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**STATISTICAL ANALYSIS OF INTER-IONIC DISTANCES AND OCCUPATION
PREFERENCES IN TERNARY ZINCBLENDE AND WURZITE STRUCTURED
CRYSTALS**

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Abstract

The statistical *strained-tetrahedron* model was developed to overcome two common assumptions of previous models: 1) *rigid undistorted ion sublattice* of regular tetrahedra throughout all five configurations and 2) random ion distribution. These *simplifying* assumptions restrict the range of applicability of the models to a narrow subset of ternary alloys for which the constituent binaries have their *lattice constants* and *standard molar enthalpies of formation* ($\Delta_f H_0$) equal or quasi-equal. Beyond these limits predictions of such models become unreliable, in particular, when the ternary exhibits site occupation preferences (SOPs). The *strained-tetrahedron* model, free from rigidity and stochastic limitations, was first developed to interpret structural information obtained with the use of x-ray absorption experimental data. It was validated on published EXAFS data of both zincblende (ZB) and intermetallide materials. The model was then extended to describe and interpret infrared spectra. The derivation and verification of the validity of our model and its assumptions are detailed in our published papers. We extend the model to cover the interpretation of far IR spectra and successfully apply it to a set of $\text{GaAs}_y\text{P}_{1-y}$ spectra. The unfolding gives the SOP coefficient values and/or specific oscillator strengths (OSs). Comparison with data available in the literature showed the good agreement of our model predictions.

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1. THE STATISTICAL STRAINED-TETRAHEDRON MODEL

The abundant literature on sphalerite (ZB) ternary semiconductors (ABZ or AYZ, where A, B stand for cations, and Z, Y for anions) bears witness to the considerable interest they have generated. For local structural properties, the interpretation of X-ray absorption data, e.g., EXAFS, and vibration spectra in the far IR domain is paramount.

ZB f.c.c. structures are tetrahedron coordinated and characterized by a *central* ion surrounded by four *nearest-neighbor* (NN) ions (i.e., 1st shell coordination) defining the four vertices of a tetrahedron, and twelve *next nearest-neighbor* (NNN) ions (i.e., 2nd shell). Binary compounds AZ have successive shells alternately filled by A and then Z ions. All tetrahedra are symmetric, regular and identical so, by simple trigonometry, equal inter-bond angles $\alpha_{A:Z:A} = \alpha_{B:Z:A} = 109.47^\circ$ and inter-ion distances (^{ij}d) are defined in terms of the lattice constant *a* (known from X-ray diffraction analysis): $^{AZ}d = 3^{1/2} a/4$, $^{AA}d = ^{ZZ}d = a/2^{1/2}$.

For ternary $A_{1-x}B_xZ$, in the binary compound AZ, A cations are partially substituted by B anions. This leads to the formation of five different elemental tetrahedra $\{T_k\}_{k=0,4}$, where the subscript *k* indicates the number of B ions at the vertices of the tetrahedron, with (4-*k*) A ions (see Fig.1). In the case of a random distribution, the filling (of *k* B ions into a shell with *N* sites (4 in the 1st shell, and 12 in the 2nd shell), from relative contents *x* & *1-x*) is precisely described by the Bernoulli binomial polynomials

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

In the *strained-tetrahedron* model [1], tetrahedra are free to deform from one configuration to the other, and the distribution is free to be non-stochastic. This model is a successful generalization of the rigid cation approximation [2] and random iterative cluster model [3]. Simulation of the local structure of ZB-ternary alloys requires 50 parameters (31 to weigh each of the Bernoulli binomials involved and to account for free distributions in the first two shells and 19 for the inter-ion distances).

The experimental observations of SOPs show that natural distributions generally deviate from a Bernoulli-binomial description. The inequality of the $\Delta_f H_0$ of the two binary constituents of the observed alloy causes deviations. To quantify them we associate to each Bernoulli binomial a weighted SOP coefficient “ W_{binomial} ”, a total of 31 SOP coefficients to cover the distribution of the NN and NNN sites.

Fortunately, the overall 50 parameters are linked by 40 identifiable constraints: i) NN preference parameter values determine NNN preferences and beyond; ii) though distorted, tetrahedra preserve proper symmetries; iii) to avoid destructive stresses, the average tetrahedron volumes of both sublattices locally relax to equal values. Thus, configuration probabilities have three degrees of freedom, with ≤ 7 distance free-parameters. (\leq when due to SOP extreme values, some configuration(s) are forbidden and their distances become

inexistent.);

Distribution-wise, while A and B ions are deterministically surrounded by Z ions, the Z ion selects its A or B neighbor ions. We thus **claim** that ALL higher shell preferential fillings are determined by linear expressions of the five NN SOP coefficients $\{W_k\}_{k=0,4}$. Binary tetrahedron configurations T_0, T_4 cannot have preferences, hence $W_0 = W_4 \equiv 1$. The probability of finding B and A ions in a T_k configuration is proportional to $\{kW_k\}_{k=0,4}$ and to $\{4-kW_k\}_{k=0,4}$, respectively. As probabilities are ≥ 0 , hence $0 \leq W_k \leq 4/k$.

The **three bounded free parameters** $0 \leq W_1 \leq 4, 0 \leq W_2 \leq 2, 0 \leq W_3 \leq 4/3$ define the distribution probability. The NNN shell coefficients $\{^A W_k\}_{k=0,1,2}$ and $\{^B W_k\}_{k=0,1,2}$ are determined by *combinatorial* probabilities associated with the Z ions of the NN shell; this leads to linear expressions of NNN SOP coefficients $^A W_k$ and $^B W_k$ as functions of the three W_k 's. For **ZB** structures these expressions are given in refs. [1] and Table 1. This hypothesis is general, and is fulfilled even in other crystal structures as $M_3(X_{1-x}X'_x)_1$ intermetallic alloys [4].

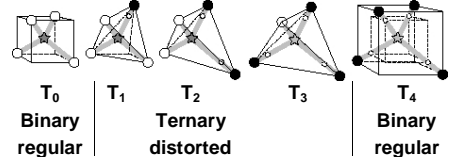


Fig.1 Aspect of the five elemental tetrahedron configurations $\{T_k\}_{k=0,4}$ of ABZ (or AYZ) ternary alloys. Small open circles indicate the would-be ion-positions as per *rigid tetrahedron* hypothesis.

Table 1 All possible B ion distributions in a NNN shell of a ZB ternary ABZ, and expressions for NNN SOP coefficients $\{^A W_k\}_{k=0,1,2}$ and $\{^B W_k\}_{k=0,1,2}$ around A and B, respectively. The distribution is determined by the combinatorial probabilities, in terms of SOP coefficients $\{W_k\}_{k=0,4}$ around Z ions of the 1st shell. Detailed explanation is given in [1].

k	All 12 possible NNN B-ion fills of the 4 tetrahedra	Resulting B-weights	Resulting A-weights
		$^B W_k \stackrel{[12]}{=} \sum_{j=0,4} \{^B M_{j,k} W_j^{[4]}\}$	$^A W_k \stackrel{[12]}{=} \sum_{j=0,4} \{^A M_{j,k} W_j^{[4]}\}$
0	0 0 0 0	W1	W0 = 1
1	0 0 0 1	$(3W_1 + W_2)/4$	$(3W_0 + W_1)/4$
2	0 0 0 2 / 0 0 1 1	$(5W_1 + 2W_2 + W_3)/8$	$(5W_0 + 2W_1 + W_2)/8$
3	0 0 0 3 / 0 0 1 2 / 0 1 1 1	$(6W_1 + 4W_2 + W_3 + W_4)/12$	$(6W_0 + 4W_1 + W_2 + W_3)/12$
4	0 0 1 3 / 0 0 2 2 / 0 1 1 2 / 1 1 1 1	$(5W_1 + 7W_2 + 3W_3 + W_4)/16$	$(5W_0 + 7W_1 + 3W_2 + W_3)/16$
5	0 0 2 3 / 0 1 1 3 / 0 1 2 2	$(4W_1 + 3W_2 + 3W_3 + 2W_4)/12$	$(4W_0 + 3W_1 + 3W_2 + 2W_3)/12$
6	0 0 3 3 / 0 1 2 3 / 1 1 1 3 / 0 2 2 2 / 1 1 2 2	$(4W_1 + 6W_2 + 6W_3 + 4W_4)/20$	$(4W_0 + 6W_1 + 6W_2 + 4W_3)/20$
7	0 1 3 3 / 0 2 2 3 / 1 1 2 3	$(2W_1 + 3W_2 + 3W_3 + 4W_4)/12$	$(2W_0 + 3W_1 + 3W_2 + 4W_3)/12$
8	0 2 3 3 / 1 2 2 3 / 1 1 3 3 / 2 2 2 2	$(W_1 + 3W_2 + 7W_3 + 5W_4)/16$	$(W_0 + 3W_1 + 7W_2 + 5W_3)/16$
9	0 3 3 3 / 1 2 3 3 / 2 2 2 3	$(W_1 + W_2 + 4W_3 + 6W_4)/12$	$(W_0 + W_1 + 4W_2 + 6W_3)/12$
10	1 3 3 3 / 2 2 3 3	$(W_2 + 2W_3 + 5W_4)/8$	$(W_1 + 2W_2 + 5W_3)/8$
11	2 3 3 3	$(W_3 + 3W_4)/4$	$(W_2 + 3W_3)/4$
12	3 3 3 3	W4 = 1	W3

A random integer ion distribution (k and 4-k) fully respects stoichiometry. With SOP coefficients $W_k \neq 1$ the scenario departs from the stochastic equilibrium: an **attenuation** of the three “ternary” configuration populations due to the asymmetry of the two ion populations,

while the excess enhances the binary probabilities, $W_k < 1$ that of AZ populations, $W_k > 1$ that of BZ. If $\{C_k(W_k)\}_{k=1,3}$ are the corrective weight factors imposed by stoichiometry, with $0 \leq \{C_k = \min[W_k, 1, (4-kW_k)/(4-k)]\}_{k=1,3} \leq 1$, we have:

$$\begin{aligned} \{P_k^{[4]}(x) = C_k p_k^{[4]}(x)\}_{k=1,3} & \quad \text{for ternary } T_k \\ P_0^{[4]}(x) = p_0^{[4]}(x) + \sum_{k=1,3} \{\max(0, 1-W_k) p_k^{[4]}(x)\} & \quad \text{for binary AZ configuration } T_0 \\ P_4^{[4]}(x) = p_4^{[4]}(x) + \sum_{k=1,3} \{\max(0, k(W_k-1)/(4-k)) p_k(x)\} & \quad \text{for binary BZ configuration } T_4 \end{aligned} \quad (1)$$

In the random case, when $\{W_k \equiv 1\}_{k=1,3}$, $\{P_k(x) \rightarrow p_k(x)\}_{k=0,4}$.

We must stress that while the observed SOPs enhance the probability of the binary-tetrahedron populations with respect to those of the random case, their spatial distribution remains stochastic, with NO tetrahedron clustering, as confirmed experimentally .

Once the probabilities are defined as a function of x , all the expressions for the average pair coordinations $\langle^{ij}CN(x)\rangle$ and for distances $\langle^{ij}d(x)\rangle$ for any two-ion pair $i:j=\{AZ, BZ, BB, BA, AA, ZAZ, ZBZ\}$ of ABZ ZB-ternary can be explicitly written (see ref. [1]). To illustrate, we recall one equation for each set: $\langle^{BZ}CN(x)\rangle = \sum_{k=0,4} \{kW_k p_k^{[4]}(x)\}$, and $\langle^{AZ}d(x)\rangle = \{\sum_{k=0,3} [(4-k) C_k]^{AZ} d_k + 4 \text{Max}(0, 1-W_k)^{AZ} d_0\} p_k^{[4]}(x) / \{\sum_{k=0,3} [(4-k) C_k] + 4 \text{Max}(0, 1-W_k)\} p_k^{[4]}(x)$. Applying these equations to unfold a set of EXAFS data such as GaAsP [5], we obtain, besides the SOP-coefficient values, the dimensions of all the elemental tetrahedra involved: inter-ion distances and angles (see ref. [1]). For example, inter-ion distances [\AA] in GaAsP are $\{\text{GaAs} d_k\}_{k=1,4} = \{2.42, 2.43, 2.44, 2.450\}$, $\{\text{GaP} d_k\}_{k=0,3} = \{2.359, 2.37, 2.37, 2.38\}$, $\{\text{AsGaAs} d_k\}_{k=2,4} = \{3.90, 3.90, 4.001\}$, $\{\text{PGaP} d_k\}_{k=0,2} = \{3.852, 3.88, 3.98\}$, $\{\text{AsGaP} d_k\}_{k=1,3} = \{3.91, 3.90, 3.99\}$, $\{\text{GaAsGa} d_k\}_{k=1,4} = \{3.95, 3.97, 3.98, 4.001\}$, $\{\text{GaPGa} d_k\}_{k=0,3} = \{3.852, 3.87, 3.87, 3.89\}$

To check the validity of the model and its assumptions of limited number of free parameters, we compare a) the experimental EXAFS distance-data available in the literature with the model fit curves [1,4] b) ‘‘co-ordination number’’ curves predicted on the basis of SOP values obtained from distance EXAFS-measurements, against independently measured coordination number values [1,4]; c) the correlation between the relative values of $\Delta_r H^0$ of the two constituents [1] and the corresponding SOP coefficient values obtained. *The comparison confirms the validity of the model and in particular the restrictive assumptions we proposed.*

2. FIR DIELECTRIC FUNCTION $\varepsilon(\omega, x)$ FOR TERNARY ZINCBLLENDE alloys

The dielectric function $\varepsilon(\omega) = \varepsilon_\infty + \sum_{j=1,n} \{S_j \omega_j^2 / [(\omega^2 - \omega_j^2) + i \omega \Gamma_j]\}$ of crystal systems can be extracted from the experimental reflectivity or transmission coefficients of the crystal. Careful fitting of spectra via the Kramers-Kronig analysis (as the experimental ω -range is finite) yields $\text{Im}[\varepsilon(\omega)]$ as output, whence directly the maxima for each oscillator line, assumed Lorentzian, each with its three parameters $\{\omega_j, \Gamma_j, \text{and } S_j\}$, respectively, the frequency, the line half-width, and its OS. Note that while $\{^iZ\omega_k$ and $\{^iZ\Gamma_k\}$ are prime values, $\{^iZS_k\}$ are sums over all the

specific OSs $\{iZ_{S_k}\}$ multiplied by the relative ion-pair populations and their multiplicities (Eq.4), and by *three* SOP parameters $\{W_1, W_2, W_3\}$, thermodynamic expression of the considered alloy. The introduction of SOPs links them to the OS of each ternary line. The sum

$$\text{Im}[\varepsilon(\omega, x)] = \sum_{j=1,n} \{S_j \omega_j^2 \omega \Gamma_j / [(\omega^2 - \omega_j^2)^2 + \omega^2 \Gamma_j^2]\} \quad (2)$$

describes the total activity of all the oscillators over the considered frequency range. In ZB ternary alloys, each vibrating ion dipole-pair, from each of the five elemental tetrahedron configurations $\{T_k\}_{k=0,4}$, contributes with a phonon line to the spectrum, as first suggested by Verleur and Backer [6] with their pioneer single-parameter model. We discussed the limits of the model in ref. [7]. With $P_k(x)$'s defined (Eqs.1) the $\text{Im}[\varepsilon(\omega, x)]$ of $A_{1-x}B_xZ$ spectra can be written as

$$\begin{aligned} \text{Im}[\varepsilon(\omega, x)] = & \{4 \text{}^{AZ}S_0 \text{}^{AZ}\omega_0^2 \text{}^{AZ}\Gamma_0 \omega / [(\omega^2 - \text{}^{AZ}\omega_0^2)^2 + \text{}^{AZ}\Gamma_0^2 \omega^2]\} P_0(x) && \text{binary AZ} \\ & + \sum_{k=1,3} \{k \text{}^{BZ}S_k \text{}^{BZ}\omega_k^2 \text{}^{BZ}\Gamma_k \omega / [(\omega^2 - \text{}^{BZ}\omega_k^2)^2 + \text{}^{BZ}\Gamma_k^2 \omega^2] + (4-k) \text{}^{AZ}S_k \text{}^{AZ}\omega_k^2 \text{}^{AZ}\Gamma_k \omega / [(\omega^2 - \text{}^{AZ}\omega_k^2)^2 + \text{}^{AZ}\Gamma_k^2 \omega^2]\} P_k(x) && \text{ternary ABZ} \\ & + \{4 \text{}^{BZ}S_4 \text{}^{BZ}\omega_4^2 \text{}^{BZ}\Gamma_4 \omega / [(\omega^2 - \text{}^{BZ}\omega_4^2)^2 + \text{}^{BZ}\Gamma_4^2 \omega^2]\} P_4(x) && \text{binary BZ} \end{aligned} \quad (3)$$

With the *specific* OSs $\text{}^{AZ}S_0 = \text{}^{AZ}S$ and $\text{}^{BZ}S_4 = \text{}^{BZ}S$ proper to the two binary constituents, and $\{\text{}^{AZ}S_k\}_{k=0,3}$ and $\{\text{}^{BZ}S_k\}_{k=1,4}$ of the three ternary configurations, the OS iZ_{S_k} of each mode can be expressed by

$$\text{}^{BZ}S_k(x) = \text{}^{BZ}S_k P_k(x) \text{ and } \text{}^{AZ}S_k(x) = \text{}^{AZ}S_k (4-k) P_k(x), \quad (4)$$

If all four specific OSs for a given iZ pair are equal and independent of x , i.e., $\{\text{}^{BZ}S_k\}_{k=1,4} = \text{}^{BZ}S$ and $\{\text{}^{AZ}S_k\}_{k=0,3} = \text{}^{AZ}S$, for a random distribution of A and B ions, the total OS of the respective modes AZ and BZ of $A_{1-x}B_xZ$ alloys is reduced identically to two linear functions of x (often referred to as the *OS linear dependence on x*)

$$\sum_{k=0,4} \text{}^{BZ}S_k(x) = 4x \text{}^{BZ}S \text{ and } \sum_{k=0,4} \text{}^{AZ}S_k(x) = 4(1-x) \text{}^{AZ}S, \quad (5)$$

To treat FIR spectra we make **two** additional **FIR assumptions**: **1)** Specific OSs relative to a given ion pair are the same throughout all configurations, $\{\text{}^{BZ}S_k\}_{k=1,4} = \text{}^{BZ}S$, $\{\text{}^{AZ}S_k\}_{k=0,3} = \text{}^{AZ}S$. **2)** Analogously, we assume that for each of the two constituent ion-pair populations, line-widths Γ 's of any given composition spectrum are invariant: $\{\text{}^{AZ}\Gamma_k\}_{k=0,3} = \text{}^{AZ}\Gamma$ and $\{\text{}^{BZ}\Gamma_k\}_{k=1,4} = \text{}^{BZ}\Gamma$.

Thus, to unfold a ternary spectrum with its 8 lines per spectrum, we have 3 SOP and 2 OS coefficients.

As demonstrated above, *true tetrahedron populations* in crystal lattices are determined by the alloy composition “ x ” (or “ y ” for AY_yZ_{1-y}) and by the three SOP coefficients $\{W_1, W_2, \text{ and } W_3\}$. To assess the validity of the two FIR assumptions and with knowledge of GaAsP SOP values [1] from the EXAFS documentation [4], a best-fit test was carried out on GaAsP spectra [8]. The two binary OS values $\{\text{}^{AZ}S, \text{}^{BZ}S\}$ “derived” as per the model overlap with the corresponding $\text{}^{AZ}S, \text{}^{BZ}S$ values available in the literature.

3. SUMMARY and CONCLUSIONS

The spectrum of any pure canonical ZB ternary ABZ (or AYZ) material with its five tetrahedron configurations $\{T_k\}$ exhibits **eight phonon lines** (4 AZ + 4 BZ) and less than 8 when extreme preferences prevent the formation of some configuration, as is observed with a transient element in $B=\{\text{Mn, Fe, ...}\}$: ZnMnSe lacks one, ZnMnS lacks two, whence only six and four phonon lines, respectively. More than eight lines are vibration frequencies due to the presence of point defects, as in HgCdTe [9] or impurities. The *statistical model of the dielectric function* is applied to five GaAs_yP_{1-y} FIR spectra [8]. In spite of the restricted number of parameters, the fit of the spectra with $y_{As}=\{0.01, 0.15, 0.44, 0.72, 0.94\}$, and with all five taken together yields the following values for $\epsilon_{As}^{\text{GaAs}}=\{*, 2.18, 1.68, 1.58, 2.00\}$, and $\epsilon_{S}^{\text{GaP}}=\{1.97, 1.98, 2.49, 2.77, *, 1.98\}$ i.e., respective experimental averages 1.84 ± 0.11 and 2.24 ± 0.17 , while the literature reports 1.815 ± 0.21 , 2.06 ± 0.16 . Thus, the values obtained overlap the literature values within reference-uncertainty bars. The satisfactory reproduction makes the model assumptions credible and supports our belief that the model will be useful for a better understanding of FIR lattice dynamic analysis.

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REFERENCES

- (1) B.V.Robouch, A.Kisiel, J.Konior, *J. Alloys Compounds* **339**, 1 (2002); idem: **340**, 13 (2002)
- (2) A.Balzarotti, M.T.Czyżyk, A.Kisiel, N.Motta, M.Podgórný, M.Zimnal-Starnawska, *Phys.Rev.B* **30**, 2295 (1985)
- (3) M.R. Wiedmann, J.R. Gregg, K.A. Newman, *J. Phys. Condensed Matter*, **4**, 1895 (1985)
- (4) B.V.Robouch, E.Burattini, A.Kisiel, A.L.Suvorov, A.G.Zaluzhnyi, *J. Alloys Compounds* **359**, 73-78 (2003)
- (5) Z. Wu, K. Lu, Y. Wang, J. Dong, H. Li, Ch. Li, Zh. Fang, *Phys. Rev. B* **48**, 8694 (1993)
- (6) H.W.Verleur and A.S.Barker, *Phys.Rev.* **149**,715 (1966)
- (7) B.V.Robouch, A.Kisiel, E.M.Sheregii, *Phys. Rev.B* **64**, 73204 (2001)
- (8) B.V.Robouch, E.M.Sheregii, J.Polit, J.Cebulski, E.Burattini, *Fiz.Nizkikh Temp: Low Temp. Phys.* **30**, 1225 (2004)
- (9) S.P.Kosyrev, L.K.Vodopyanov, R.Triboulet, *Phys. Rev. B* **58**, 1374 (1998)