, 10674 (1988)
Hund's Rule

<table>
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<tr>
<th>RE element</th>
<th>No F electrons</th>
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J=L-S

J=L+S

J=5/2 is very different from one electron missing in a full DFT SO split Sm2+ band
SmB$_6$ – Multiplets and Spin-orbit splitting  Robert Green electron removal and addition spectra for the free ions in a mixed valent scenario
From Hirst PRB 15,1 (1977)
Gerken J. Phys. F: Met. Phys. 13 (1983) 703-713. These are the factors reducing the hoping Integrals and increasing the effective mass Because of local atomic correlations

Coefficients of fractional parentage

Sm 2+7F0 to Sm3+ 6H5/2 ~ 0.03
Sm3+ 6H5/2 to Sm2+7Fo ~ 0.03
Effective hopping integral pre-factors multiplying the DFT obtained hoping integrals

\( \text{fp6} = \) coefficient of fractional parentage to remove an electron from the \( J=0, S=3, L=3 \) f6 state leaving a \( f5(J=5/2, S=5/2, L=5) \) state

\( \text{fp5} = \) same for the addition of an electron from the \( J=5/2, S=5/2, L=5 \) f5 state to \( J=0, S=3, L=3 \) f6 state

This can be described by a spinless Fermion model
Switch on f-Smd; f-Bp Hybridization

Must be Sm2+ J=0 to Sm3+ J=5/2 Exist around K=0

Must be Sm3+ J=5/2 to Sm2+ J=0 Exist around X

INDIRECT GAP

N to N+1 electron Addition

N to N-1 electron Removal
Fig. 4. (Color online) (a-d) Progressive zoom of the X-Γ-X valence band spectra measured at $\hbar \omega = 70$ eV using a sum of LH and LV photon polarizations and with comparison to theoretical B 2$p$ (dotted) and 5$d$ (solid) bands from LaB$_6$. X-point $d$-band velocity values in units of eV-Å are also labeled.
Summary

• Oxides with formally high oxidation states - negative CT
• The mobile charge degrees of freedom mainly O 2p bands
• Nickelates - lowest energy O2p hole states- eg symmetry
• Bismuthates- they are of a1g symmetry , in cuprates eg
• Short bond length states- O2p hole (bi) polarons condensing into a bond disproportionated ground state
• SmB6 fascinating “mixed valent state in momentum space”
• Strongly further reduced f-f hoping due to low coefficients of fractional parentage ---- strong atomic increase of effective mass
• The “pseudo” Fermi surface gives a Luttinger count which agrees with the concentration of Sm3+