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PROBABILISTIC ANALYSIS OF SITE-OCCUPATION PREFERENCES IN $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{Sb}_{1-y}$ AND $\text{Cd}_{1-x}\text{Mn}_x\text{Se}_y\text{Te}_{1-y}$ QUATERNARY COMPOUNDS

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Site-occupation preferences in quaternary GaInAsSb and CdMnSeTe compounds in tetrahedrally coordinated zinc-blende structures are discussed. Probabilistic eigenfunctions are defined to determine individual component pair-populations from measured average-pair distributions. The methodology and possible traps in interpreting site-occupation preferences of published EXAFS experimental overall average-pair distributions are discussed. The approach allows a deeper understanding of individual pair selective preferences in semiconducting multinary compounds. EXAFS reported departures from Bernoulli random distributions point to changes within elemental tetrahedral average-populations. Resolution requires that for tetrahedral structures experimental data best-fit be a 4th degree polynomial, product of a parabola by the factor $x(1-x)$. The analysis shows that both materials have a marked preference for elemental tetrahedra with odd numbers of competing species of ions around a central ion.

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1. Introduction

Site-occupation preferences (S-OP) of infrared lattice vibration spectra for tetrahedrally coordinated III-V and II-VI group ternary compounds [1, 2] are confirmed by extended X-ray absorption fine structure (EXAFS) analysis in ternary ZnMnSe [3] and quaternary $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{Sb}_{1-y}$ [4], $\text{Cd}_{1-x}\text{Mn}_x\text{Se}_y\text{Te}_{1-y}$ [5] and

$\text{Zn}_{0.5}\text{Cd}_{0.5}\text{Se}_{0.5}\text{Te}_{0.5}$ [6]. It has been shown that Ga-As and In-Sb pairs are preferred to In-As and Ga-Sb pairs in GaInAsSb [4], Mn-Se and Cd-Te to Mn-Te and Cd-Se in CdMnSeTe (for $x < 0.2$; $y < 0.2$) [5], and Zn-Se and Cd-Te to Zn-Te and Cd-Se in ZnCdSeTe [6]. Magnetic susceptibility analysis on CdFeSeTe [7] shows S-OP of the tetrahedral configuration of 1Se:3Te ions around Fe-ions. Experimental results for GaInAsSb are consistent with the pair-approximation method [8], in which pair distribution depends on the quaternary interaction parameter with near-neighbors (NN) and next-near-neighbors (NNN). The results suggest that certain ions tend to pair preferentially in solid solutions. EXAFS data for quaternary, and infrared studies for ternary compounds show S-OP for some ions, but do not indicate which tetrahedral ion-configurations contribute the most. The present paper reports a general probabilistic analysis of elemental tetrahedral configurations applied to GaInAsSb and CdMnSeTe in order to solve this problem.

2. Random and biased site-occupation analysis

In tetrahedrally coordinated zinc-blende (ZB) structure quaternary crystals, an anion/cation occupies a *central* site (c), with cations/anions in the peripheral (p) sites. An *anion* $\leftrightarrow$ *cation* correlation exists between the c-ions and each of the p-ions and is symbolized by "cp-pairs".

In a random-distribution model no interaction distorts this distribution. When in nature the random distribution is distorted, the distribution is biased. For experimental reasons proper to EXAFS on quaternary compounds, observations are limited to NN cp-pairs. Both random and biased site-occupation and resulting pair populations are considered. Random is a particular case of the general biased site-occupation and all its expressions are labeled with the subscript ∞ (selective-pair interactions $\ll$ random-chaos). General expressions for all probabilities are derived, introducing biasing weight factors. Equations relating the weight factors to best-fit parameters of experimental data are given. This methodology is applied to resolve quaternary experimental observations of published average pair-populations into their individual pair-population components.

The probability to fill k and $N_s - k$ of the N_s available peripheral (p) sites around each center (c) ion, with draws from a total population of two competing species with x and $1 - x$ respective relative contents, is

$$\{p_k^{[N_s]}(x)\}_{k=0, N_s} = \{x^k(1-x)^{(N_s-k)} / [k!(N_s-k)!]\}_{k=0, N_s} \quad (1)$$

distinct draws, since permutations between sites are undetectable. The maximum effect of a k -population occurs at $x = k/N_s$. The k -fill leads to k cp-pair interactions. Other interactions are not considered here. The total number of cp-pairs $B(x)$ for a given k -filling is

$$B_k^{[N_s]}(x) = k p_k^{[N_s]}(x). \quad (2)$$

Particular ion-ion interactions may or may not be negligible in preferring one site-occupation to another, i.e., the selections have, respectively, random or biased distribution. In general, let $w_k^{[N_s]}$ stand for the site-occupation biasing weights

(dependent on selective forces) for a k -fold filling. When selection is random, all $w_k^{[Ns]} \equiv 1$. Thus, in general, the overall "average-pair population" is

$$B^{[Ns]}(x) = (Ns - 1)! \sum_{k=1}^{Ns} B_k^{[Ns]}(x) \\ = x(Ns - 1)! \sum_{k=1}^{Ns} [w_k^{[Ns]} x^{k-1} (1-x)^{(Ns-k)} / [(k-1)!(Ns-k)!]]; \quad (3)$$

$(Ns - 1)!$, the normalizing factor, ensures pair-population $B^{[Ns]}(x = 1) = 1$ and implies that the saturated Ns -fill (concentration dependence) is taken as a reference for all other populations. Achieving this normalization allows a comparison of different measurements. $w_k^{[Ns]} > 1$ implies a S-OP shift from competing c' -centered tetrahedra to c -centered ones.

When ion-ion pair interactions are negligible, site-occupation is random, ($w_k^{[Ns]} \equiv 1$), and the expressions simplify to Bernoulli's binomial distributions, with

$$B_{\infty}^{[Ns]}(x) \\ = x(Ns - 1)! \sum_{k=1}^{Ns} \{w_k^{[Ns]} x^{k-1} (1-x)^{(Ns-k)} / [(k-1)!(Ns-k)!]\} \equiv x. \quad (4)$$

Random case formulas are illustrated (Fig. 1) as resolved components and resulting average populations for both tetrahedral and octahedral coordination.

Departures, $D(x)$, from the random expressions for any Ns -coordination

$$D^{[Ns]}(x) = B^{[Ns]}(x) - B_{\infty}^{[Ns]}(x) = B^{[Ns]}(x) - x \equiv x(1-x)P^{(Ns-2)}(x); \quad (5)$$

with $P^{(Ns-2)}(x)$ polynomial of degree $Ns - 2$.

For tetrahedra ($Ns = 4$), whence

$$\{w_k\}_{k=1,4} = \{1 + a_0, 1 + (2a_0 + a_1)/3, 1 + (a_0 + a_1 + a_2)/3, 1\}$$

as

$$x(1-x) \sum_{k=0}^2 a_k x^k \equiv x[x^3(w_4 - 3w_3 + 3w_2 - w_1) \\ + 3x^2(w_3 - 2w_2 + w_1) + 3x(w_2 - w_1) + w_1 - 1].$$

Fitting these polynomials to experimental results, and deriving the relative biasing weight factors $w_k^{[Ns]}$, we decompose the experimental results into their component eigen k -pair terms. Evaluating set $\{w_k^{[Ns]}\}$ from set $\{a_k\}$ (best-fit of experimental data — for example a least mean square, LMS, fit) is just an elementary algebra problem.

In analyzing tetrahedral coordination experimental results, $D(x)$ (then a 4th power curve) is often approximated by a parabola $P^*(x)$ [2, 4, 5]. To satisfy normalization and conditions at the limits, $P^*(x)$ must be of the form

$$P^*(x) = x(a-x)/(a-1),$$

implying

$$\{w_k\}_{k=1,4} = \{(3a+1-k)/[3(a-1)]\}_{k=1,4} \quad (6)$$

Fig. 1. Random component pair-populations in ternary/quaternary materials and their $B_{\infty}(x) = x$, average cp-population, as a function of relative content x , for tetrahedral (left part) and for octahedral (right part) coordination.

is an arithmetic series with decrement $1/3(a-1)$. This simple law is useful when there is insufficient coverage and is a good start for a best-fit iteration. But, if the parabolic fit does not have the two roots 0 and 1, the proceeding with the $P^*(x)$ approximation can lead to erroneous conclusions.

3. Experimental evidence of site-occupation preference

The complex EXAFS formula carries information on neighbors of the excited ion [9] with the amplitude of the signal proportional to the number of neighbors in each shell. Scattering losses cause large tuning of electron wavelength; hence, the materials are usually studied through relations between the "central" atom and its NN and only in convenient cases, NNN.

Quaternary $Ga_xIn_{1-x}As_ySb_{1-y}$ and $Cd_{1-x}Mn_xSe_yTe_{1-y}$ ($x < 0.2, y < 0.2$) crystallize in a tetrahedral coordinated ZB-structure, with each cation surrounded by four equidistant anions, and vice versa. In a tetrahedral coordination, there are five distinct elemental tetrahedral configurations for each *central* anion a : $a - 4c_1 + 0c_2$, $a - 3c_1 + 1c_2$, $a - 2c_1 + 2c_2$, $a - 1c_1 + 3c_2$, $a - 0c_1 + 4c_2$ (where c_1 and c_2 are the competing peripheral cations at the tetrahedron vertexes, i.e., the NN, 1st shell).

3.1. $Ga_xIn_{1-x}As_ySb_{1-y}$

$Ga_xIn_{1-x}As_ySb_{1-y}$ semiconducting material is stable for all ($0 \leq x \leq 1$ and $0 \leq y \leq 1$) contents against phase segregation and spinodal decomposition [10]. EXAFS observations [4] of As K -edges for various Ga_x and As_y compositions (i.e., analyzing NN Ga ions of the As ion) show S-OP (see Fig. 2a). Using the probabilistic analysis and a 4th power polynomial (proper to tetrahedral coordination) LMS-fit to the whole set of values [4], we get

$$D^{[Ns]}(x) = x(1-x)(2.89x^2 - 2.16x + 1.19),$$

i.e.,

$$\{w_k\} = \{T_k\} = \{2.19 \pm 0.2 : 1.07 \pm 0.2 : 1.64 \pm 0.2 : 1\}.$$

From these data, selective forces favor odd/odd fillings twice more than even/even!

3.2. $Cd_{1-x}Mn_xSe_yTe_{1-y}$

EXAFS analysis of $Cd_{1-x}Mn_xSe_yTe_{1-y}$ has a complex phase transition diagram [11], with its ZB structure limited to $x < 0.2$ and $y < 0.2$. The data obtained for Se and Mn K -edges allow (see Fig. 2b) comparative analysis of Se-Mn and Mn-Se pair populations [5]. All observed values have $x < k/N_s = 0.25$ ($k = 1$, $N_s = 4$), i.e., T_1 -population dominates throughout, with higher site-occupations T_2 and T_3 by at least one order of magnitude lower and smaller than uncertainty bars. The resolution process fails since one of the weight factors is negative. However, the dominance of T_1 over T_2 and T_3 populations (see Fig. 1)

Fig. 2. Resolution into component pair-populations of experimentally observed average pair-populations, as a function of x , for quaternary compounds in tetrahedral coordination: (a) GaInAsSb [4], (b) CdMnSeTe [5].

allows at least the $T_1 : T_4$ ratio to be determined. The local normalized average pair-population fits (LMS) the parabolic expression (Eq. (2)):

$$B_{\text{exp}}(x) = x(2.14 - x)/1.14,$$

whence

$$\{w_k\} = \{T_k\} \sim \{1.9 \pm 0.11 : (1.6) : (1.3) : 1\} \quad (7)$$

(values in parentheses are estimates with a large uncertainty).

The preference for Mn-Se pairs T_1 , just as for GaInAsSb, is twice that for a random Bernoulli distribution (with T_4 the reference population, since $B(x = 1) = 1$). Conclusions about T_2 and T_3 values are hazardous due to their small contribution.

4. Conclusion

This work develops a probabilistic approach of random and biased site-occupation preferences in tetrahedrally coordinated systems and applies it to analyze EXAFS results for GaInAsSb and CdMnSeTe. The analysis confirms, for both the quaternary compounds, a particular preference for elemental tetrahedra with odd numbers of competing species around the central ion.

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