Which multinary site occupation preferences can be unfolded from EXAFS observations

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Introduction

$C_mI_{m'}$ binary is perfectly defined by Wyckoff , its lattice constant, and known are its *C*-ion-radius R_C and its enthalpy of formation $^{IC}\Delta_fH^0$

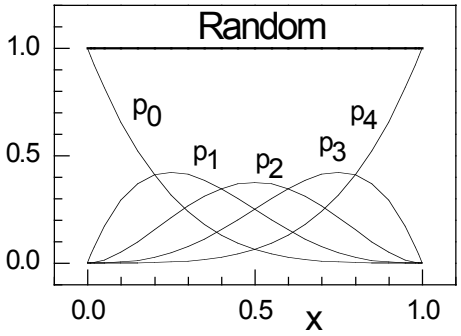
Doping $C_mI_{m'}$ with C′, C″… leads to a multinary alloy

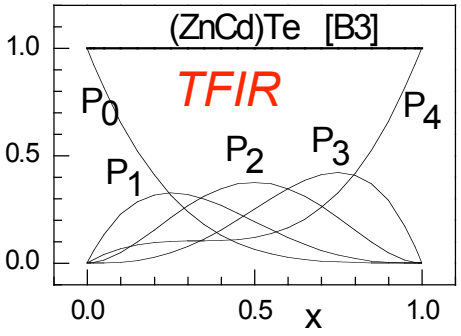
- If $R_C = R_{C'}$ and $^{IC}\Delta_fH^0 = {}^{IC'}\Delta_fH^0$, the substitution thermodynamically has no preferences ➔ site occupation is Bernoulli random
- Whenever $R_C \neq R_{C'}$ and $^{IC}\Delta_fH^0 \neq {}^{IC'}\Delta_fH^0$ preferences occur ➔ occupation is ≠ Random altering the crystal configuration composition and crystal properties\behavior

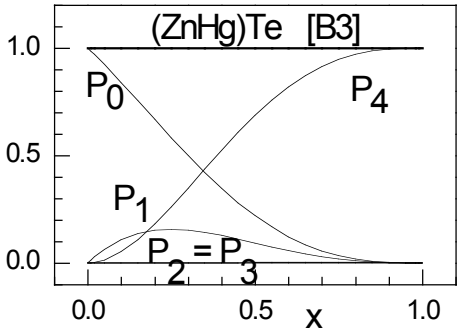
That is why we are concerned to evaluate the departure of probabilities from random, from EXAFS or FTIR observations

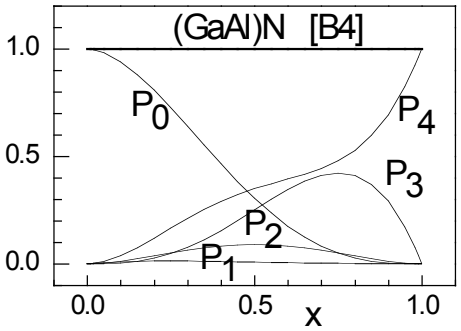
Distribution deviation from random

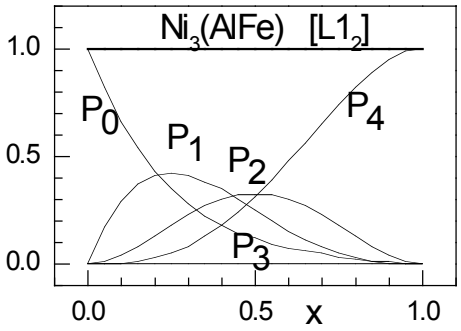
N=4



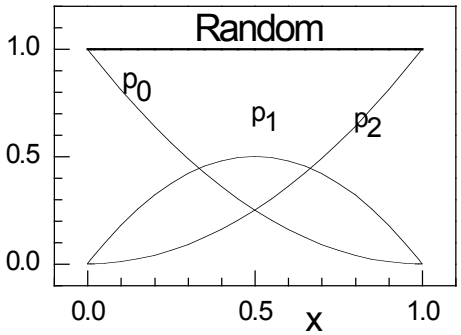


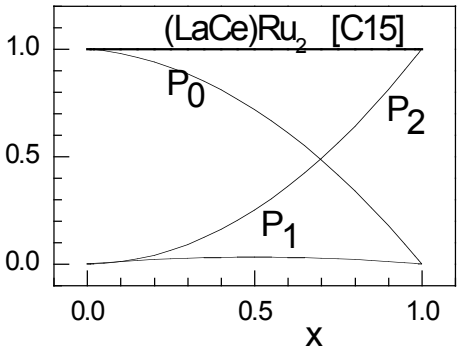






N=2





EXAFS

My previous presentations

2004	-sphalerite (B3); wurtzite (B4); intermetallide ($L1_2$) - full NN-NNN level from **EXAFS** ➔ bond distances, angles, ➔ **probability deviation** (from random Bernoulli) -CdMnTe, CdZnTe, GaAsP, GaInAs, GaAlN, HgMnTe, ZnMnS, ZnMnSe, ZnMnTe and $Ni_3(AlFe)$
	-sphalerite (B3) ZnCdTe from **far-IR** ➔ **probability deviation** validation
2008	Laves (C15): $LaCeRu_2$ – NN level from **EXAFS**

A quest

"EXAFS analysis is a powerful tool that gives average values"

*"**How** and **for which** structures can we expect to extract the maximum local information?"*

(Prof. W. Barduszewski, 2008)

… response

We shall here try to answer to this quest

indicating limits both formal and practical

Binary Compounds $C_mI_{m'}$

- Wyckoff's *Basic* and *Relative* vectors define site numbers *N* & distribution ➔ configurations T_0
- lattice constants ➔ size

✓ Wyckoff description ➔ Our model parameters

- Deviations, asymmetry, multi.shells ➔more parameters

➢ Exclude:
point defects; vacancies; antisites; intersites; impurities

➢ too many competition sites (*N* > *6*):

* *m* = *1* - (B2) CsCl (*N* = *8*)

* *m* > *1* - (C1) $(F_{1-x}Cl_x)_2Sr$ (*N* = *8*)

($L1_2$) $(V_{1-x}P_x)_3Ni$ (*N* = *12*)

C_mI_m excluded structures

- Group IV-IV - covalent compounds - already at the binary stage atoms fill indifferently sublattice sites
- Group II-V - periodic vacancies:
  metal-pnictide C_3I_2 ($D5_3$) Mn_2O_3-prototype (Zn_3As_2…)

Undefined at the ternary level (multi-shell sublattice)

- metal-pnictide ($B8_1$) NiAs prototype: Ni , As have different environments and non-interchangeable positions
- (B10) PbO-prototype FeSe structures (N=5) sites on two spheres with asymmetrical configuration.

Limits imposed by EXAFS

<*CN*(x)> measurement **accuracy** ~10-20% limits unfoldable structures to $N \leq 6$.

(B3, B4, $L1_2$) N=4 <6 1 atom =25% > uncertainty reliable

(B1) N=6, 1 atom >16% of configuration - limit of EXAFS precision - with suitable S/N ratio.

(B2) N=8 >6 uncertainty > 1 atom, limits reliable extraction

For N ≤ 6 to determine $\{W_k\}_{k=1,N-1}$ from <CN> data requires **≥ 6** observations.

$<{}_I{}^C d(x)>$ accuracy is relatively high, but at NN level

➔ $3(N\text{-}1)$ parameters $\{W_k , {}_I{}^C d_k , {}_I{}^{C'} d_k\}_{k=1,N-1}$

➔ **>** 3(N-1) observations

For ***N* ≥ 8** needed **too many observations**

Invariant boundary conditions

- Binary C_1I_m
  - ➔ Around "central" photoabsorber site I, shells of sites $\{C,C'\}$ & of sites I alternate
  - ➔ "competition" shells $\{C,C'\}$ surrounded by exclusively homogeneous sites I
  - ➔ **constant boundary conditions** for competing sites

- W_k of each configuration T_k is independent of relative content x
- multinaries derived from these binaries are addressed

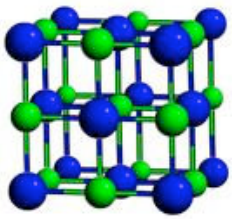
Some ternary structures and those already treated

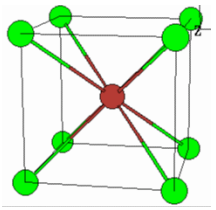
(CC')I

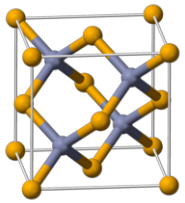
NaCl B1 N=6

CsCl B2 N=8

sphalerite,wurtzite B3,B4 N=4





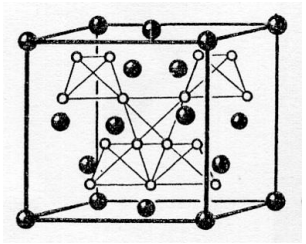


$(CC')I_2$

cubic Laves

C15

N=2 $(La_{1-x}Ce_x)Ru_2$



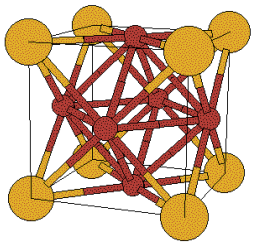
$(CC')I_3$, $(CC')_3I$

Intermetallide

$L1_2$

N_C =4 $Ni_3(Fe_{1-x}\ Al_x)$

N_I =12 $(V_{1-x}P_x)_3Ni$



Ternary $(C_{1-x}C'_x)_1I_{m'}$ alloys

Sites I with around NN shell of competing N sites: configurations $\{T_k\}_{k=0,N}$ $(N+1)$ with $(N-k)$ C + k C' ➔

- **Binary** T_0 $(CI_{m'})$ & T_N $(C'I_{m'})$,
- **Ternary** $\{T_k\}_{k=1,N-1}$ N-1 with all three (I, C , C')

substitutions modify configurations altering the respective bond distances, whence :

strained configuration statistical model.

T_k configuration probabilities

- NO preferences ➔ Bernoulli binomials $\boldsymbol{p_k}$.
- Preferences ➔ $\boldsymbol{p_k}$ **weighted** by its SOP coeff. $C_k(W_k)$

N.B.: Configurations $\{T_k\}_{k=0,N}$ independently modified & randomly distributed through crystal

...more comments

$(CC')_1 I_{m'}$ ➔ T_0 or T_N, the loci of ***N*** competing sites - single spheres.

But ternary $\{T_k\}_{k = 1,N-1}$, ➔

- $N \leq 4$ ➔ **2** concentric spheres for each T_k
- $N > 4$ ➔ **> 2** spheres

  ➔ ${}_I{}^C\underline{\boldsymbol{d}}_k = \langle {}_I{}^C d_k \rangle$ averages not ${}_I{}^C d_k$ individually
- $N \geq 8$ unfolding of bond distances is questionable.

Higher multinary alloys $(CC'...C'')_m(cc'...c'')_{m'}$

chemically classified N_M (= N_C+N_c) multinaries,

structurally 2 distinct families:

- **truly**-multinary $(CC'...C'')_m I_{m'}$

  $\{C,C',..,C''\}$ shells surrounded by non-varying boundary condition of ***I*** shells as in

  $(Zn_xCd_{x'}Hg_{1-x-x'})Te$

- **pseudo**-multinary $(CC'...C'')_m(cc'...c'')_{m'}$

  all shells with variable contents of competing elements.

  No constant content boundary conditions.

  Preferences vary with the relative contents and have no physical meaning as in

  $(Cd_{1-x}Mn_x)(Se_yTe_{1-y})$ or $(Ga_{1-x}In_x)(As_yTe_{1-y})$

  - **not addressed**.

Quintanary (*CC'I*)(*I'I"*)

doped quaternary AsCuSiZr-prototype "di-binary" (*CI*)(*I'I"*) alloys

Fluorine doped Lanthanide transition-metal oxy-pnictides or oxy-chalcogenide - $La(O_{1-x}F_x)FeAs$ quintanary **superconductors** (T_c > 50K) ➔ *interest*

- Structure maintains a bonding framework independent of *x* with, around the $O_{1-x}F_x$ shells, **boundary** reminiscent of quaternary complement *I*(*I'I"*).
- with *N* = 4 occupation sites, allows unfolding these "quintanary" alloys **in spite** of the asymmetry.
- Asymmetry ➔ an extra ternary configuration; parameterization requires 4 SOP coefficients + 10 NN bonds ➔ 14 independent parameters ➔ extra 5 parameters.

Discussion

Describing complex structures is often prohibitive

NN level investigations can unfold basic $\{W_k$, ${}_I{}^{C}d_k$, ${}_I{}^{C'}d_k\}$ without description ➔ (C15) $(Ce_{1-x}La_x)Ru_2$.[17]

NN scatter photoabsorber must be *I* :

NN environment around {*C,C′,..C″*} sites are sites *I* - binary with constant coordination value N_I

Coefficients $\{W_k\}_{k=1,N-1}$ evaluated observing $<{}_I{}^{C}CN(x)>$ &\or $<{}_I{}^{C'}CN(x)>$ ➔ *sum* $=<{}_I{}^{C}CN(x)>+<{}_I{}^{C'}CN(x)> = N$ ➔ defect-free;

< *N* ➔ vacancies; **>** *N* ➔ intersites

what NOT to do…

Boyce and Mikkelson reported NN bond distance averages for Rb(BrI) **11** and **10** for (RbK)I [29]

Octahedral rocksalt (B1) structure , $N = 6$

➔ 5 SOP coefficients W_k + 5x2=10 NN bond distance parameters ➔ 15

➔ **>15** observations.

information insufficient to perform the NN unfolding.

A complete determination at the NN level would have been possible if the coordination number averages had been reported.

…discussion.

- For $N \leq 4$ Bond distances $\{{}_I{}^C d_k$, ${}_I{}^{C'} d_k$ & $W_k\}_{N-1}$ retrieved
- Inter bond angles require all NN & NNN bonds.
- *described* structure parameters ➔ known bond constraints ➔ reduces n° of independent parameters.
- NO description ➔ bond parameters independent ➔ more samples ➔ To keep n° of observations reasonable, unfold only structures with $N<6$.
- To best fit EXAFS $<CN>$ and\or $<d>$ data minimum n° of observations must **>** n° free parameters $\{W_k$, ${}_I{}^C d_k$, ${}_I{}^{C'} d_k\}$ of structure
- Conclusions made on *a priori* random distribution are **not** reliable ➔ preferences can strongly deform experimental configuration probabilities respect to random.

Observations

EXAFS reports <*CN*> and\or <*d*> averages .

Unfold ➔ for each $\{T_k\}_{k=1,N-1}$
coefficients W_k & bond distances $\{{}_{I}{}^{C}d_k, {}_{I}{}^{C'}d_k\}$

- bond distances cannot be independently verified ➔ only qualitative estimations
- preference coefficients $\{W_k\}_{k=1,N-1}$ **<u>can be</u>** independently validated by FTIR unfold.
- Knowing local crystal parameters, as W_k's, explains characteristic & *unexpected* behaviors: in

$Ga_{1-x}Al_xN$ the lack of 4 of the 8 phonon modes of its far IR spectrum, and crystal inhomogeneity beyond 50% Al relative content.

Inter bond angles require all NN and NNN bond distances ➔ more observations.

Conclusions

Model unfolds

- EXAFS data at full (**NN & NNN**) level of (B3), (B4), ($L1_2$) structures ➔ probabilities, bond distances, angles for component configurations.
- EXAFS **NN** observations allow complex structures unfold avoiding configuration description, see (C15) $LaCeRu_2$
- ternary compounds from subset of $C_1I_{m'}$ binary structures, if **N ≤ 6**, & **photoabsorber *I***
- unfold valid over *x* range where structure has **NO phase transitions** - DMSs *diluted magnetic semiconductors* of Mn-metal-chalcogenides.

Ternary $(CC')_1I_{m'}$, higher truly-multinary $(CC'...C''')_1I_{m'}$, stacked $(C_{1-x}C'_xI)(I'I'')$ quintanery - can be unfolded.

To unfold: n° experimental data **>** n° independent parameters

Abundance of samples improves statistics & accuracy of data.

Спасибо за внимание

Thank you for your attention

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