

# Occupation preference values in doped $C_mI_{m'}$ multinaryes from EXAFS and FTIR correlative analysis

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We discuss which x-ray absorption fine structure (EXAFS) data of binary doped  $C_mI_{m'}$  compound structures can be unfolded to determine elemental bond distances and the deviations from random configurations due to site preference occupations (SOPs). SOP-deviation estimations can be further confirmed by independent Fourier transform infrared (FTIR) data analysis. The limits and restrictions of our model are presented and discussed.

PACS: 74.70.Dd Ternary, quaternary, and multinary compounds (including Chevrel phases, borocarbides, etc.);  
78.70.Dm X-ray absorption spectra;  
87.64.km Infrared.

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## 1. Introduction

A statistical strained configuration model was recently introduced to extract basic elemental data from experimental x-ray absorption fine structure (EXAFS) data of complex alloys [1–4]. This mathematical tool determines for each configuration bond distances and bond angles, and quantifies the probability deviation from random as a result of site occupation preferences (SOPs). For each component configuration  $T_k$ , the model also determines the ratio  $C_k$  of the experimental distribution to the random. Such deviations significantly affect the crystal behavior and its characteristics. It is important to stress that the model is purely statistical without any physical assumptions such as short- or long-range atomic interactions, hence it is necessary to explain a posteriori why some configurations are either absent or are present with negligible probability. This model does not require Monte Carlo, Molecular Dynamics, or similar computer simulations. An attempt to describe a real system is obtained by applying a general theoretical model to the complete set of experimental data. The crystal structure notations of the US Naval Research Laboratory are used throughout the paper [5].

A single element is denoted as an “A type” structure. The combination of two elements, C and I, gives rise to a wide variety of binary compounds with the generic formula  $C_mI_{m'}$  typically classified as “D type” structures, including:

- CI compounds (B type), such as the simple rocksalt (B1) NaCl prototype, (B2) CsCl prototype, (B3) zincblende/sphalerite, and (B4) wurtzite ZnS prototype structures;
- $CI_2$  compounds (C type), such as the fluorite (C1)  $CaF_2$  prototype, Laves cubic phase (C15)  $MgCu_2$  prototype, and the hexagonal  $\omega$  (C32) structured  $AlB_2$  prototype crystals; and
- $CI_3$  compounds, such as the “L type” tetrahedron intermetallide ( $L1_2$ )  $Cu_3Au$  prototype and the Heusler ( $L2_1$ )  $Fe_3Al$  prototype structures [5].

Two independent experimental techniques are typically used to investigate the local structure of a crystal: EXAFS [6] and FTIR [7] spectroscopy. When unfolding data collected by these two independent techniques the model should return two comparable sets of SOP coefficients [8,9].

FTIR spectroscopy probes throughout the crystal sample, the phonon and the vibrational modes of NN ion/atom

dipoles in the far-IR range, and determines their frequencies and oscillator strengths.

EXAFS analysis probes over a small cluster — whose size depends on the mean free path of electrons in the material [10] — all the single scattering contributions from the atoms surrounding a selected photoabsorber, such as the NN, the NNN and eventually the next-next nearest neighbor (NNNN) sites. EXAFS provides local average structure information, such as bond distances  $\langle d \rangle$  with high accuracy and coordination numbers  $\langle CN \rangle$ . Although EXAFS is mainly sensitive to single scattering processes, EXAFS data must be carefully evaluated as their accuracy is strongly affected by many concurrent contributions (i.e., sample quality, data acquisition, and treatment) [11,12]. In order to extract all the relevant parameters from the EXAFS spectra, a sufficient number of experimental data must be collected. The model then allows complete determination of the component configurations of nearest neighbor (NN) and next nearest neighbor (NNN) observations of (B3), (B4), (L1<sub>2</sub>) structured crystalline materials [1–4]. An analysis of the (C15) cubic Laves phase complex structure was restricted to the NN level [6].

Several EXAFS data of the tetrahedron CI (B3), (B4), and CI3 (L1<sub>2</sub>) structures were successfully unfolded using our statistical strained configuration model to derive local configuration details, such as (i) elemental component configuration probabilities, (ii) bond distances, and (iii) bond angles for CdMnTe, CdZnTe, GaAsP, GaInAs, GaAlN, HgMnTe, ZnMnS, ZnMnSe and ZnMnTe semiconductors [1,2,4] and intermetallide (AlFe)Ni<sub>3</sub> [3] materials. While the unfold of C<sub>3</sub>I structures such as the (V<sub>1-x</sub>P<sub>x</sub>)<sub>3</sub>Ni system is formally possible, but a large amount of data has to be collected [3].

In the next we will try to answer to the following questions:

— How can the maximum local elemental information be extracted from EXAFS data?

— What are the limitations of the model? Which  $C_mI_{m'}$  binary structures can be unfolded?

## 2. Structures and parsamerization

The parameters for binary  $C_mI_{m'}$  crystal compound configurations are the Primitive and Basic Vectors defining the distribution of sites through space [5]. This canonical distribution of sites determines the number of NN occupation sites around each atom ( $N_C$  C sites around I, and  $N_I$  I sites around C), and the shape of the binary single  $T_0$  configuration [13]. The size of  $T_0$  is determined by using the lattice constant  $a_{C_mI_{m'}}$  available from the literature [13–15].

Real crystals may depart significantly from the canonical description because of impurities, point defects such as vacancies, intersites or antisites. Such deviations may be treated case by case, including additional *ad hoc* parameters, but will not be discussed here.

Some binary structures may depart from the canonical description:

— In Group IV–IV covalent compounds atoms are free to fill arbitrarily sites in either of the two sublattices.

— The metal-pnictide C<sub>3</sub>I<sub>2</sub> (D5<sub>3</sub>) Mn<sub>2</sub>O<sub>3</sub>-prototype structures of Group II–V (i.e., Zn<sub>3</sub>As<sub>2</sub>, or Cd<sub>3</sub>As<sub>2</sub>) are characterized by consistent vacancies distributed periodically throughout the crystal [14].

Other binary structures present asymmetric or (when doped) ambiguous site distributions:

— In Group II–V of metal-pnictide (B8<sub>1</sub>) NiAs-prototype structured compounds, Ni and As atoms have different environments with non-interchangeable positions [16], while

— the (B10) PbO-prototype FeSe structures have five sites distributed on two spheres with asymmetrical configurations.

We will focus only on binary ionic-compounds characterized by a central (photoabsorber) site I surrounded by successive sublattice shells, alternatively occupied by C and I sites. Doping such a binary compound by a *competing* element C' generates a ternary  $(C_{1-x}C'_x)_m I_{m'}$  alloy of relative content  $x$ . Each competition-shell  $\{C, C'\}$  is surrounded exclusively by *invariant* sites I, thus defining a constant boundary condition. The ratio ( $W_k$ ) of experimentally observed dipole pairs IC' vs. random distribution of each ternary configuration  $T_k$  is independent of  $x$ . Both  $T_0$  (CI <sub>$m'$</sub> ) and  $T_N$  (C'I <sub>$m'$</sub> ) are binary configurations. In the absence of preferences, the configuration distribution probabilities of  $T_k$  are described by the Bernoulli binomials  $p_k(x)$ . The  $N+1$   $T_k$  configurations are independent and randomly distributed throughout the crystal, each configuration being independently modified. In the presence of SOPs, the respective occurrence probability is determined by  $p_k(x)$  weighted by its SOP coefficient  $C_k$  [1]. Beyond a single element C' doping, the association of further elements gives rise to higher multinary alloys  $(CC' \dots C'')_m (cc' \dots c''')_{m'}$  with  $N_C$  competing elements  $\{CC' \dots C''\}$  and  $N_c$  competing elements  $\{cc' \dots c'''\}$ , classified as  $N_M (= N_C + N_c)$  multinationaries, resulting in two distinct families [17]:

— The *truly*-multinary  $(CC' \dots C'')_m I_{m'}$  alloys, characterized by competing element  $\{C, C' \dots C''\}$  shells surrounded by a constant non-varying boundary condition of identical site-I shells. These structures have constant preference coefficients independently of the relative content of the components  $\{CC' \dots C''\}$  — as observed in the truly-quaternary  $(Zn_x Cd_x Hg_{1-x-x'})Te$  system [17].

— The *pseudo*-multinary  $(CC' \dots C'')_m (cc' \dots c''')_{m'}$  alloys are a mixture of lower degree multinationaries with all shells hosting variable amounts of competing elements. In such systems preferences vary with the relative contents and have no physical meaning; no invariant content boundary condition exists. Pseudo-multinary alloys such as

(Cd<sub>1-x</sub>Mn<sub>x</sub>)(Se<sub>y</sub>Te<sub>1-y</sub>) or (Ga<sub>1-x</sub>In<sub>x</sub>)(As<sub>y</sub>Te<sub>1-y</sub>) systems [17] are not discussed in this paper.

Quintanary (C<sub>1-x</sub>C'<sub>x</sub>)I(I'') alloys derived from doped quaternary alloys of the AsCuSiZr-prototype (such as fluorine doped La(O<sub>1-x</sub>F<sub>x</sub>)FeAs) are characterized by a stack of alternating binary layered structures along the crystal *c*-axis [18,19]. They present four occupation sites with a constant boundary condition around the O<sub>1-x</sub>F<sub>x</sub> shells, reminiscent of the quaternary complement I(I''). This asymmetric structure includes a first sublattice zone along two spheres with an additional ternary configuration [19].

### 3. Discussion

A full description of the configuration of complicated (C<sub>1-x</sub>C'<sub>x</sub>)<sub>m</sub>I<sub>m'</sub> structures is a complex task to perform. At the NN level, the EXAFS investigation allows the unfolding of the basic parameters {W<sub>k</sub>, <sup>C</sup><sub>I</sub>d<sub>k</sub>, <sup>C'</sup><sub>I</sub>d<sub>k</sub>}<sub>k</sub> [6] for a wide range of structures (S<sub>CmIm'</sub>). When a large number of parameters have to be determined (m > 1) a great deal of experimental data has to be gathered.

For the analysis of NN EXAFS data, the photoabsorber must be the element I; indeed, the NN environment around any of the competing {C, C', ...C''} scattering elements is "binary", consisting exclusively of sites I of the "boundary", thus returning an a priori constant coordination value N<sub>I</sub>, typically available from the literature [13]. The coeffi-

cients {W<sub>k</sub>} can be evaluated from average coordination numbers (⟨<sup>C</sup><sub>I</sub>CN(x)⟩ and/or ⟨<sup>C'</sup><sub>I</sub>CN(x)⟩, where I is the photoabsorber; C and C' are the scattering sites). For a canonical defect-free crystal ⟨<sup>C</sup><sub>I</sub>CN(x)⟩ + ⟨<sup>C'</sup><sub>I</sub>CN(x)⟩ = N. This sum is smaller than N when vacancies occur; and larger than N when intersites are present.

Determination of the (N - 1) preference coefficients W<sub>k</sub> is formally possible from reliable ⟨<sup>C</sup><sub>I</sub>CN(x)⟩ and/or ⟨<sup>C'</sup><sub>I</sub>CN(x)⟩ available EXAFS data for structures with N ≤ 6. The limit is due to the 10–20% accuracy of the <CN> EXAFS analysis. Indeed, in a rocksalt octahedral fcc structure with N = 6, one atom (=1/6) represents 16.7% of the configuration population and this value is still detectable by EXAFS analysis. For N > 6, as for (B2) structures, "one atom" probability is less than the EXAFS precision, whence the limit on extracting reliable values from coordination averages.

The accuracy of average bond distance <d(x)> EXAFS measurements is relatively high. However determination at the NN level of the 3(N - 1) parameters {W<sub>k</sub>, <sup>C</sup><sub>I</sub>d<sub>k</sub>, <sup>C'</sup><sub>I</sub>d<sub>k</sub>}<sub>k=1,N-1</sub> requires at least "3(N - 1) + 1" experimental data, which for N ≥ 8 may be too high. Note that for N ≤ 4, unfolding returns the bond distance values; while for structures with N ≥ 5, the derived bond distances are "average value" estimations over the different ternary subshell spheres.

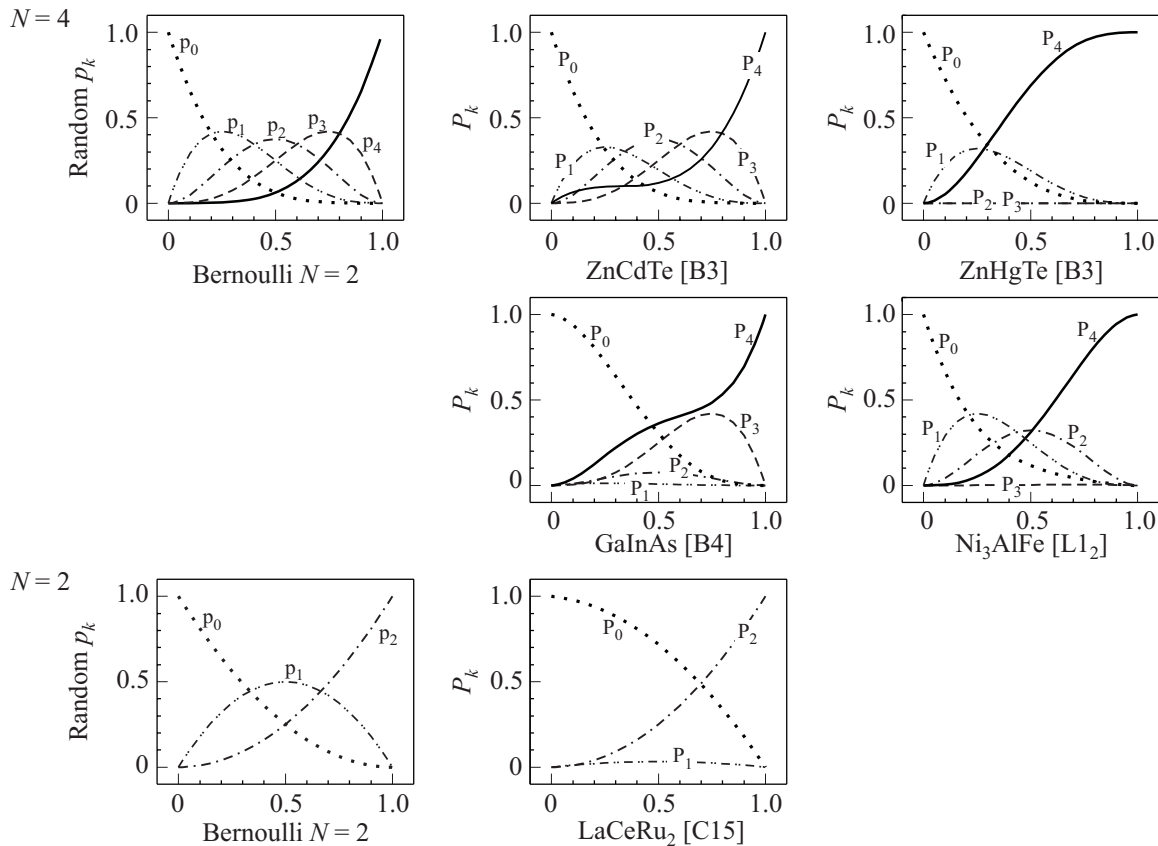


Fig. 1. Configuration probabilities random  $p_k(x)$  and experimental distributions  $P_k(x)$  of different ternary systems [structures are in brackets].

For a rocksalt octahedron fcc (B1) structure with  $N = 6$ , the number of SOP coefficients ( $W_k$ ) is 5; the number of  $NN$  bond distance parameters is 10, i.e.  $5 \times 2$ . To determine these 5+10 parameters, more than 15 values are required. Boyce and Mikkelsen reported insufficient information: only eleven  $NN$  bond distance averages for the Rb(BrI) system, and ten for the (RbK)I [20]. Had the coordination number averages been reported, complete determination at the  $NN$  level would have been possible.

Determination of bond angles is quite demanding. A well-described structure implies known constraints on the bond parameters and reduces the number of independent parameters to be unfolded, and hence the number of samples to be measured. When the full description of complex configuration structures is unavailable, all bond parameters are considered independent, thus requiring a larger number of samples. To keep reasonable the number of samples to be analyzed  $N$  has to be contained since in this situation there are twice as many “independent” parameters, requiring twice as much measured data.

Lacking a statistical description of distributions, conclusions based on *a priori* random distribution are not reliable, since preferences may strongly distort experimental configuration probabilities from the corresponding random distributions [1–3,6]. Figure 1 illustrates the deformation of experimental configuration probabilities (vs. content  $x$ ) induced by preferences compared to the corresponding random distribution curves for several ternary materials. The plots have been derived from published FIR data of ZnCdTe [21] and EXAFS data of ZnHgTe [22], GaAlN [23], Ni<sub>3</sub>FeAl [24], and LaCeRu<sub>2</sub> [25]. While the ZnCdTe unfolding can be reasonably approximated by a random distribution, such assimilation does not apply to the other materials. A knowledge of all local crystal parameters, such as the coefficients  $W_k$ , helps to understand the crystal behavior. In the case of Ga<sub>1-x</sub>Al<sub>x</sub>N such observations could explain: why four of the eight phonon modes describing the far-IR spectrum are missing, and the reason for the reported crystal inhomogeneity of crystals beyond a 50% Al relative content [4].

#### 4. Conclusion

Our model parameterizes doped binary  $C_mI_{m'}$  structures, using the canonical description [1]. Additional *ad hoc* parameters are required to account for non-negligible deviations, such as antisites, vacancies, intersites, and impurities. The number of parameters is a serious limit for successful unfolding. Our general model does not consider crystals, such as covalent Group IV–IV, or Group II–V (D5<sub>3</sub>), nor those such as (B8<sub>1</sub>) or (B10) structures, which once doped, require more than the canonical parameters for their description. For (B3), (B4) and (L1<sub>2</sub>) structures the model returns the full set of parameters (component elemental configuration probabilities, bond distances, and

bond angles) [1–3]. For (C15) structures only parameters proper to the NN level are derived [6]. The model is valid for an  $x$  range where the structures do not exhibit phase transitions [2].

Limiting EXAFS  $\langle CN \rangle$  and/or  $\langle d \rangle$  data to the NN shell level allows complex structures to be unfolded without a description of their configuration [25], but requires that the photoabsorber be the atom I. The model unfolding returns for each configuration  $T_k$  its coefficient  $W_k$  and the two bond distances at the NN level  $\{ {}^C_I d_k, {}^{C'}_I d_k \}$ . The latter cannot be independently verified so the estimations remain qualitative. However, comparison with the preference coefficients  $W_k$  obtained from FTIR spectroscopy data [8,9] allows an independent confirmation [7].

Bond angles require a full configuration description [1–3], or the measurements of all NN and NNN bond distances, i.e., a large set of experimental EXAFS data.

The parameterization and unfolding of ternary and higher truly-multinary  $(CC' \dots C''')_1 I_{m'}$  and even of stacked  $(C_{1-x}C'_x)_1(I'')$  asymmetrically structured alloys such as quinary La(O<sub>1-x</sub>F<sub>x</sub>)FeAs is feasible. However, a reliable unfolding would require that the number of experimental data to be collected be greater than the number of independent parameters to be determined, and may turn out to be a practical limitation when unfolding such structures. However, increasing the number of samples analysed improves the accuracy and the reliability of the measurement results.

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