STATISTICAL STRAINED-TETRAHEDRON MODEL OF LOCAL TERNARY ZINCBLENDE CRYSTAL STRUCTURES

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Abstract

A statistical strained-tetrahedron model developed to better describe and understand the local structure of ternary zincblende crystals, interprets experimental EXAFS and far-infrared spectra. It considers five tetrahedron configurations distorted in shape and size, characteristic of ternary zincblende alloys, allows non random distributions, hence site occupation preferences, conserves coordination numbers, respects stoichiometry, and assumes next neighbor values determine preferences beyond next neighbor. Configuration probabilities have three degrees of freedom.

The nineteen inter-ion crystal distances are constrained by tetrahedron structures; to avoid destructive stresses, we assume average tetrahedron volumes of both sublattices to relax to equal values. The number of distance free-parameters ≤ 7. Model estimates, compared to published EXAFS results, validate the model.

Knowing configuration probabilities, one writes the dielectric function for the phonon spectral region. Constraining assumptions restrict the number of degrees of freedom. Unfolding experimental spectra yields SOP coefficient values and\or specific oscillator strengths. Validation again confirms the model.

PACS : 61.43.Dq

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1   INTRODUCTION

To quantitatively interpret phenomena one often resorts to modeling. An ideal model should perfectly describe the phenomenon predicting through the use of the related parameters all the behavior of the phenomenon. In practice the model assumes simplifying approximations to render the description and\or the calculation easier to handle. This inevitably restricts the range of applicability of the model, defining range-limits beyond which model-predictions become unreliable. This is a general statement, and we shall soon apply this notion to the problem of our concern.

The interest to sphalerite (zincblende) ternary semiconductors stems from their predominant importance as semiconductor devices, as amply evidenced by the abundance of articles in literature devoted to them. Paramount is the interpretation of extended x-ray absorption fine structure (EXAFS) (see theoretical considerations [1,2] since 1981) and vibrational spectra observed in far infrared region (FIR spectra). EXAFS were applied soon after [3,4] with alas no review paper covering the abundant literature hereto devoted. For FIR spectra literature, one can refer to for instance review articles [5-7] and book [8]).

Eager to understand the local structure of ternary zincblende semiconductors $A_{1-x}B_xZ$ (or $AY_yZ_{1y,}$ we use A, B, for cations, and Z, Y, for anions), several models have been considered. Though each has its distinct particularity, all have in common TWO simplifying assumptions: 1)- the competing ions (cations or anions) occupying the four vertices of the tetrahedron around the ion (of opposite polarity, i.e. anion or cation respectively) inside of it, form a RIGID tetrahedron that does not deform as competing ions replace each other going from one configuration to the other. 2)- Competing ions occupy available sites in a RANDOM way, with ion distribution filling (k B-ions into a shell with N sites, from relative contents x and $1-x$) assumed stochastic and probabilities perfectly defined by the random Bernoulli binomial polynomials

$$p_k^{[N]}(x) = N!/[k!(N-k)!]x^k(1-x)^{N-k} \quad \text{with } k=0,\dots,N .$$

The consequence of such assumptions, is the reduction of the range of applicability of these models to the following subset of materials:

- The invariance of the tetrahedron for the various configurations, implies the lattice constants of both binary constituents AZ and BZ should be equal (or quasi equal), thus restricting correspondingly the range of applicability of the model.
- RANDOM distribution statistically implies assuming a stochastic filling around Z with ions A and B, i.e. that the Z-ion preference for either is the same. Thermodynamically this implies that the potential well for A around Z is identical to that of B around Z. But we are aware that in nature equality is the exception that confirms the rule of inequality. Indeed, standard molar enthalpies of formation, $\Delta_f H_0$ [kJ/mol] of binaries are generally different. That is why the stochastic approach is unable to describe and interpret materials presenting site occupation preferences (SOPs) as reported experimentally!

To be free of these limitations, we developed the statistical *strained-tetrahedron* model with tetrahedra freely distorting from configuration to the other, and free to account for SOPs. The model was validated on published EXAFS zincblende data [9,10], and, after an adaptation, on even intermetallide materials [11]. The model was then extended to describe and interpret FIR spectra.

We propose to briefly recall here the developed model, its validation, and dwell on FIR-spectrum interpretation, applicability and limits.

2   THE STATISTICAL *STRAINED-TETRAHEDRON* MODEL

To create any model, one has to 1) describe as closely as possible the *object* under study using for that proper parameters; 2) reduce the set of these parameters through motivated constrains to determine the minimum number of degrees of freedom parameters; 3) check model-predicted values against experimental ones; 4) consequently, trash or retain valid the model depending on the reproducibility thus obtained. With this in mind we recall our modeling.

2.1   The object under study

Zincblende fcc structures are tetrahedron coordinated, characterized by a *central* ion surrounded by four *nearest-neighbor* (NN) ions (first shell) defining the four vertices of a tetrahedron, and 12 *next nearest-neighbor* (NNN) ions (second shell). Binary compounds AZ have their successive shells alternately fully filled by A then Z ions. All tetrahedra are symmetric, regular, and identical; thus, by simple trigonometry, equal inter-bond angles $\alpha(A:Z:A) = \alpha(B:Z:A) = 109.47°$, and the inter-ion distances (^{ij}d) are defined in terms of the lattice constant a (known from interferometry literature): $^{AZ}d = 3^{1/2}\,a/4$, $^{AA}d = {}^{ZZ}d = a/2^{1/2}$.

For ternary $A_{1-x}B_x Z$ (or $AY_y Z_{1-y}$), in the binary compound AZ, cations A are partially substituted by B ions. This, leads to 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 [$T_0(Z:^4A)$, $T_1(Z:^3A+^1B)$, $T_2(Z:^2A+^2B)$, $T_3(Z:^1A+^3B)$, $T_4(Z:^4B)$]. Prior to us, simulations considered the five $\{T_k\}_{k=0,4}$ tetrahedra as externally rigid with the central ion free to be displaced, and around a central Z-ion the 1st shell four A\B ions are described by $p_k^{[4]}(x)$, while the 2nd shell contains twelve Z-ions! On the other hand, around an A or B ions, the 1st shell contains four Z-ions, while the 2nd shell distribution of the twelve ions A\B is described by $p_k^{[12]}(x)$. This allows approximate evaluations, avoiding analytical difficulties, provided NO SOPs are observed for the material.

2.2   Statistical strained-tetrahedron model assumptions

We build our model discarding both restrictions: 1)- deviating from stochastic filling of ions, and 2)- freeing the tetrahedra of the unnatural constraint of rigidity.

The price for such a more general model is the number of parameters needed to describe the crystal structure. But as we shall demonstrate, adequate assumptions (checked correct at the end) reduce the degrees of freedom, to an acceptable value.

To quantify results departing from stochastic distribution, we attribute to each Bernoulli binomial a SOP weight-coefficient. This leads to five NN terms $W_k\, p_k^{[4]}(x)$, thirteen NNN $^A w_k\, p_k^{[12]}(x)$ (for central A-ions), and thirteen $^B w_k\, p_k^{[12]}(x)$ (for central B-ions), a total of 31 w-parameters! Fortunately it is the Z-ion that determines the choices (while ions A and B deterministically are surrounded by Z ions); thus we **claim** that ALL higher shell fillings are determined by linear expressions of the NN five SOP-coefficients $\{W_k\}_{k=0,4}$. But binary tetrahedron configurations T_0, T_4 have NO preferences. Thus $W_0 = W_4 \equiv 1$! and we are left with only $\{W_1, W_2, W_3\}$.

The probabilities to find B and A ions in a T_k-configuration are proportional respectively to $\{kW_k\}_{k=0,4}$ and to $\{4-kW_k\}_{k=0,4}$ (conservation of coordination numbers). As probabilities **cannot** be negative, we have $0 \leq W_k \leq 4/k$. *There are thus only **three** bounded free parameters* $0 \leq W_1 \leq 4$, $0 \leq W_2 \leq 2$, $0 \leq W_3 \leq 4/3$.

Expressions $\{^A w_k\}_{k=0,12}$, $\{^B w_k\}_{k=0,12}$ for the NNN shell, are determined by combinatorial probabilities in terms of those around the Z-ions of the NN shell. This hypothesis leads for the **zincblende** structure, to the linear expressions of NNN SOP-coefficients $^A w_k$ and $^B w_k$ as functions of the three W_k's given in Tab.1a [9]. To illustrate that the assumption is general and applies even to other crystal structures, the expressions for intermetallic alloys of type $M_3(X_{1-x}X'_x)_1$ are given in Tab.1b [11].

TAB. 1a: NNN SOP-coefficients in terms of NN SOPs**:** All possible NNN distributions and resulting SOP-coefficients for ternary. $0 \leq \{W_k\}_{k=1,3} \leq 4/k$, while $W_0 = W_4 = 1$. Zincblende $A_{1-x}B_xZ$ with a B or A as *central* ion [9].

a) k	All 12 possible NNN B-ion fills of the 4 tetrahedra	Resulting B-weights $^B w^{[12]}_k = \Sigma_{j=0,4}\{^B M_{j,k} W^{[4]}_j\}$	Resulting A-weights $^A w^{[12]}_k = \Sigma_{j=0,4}\{^A M_{j,k} W^{[4]}_j\}$
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

TAB. 1b: NNN SOP-coefficients in terms of NN SOPs**:** All possible NNN distributions and resulting SOP-coefficients for ternary. $0 \leq \{W_k\}_{k=1,3} \leq 4/k$, while $W_0 = W_4 = 1$. Intermetallide $M_3(XX')_1$ around X or X' [11]

b) $\{^X w_k = \Sigma_{j=0,4} {}^X M_{kj} W_j\}_{k=0,6}$	$\{^{X'} w_k = \Sigma_{j=0,4} {}^{X'} M_{kj} W_j\}_{k=0,6}$
$^X w_0 = \frac{1}{3}W_1 + \frac{2}{3}W_2$	$^{X'} w_0 = \frac{1}{3}W_0 + \frac{2}{3}W_1$
$^X w_1 = \frac{10}{36}W_1 + \frac{23}{36}W_2 + \frac{3}{36}W_3$	$^{X'} w_1 = \frac{10}{36}W_0 + \frac{23}{36}W_1 + \frac{3}{36}W_2$
$^X w_2 = \frac{16}{72}W_1 + \frac{41}{72}W_2 + \frac{13}{72}W_3 + \frac{2}{72}W_4$	$^{X'} w_2 = \frac{16}{72}W_0 + \frac{41}{72}W_1 + \frac{13}{72}W_2 + \frac{2}{72}W_3$
$^X w_3 = \frac{6}{36}W_1 + \frac{15}{36}W_2 + \frac{11}{36}W_3 + \frac{4}{36}W_4$	$^{X'} w_3 = \frac{6}{36}W_0 + \frac{15}{36}W_1 + \frac{11}{36}W_2 + \frac{4}{36}W_3$
$^X w_4 = \frac{2}{72}W_1 + \frac{13}{72}W_2 + \frac{41}{72}W_3 + \frac{16}{72}W_4$	$^{X'} w_4 = \frac{2}{72}W_0 + \frac{13}{72}W_1 + \frac{41}{72}W_2 + \frac{16}{72}W_3$
$^X w_5 = \frac{3}{36}W_2 + \frac{23}{36}W_3 + \frac{10}{36}W_4$	$^{X'} w_5 = \frac{3}{36}W_1 + \frac{23}{36}W_2 + \frac{10}{36}W_3$
$^X w_6 = +\frac{2}{3}W_3 + \frac{1}{3}W_4$	$^{X'} w_6 = +\frac{2}{3}W_2 + \frac{1}{3}W_3$

A random integer ion distribution (k and 4-k) fully respects stoichiometry. With SOP coefficients $W_k \neq 1$ the situation departs from the stochastic equilibrium, with a consequent

attenuation of the three "ternary" configuration populations caused by the observed scarcity of one of the two ion populations

$$\{P_k^{[4]}(x) = C_k \, p_k^{[4]}(x) \}_{k=1,3} \qquad \textit{for ternary } T_k$$

with $\{C_k(W_k)\}_{k=1,3}$, corrective weight factors imposed by stoichiometry

$$0 \leq \{C_k = \min[W_k, 1, (4-kW_k)/(4-k)] \}_{k=1,3} \leq 1$$

$W_k < 1$ enhances binary AZ populations while $W_k > 1$ that of binary BZ, i.e.

$$P_0^{[4]}(x) = p_0^{[4]}(x) + \Sigma_{k=1,3} \{\max(0, 1-W_k) \, p_k^{[4]}(x)\} \quad \textit{for binary AZ configuration } T_0$$

$$P_4^{[4]}(x) = p_4^{[4]}(x) + \Sigma_{k=1,3} \{\max(0, k(W_k-1)/(4-k)) \, p_k(x)\} \quad \textit{for binary BZ configuration } T_4 \quad (1)$$

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

Note however, that even if SOPs enhance the two binary populations with respect to corresponding populations of the random case, it by no means leads to clustering since the spatial distribution remains perfectly stochastic.

<u>Both ion-pair</u> and <u>configuration</u> populations are NOW determined with due account of SOPs. This allows us to interpret local crystal structures.

We have five tetrahedra freed from any constraint with, content-wise, two (T_0 and T_4) binary, regular, different sized, and well defined (as remarked above), and three (T_1, T_2, and T_3) ternary, distorted (*strained tetrahedra*) with unequal inter-ionic *nineteen* ^{ij}d distance-parameters, and consequently altered inter-bond angles (see FIG.1 [9]). Geometrical symmetry of each T_k-configuration yields three constraints each, which reduces the number of independent distance-parameters from nineteen to *ten*.
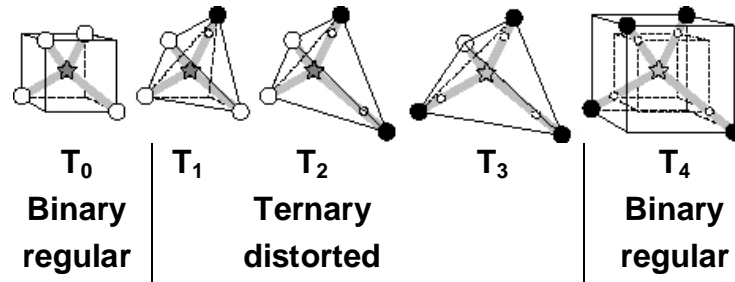

T_0	T_1	T_2	T_3	T_4
Binary		Ternary		Binary
regular		distorted		regular

FIG.1: Aspect of the five elemental tetrahedron configurations $\{T_k\}_{k=0,4}$ of $A_{1-x}B_xZ$ (or AY_yZ_{1-y}) ternary alloys [9]]; "star" for central ion; circles white: ion being displaced, black: replacing ion . Small open circles indicate the would-be ion-positions as per *rigid tetrahedron* hypothesis.

Strength of material considerations lead us, *to avoid destructive inter crystal stresses*, to impose that the average tetrahedron volume of the four vertex tetrahedra be equal to the central one! (One constraint per configuration!), leaving us with only $(10-3) \leq 7$ distance parameters!

Indeed, ≤ whenever for SOP extreme values, some configuration(s) are forbidden, and their distances become virtual!

On the basis of the above probabilities, expressions for average pair coordination $<^{i:j}CN(x)>$ and distances $<^{i:j}d(x)>$, as a function of x, for any two-ion pair i:j={AZ, BZ, BB, BA, AA, ZAZ, ZBZ} of zincblende $A_{1-x}B_xZ$ ternary can be written and are given in Tab.2 [9].

TAB.2: expressions of average pair coordinations $<^{i:j}CN(x)>$ and distances $<^{i:j}d(x)>$, as a function of x, for any two-ion pair i:j={AZ, BZ, BB, BA, AA, ZAZ, ZBZ} of zincblende $A_{1-x}B_xZ$ ternary [9].

AVERAGE	**COORDINATION NUMBERS**
	For NN ion pairs AZ, BZ
$<^{BZ}CN(x)> =$	$\Sigma_{k=0,4}\{ kW_k\ p^{[4]}_k(x)\}$
$<^{AZ}CN(x)> =$	$\Sigma_{k=0,4}\{(4-kW_k)p^{[4]}_k(x)\}$
	For NNN ion pairs BB, BA, AA
$<^{BB}CN(x)>=$	$\Sigma_{k=0,12}\{k\ ^Bw_k\ p^{[12]}_k(x)\}$
$<^{AB}CN(x)>=$	$\Sigma_{k=0,12}\{k\ ^Aw_k\ p^{[12]}_k(x)\}$
$<^{AA}CN(x)>=$	$12-<^{AB}CN(x)> =\Sigma_{k=0,12}\{(12-k\ ^Aw_k)\ p^{[12]}_k(x)\}$
$<^{BA}CN(x)>=$	$12-<^{BB}CN(x)> = \Sigma_{k=0,12}\{(12-k\ ^Bw_k)\ p^{[12]}_k(x)\}$
$<^{ZBZ}CN(x)>=$	$\Sigma_{k=0,4}\{3\ k\ W_k\ p^{[4]}_k(x)\}\quad = 3\ <^{BZ}CN(x)>$
$<^{ZAZ}CN(x)>=$	$\Sigma_{k=0,4}\{3\ (4-kW_k)\ p^{[4]}_k(x)\} = 3\ <^{AZ}CN(x)>$

AVERAGE	**DISTANCES**
	For NN ion pairs AZ, BZ
$<^{BZ}d(x)> =$	$\{ \Sigma_{k=1,4}[(k\ C_k)\ ^{BZ}d_k\ +4\ Max(0, k(W_k-1)/(4-k))\ ^{BZ}d_4]\ p^{[4]}_k(x)\ \}$
	$/\{ \Sigma_{k=1,4}[(k\ C_k)\quad +4\ Max(0, k(W_k-1)/(4-k))\quad]\ p^{[4]}_k(x)\ \}$
$<^{AZ}d(x)> =$	$\{ \Sigma_{k=0,3}[(4-k\ C_k)\ ^{AZ}d_k +4\ Max(0,1-W_k)\ ^{AZ}d_0]\ p^{[4]}_k(x)\ \}$
	$/\{ \Sigma_{k=0,3}[(4-k\ C_k)\quad +4\ Max(0,1-W_k)\quad]\ p^{[4]}_k(x)\ \}$
	For NNN ion pairs BB, BA, AA
$<^{BB}d(x)>=$	$\Sigma_{j=1,12}\ j\quad p^{[12]}_j(x)\ \Sigma_{k=2,4}\ [\ ^BM_{jk}\ C_k\ (k-1)\ ^{BB}d_k\ +4\ ^BM_{jk}\ Max(0, k(W_k-1)/(4-k))\ ^{BB}d_4]$
	$/ \Sigma_{j=1,12}\ j\quad p^{[12]}_j(x)\ \Sigma_{k=2,4}\ [\ ^BM_{jk}\ C_k\ (k-1)\quad +4\ ^BM_{jk}\ Max(0, k(W_k-1)/(4-k))\quad]$
$<^{BA}d(x)>=$	$\Sigma_{j=0,11}\ (12-j)\ p^{[12]}_j(x)\ \Sigma_{k=1,3}\ \{\ ^BM_{jk}\ (4-\ k\ C_k)\ [1+Mod(\ k+1\ ,\ 2)\ ]\ ^{BA}d_k\}$
	$/ \Sigma_{j=0,11}\ (12-j)\ p^{[12]}_j(x)\ \Sigma_{k=1,3}\ \{\ ^BM_{jk}\ (4-\ k\ C_k)\ [1+Mod(\ k+1\ ,\ 2)\ ]\quad \}$
$<^{AA}d(x)>=$	$\Sigma_{j=0,11}\ (12-j)\ p^{[12]}_j(x)\ \Sigma_{k=0,2}\ [\ ^AM_{jk}\ C_k\ (3-k)\ ^{AA}d_k\quad +4\ ^AM_{jk}\ Max(0,1-W_k)\ ^{AA}d_0]$
	$/ \Sigma_{j=0,11}\ (12-j)\ p^{[12]}_j(x)\ \Sigma_{k=0,2}\ [\ ^AM_{jk}\ C_k\ (3-k)\quad +4\ ^AM_{jk}\ Max(0,1-W_k)]$
	For NNN ion pairs Z:A:Z or Z:B:Z
$<^{ZBZ}d(x)>=$	$\{ \Sigma_{k=1,4}[(k\ C_k)\ ^{ZBZ}d_k\ +4\ Max(0, k(W_k-1)/(4-k))\ ^{ZBZ}d_4]\ p^{[4]}_k(x)]\}$
	$/\{ \Sigma_{k=1,4}[(k\ C_k)\quad +4\ Max(0, k(W_k-1)/(4-k))\quad]\ p^{[4]}_k(x)]\}$
$<^{ZAZ}d(x)>=$	$\{ \Sigma_{k=0,3}[(4-k\ C_k)\ ^{ZAZ}d_k +4\ Max(0,1-W_k)\ ^{ZAZ}d_0]\ p^{[4]}_k(x)\ \}$
	$/\{ \Sigma_{k=0,3}[(4-k\ C_k)\quad +4\ Max(0,1-W_k)\quad]\ p^{[4]}_k(x)\ \}$

On the basis of these, unfolding a given set of EXAFS data such as $GaAs_yP_{1-y}$ [12], one obtains the dimensions of all elemental involved tetrahedra: inter-ion distances, angles (see Tab.3).

TAB. 3: **GaAs$_x$P$_{1-x}$** complete set: determined SOP coefficients, distances, angles and volumes for all five elemental configuration tetrahedra. Eleven fit parameters (bold) (3 SOP + 8-distance (PGaP NNN data not reported) to check VRC. 37 available experimental points from a set of 16 measurements [9].

GaAs$_x$P$_{1-x}$					
Configurations	T_0	T_1	T_2	T_3	T_4
k	0	1	2	3	4
W_k	1	**0.93**	**1.15**	**1.07**	1
^{BZ}d [Å]	-	**2.42**	**2.43**	**2.44**	2.450
^{AZ}d	2.359	**2.37**	**2.37**	**2.38**	-
^{BZB}d	-	-	**3.90**	**3.90**	4.001
^{AZA}d	3.852	*3.88*	*3.98*	-	-
^{BZA}d	-	3.91	3.90	3.99	-
^{ZBZ}d	-	3.95	3.97	3.98	4.001
^{ZAZ}d	3.852	3.87	3.87	3.89	-
$\alpha(B:Z:B)$ [°]	-	-	106.7	106.9	109.47
$\alpha(A:Z:A)$	109.47	109.7	114.3	-	-
$\alpha(B:Z:A)$	-	109.3	107.36	112.0	-
$<Vol_{B.centred}>$ [Å^3]	-	7.28	7.37	7.41	7.55
$<Vol_{A.centred}>$	6.74	6.84	6.86	6.91	-
$<Vol_{Z.sublattice}>$	6.74	6.95	7.12	7.29	7.55
$<Vol_{Z.centred}>$	6.74	6.95	7.07	7.28	7.55
|Difference | [%]	0.0	0.1	0.1	0.2	0.0

Having defined the 31+19 parameter model, and identified the relative constrain relations reduces to 3+7 independent parameters. The model is ripe to confront its estimations with experimental data!

2.3 MODEL VERIFICATION

For the validity of the model and its assumptions, we checked the quality of the model with its restricted free parameters,

1. Comparing reported in literature experimental distance-EXAFS points and error bars with model fit curves (see FIG.2 (36 points with 10 free parameters), and curves reported in [9-11]).
2. "Coordination number" curve predictions on the basis of SOP values obtained from distance-EXAFS measurement analysis, against independently measured coordination number values (see FIG.3, also [9-11]).
3. Correlation between thermodynamic standard molar enthalpies of formation, $\Delta_f H^0$ [kJ/mol] of materials (Tab.4 [10]) and corresponding obtained SOP-coefficient values.

The validity of the model with its restrictive assumptions is thus confirmed.

TAB. 4: Standard molar enthalpies of formation, $\Delta_f H^0$ [kJ/mol], of materials and corresponding SOP coefficients. Column (§) gives origin and comments for reported

SOP coefficient values derived from: c - coordination number data, d - distance data,
0^{*} -assumed $W_3=0$ value. [10]

Material ABZ/ AYZ	components AZ+BZ/ AZ+AY	$\Delta_f H^0$[kJ/mol] AZ		BZ/ AY	SOP W_0	W_1	W_2	W_3	W_4	(§)
ZnMnSe	ZnSe +MnSe	-163.0 [a]	<	-106.7 [b]	1	**0.67**	1.67	0.04	1	c
					1	**0.62**	1.70	0	1	d
GaInAs	GaAs +InAs	-71.0 [a]	<	-58.6 [a,c]	1	**0.58**	0.25	**1.05**	1	d
GaAsP	GaP +GaAs	-88 [a]	<	-71.0 [a,c]	1	**0.93**	1.15	**1.07**	1	d
ZnMnS	ZnS +MnS	-206.0 [a], -205.98 [c]	>	-214.2 [a,c], -207.0 [b]	1	**1.78**	0	0.01	1	d
ZnMnTe	ZnTe +MnTe	-92.7 [a,c], -120.5 [b]	<	-94.7 [b]	1	**0.25**	2.	0.01	1	d
CdMnTe	CdTe +MnTe	-102.5 [b]	<	-94.7 [b]	1	**0.68**	1.33	0^{*}	1	d+0^{*}

[a] CRC Handbook of Chemistry and Physics, Ed.D.L.Lide, 76th Edition, CRC Press, Boca Raton, 1996-97
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3   DIELECTRIC FUNCTION ε(ω,x) FOR TERNARY ZINCBLENDE ALLOYS

The dielectric function $\varepsilon(\omega)= \varepsilon_\infty+\Sigma_{j=1,n}\{S_j\,\omega^2_j\,/[(\omega^2-\omega^2_j)\,+i\,\omega\Gamma_j]$ of phonon spectra of solids can be extracted from experimental reflectivity or transmission coefficients of a crystal, fitting the measured spectra via the Kramers-Kronig (KK) analysis. The KK output $\mathrm{Im}[\varepsilon(\omega)]$ directly yields the maxima for each oscillator line, assumed Lorentzian, with its three parameters $\{\omega_j,\ \Gamma_j,\ \text{and } S_j\}$, respectively, the frequency, the line half-width, and the oscillator strength (OS). Note that while $\{^{iZ}\omega_k$ and $^{iZ}\Gamma_k\}$ are prime values, $\{^{iZ}S_k\}$ are sums over all the specific OSs $\{^{iZ}S_k\}$ multiplied by the relative ion-pair populations, taking into account ion-pair multiplicities (Eq.4), and by *three* SOP parameters $\{W_1,\ W_2\ ,W_3\}$, which express the thermodynamics of the considered alloy. The introduction of SOPs links them to the OS of each ternary line. The sum

$$\mathrm{Im}[\varepsilon(\omega,x)] = \Sigma_{j=1,n}\{S_j\,\omega^2_j\,\omega\,\Gamma_j/[(\omega^2-\omega^2_j)^2+\omega^2\Gamma_j^2]\} \tag{2}$$

describes the total activity of all the oscillators over the considered frequency range. In zincblende ternary $A_{1-x}B_xZ$ (or AY_yZ_{1-y}) compounds, each vibrating ion dipole-pair AZ and BZ from each of the five elemental tetrahedron configurations $\{T_k\}_{k=0,4}$ contributes with a phonon line to the spectrum (this idea was first presented by Verleur and Backer [13] who proposed a pioneer single parameter model; the limits of the model where later discussed by us [14]). Thus $\mathrm{Im}[\varepsilon(\omega,x)]$ of $A_{1-x}B_xZ$ spectra can be written as

$$\mathrm{Im}[\varepsilon(\omega,x)] =\{\{4\,^{AZ}s_0\,^{AZ}\omega_0^2\,^{AZ}\Gamma_0\,\omega\,/\,[(\omega^2-^{AZ}\omega_0{}^2)^2+^{AZ}\Gamma_0{}^2\,\omega^2]\}\,P_0(x) \qquad \textit{binary AZ}$$

$$+\,\Sigma_{k=1,3}\,\{k\,^{BZ}s_k\,^{BZ}\omega_k^2\,^{BZ}\Gamma_k\,\omega\,/\,[(\omega^2-^{BZ}\omega_k{}^2)^2+^{BZ}\Gamma_k{}^2\,\omega^2]\,+(4\text{-}k)\,^{AZ}s_k\,^{AZ}\omega_k^2\,^{AZ}\Gamma_k\,\omega$$

$$/[(\omega^2-^{AZ}\omega_k{}^2)^2+^{AZ}\Gamma_k{}^2\,\omega^2]\}P_k(x) \qquad \textit{ternary ABZ}$$

$$+\{4\,^{BZ}s_4\,^{BZ}\omega_4^2\,^{BZ}\Gamma_4\,\omega\,/\,[(\omega^2-^{BZ}\omega_4{}^2)^2+^{BZ}\Gamma_4{}^2\,\omega^2]\}\,P_4(x)\,\} \qquad \textit{binary BZ}$$

$$(3)$$

with $P_k(x)$'s defined (Eqns.1).

Thus, the OS $^{iZ}S_k$ of each mode can be expressed by

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

with the *specific* OS $^{AZ}s_0 = {^{AZ}s}$ and $^{BZ}s_4 = {^{BZ}s}$ proper to the two binary constituents, and to $\{^{AZ}s_k\}_{k=0,3}$ $\{^{BZ}s_k\}_{k=1,4}$ of the three ternary configurations.

If all four specific OSs for a given iZ-pair are equal and independent of x, i.e.,

$$\{^{BZ}s_k\}_{k=1,4} = {^{BZ}s} \qquad \text{and} \qquad \{^{AZ}s_k\}_{k=0,3} = {^{AZ}s}$$

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

$$\Sigma_{k=0,4}\, {^{BZ}S_k}(x) = 4x\, {^{BZ}s} \qquad \text{and}$$

$$\Sigma_{k=0,4}\, {^{AZ}S_k}(x) = 4(1\text{-}x)\, {^{AZ}s}, \qquad (5)$$

often referred to as the *linear dependence on* x.

To treat FIR spectra we make **two *FIR-assumptions***

1. *Specific OSs relative to a given ion-pair is the same for all configurations*,

$$\{^{BZ}s_k\}_{k=1,4} = {^{BZ}s}, \ \{^{AZ}s_k\}_{k=0,3} = {^{AZ}s} \qquad (6)$$

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:

$$\{^{AZ}\Gamma_k\}_{k=0,3} = {^{AZ}\Gamma} \quad \text{and} \quad \{^{BZ}\Gamma_k\}_{k=1,4} = {^{BZ}\Gamma}. \qquad (7)$$

Thus to unfold a ternary spectrum with its 8 lines/spectrum, we have THREE SOP coefficients and TWO-OS coefficients!

As was shown, *true tetrahedron populations* in crystal lattices are determined by the alloy composition "x" (or "y" for AY_yZ_{1-y} compounds) and the three SOP coefficients $\{W_1, W_2, W_3\}$.

To assess the credibility of the model FIR-assumptions, a best-fit test is carried out to "derive" the two binary OSs $\{^{AZ}s, {^{BZ}s}\}$ values from $GaAs_yP_{1-y}$ spectra (Fig.4) [13] that have a rich documentation in EXAFS [12] yielding SOP values.

4   Summary and Conclusions

The spectrum of any pure canonical, zincblende ternary ABZ (or AYZ) material with its 5 tetrahedron configurations $\{T_k\}$ exhibits **8 phonon lines** (4 AZ + 4 BZ). The number of lines can be less than **8** when in pure defect-free materials extreme preferences prevent the formation of some configuration; this is observed with a transient element in B={Mn, Fe,...}: ZnMnSe lacks one, ZnMnS lacks two; however, GaAlN also lacks one; whence only 6, 4, 6 phonon lines respectively. More than **8** lines are observed when point defects occur (antisites, vacancies …), responsible for the extra lines (as reported in HgCdTe [15]). Indeed, FIR consents the detection of defects: vacancies, intersites, antisites, H-loading deformations, quantifying amount of impurity ions [16].

The ***Statistical model*** *of the dielectric function* is applied to five $GaAs_yP_{1-y}$ (of type AY_xZ_{1-x}) FIR spectra [13] (see Fig.4). In spite of the restricted number of parameters, results show a good fit of the spectra (Fig.5, Tab.5); but most important, the best fit yields for ^{GaAs}s and ^{GaP}s values that overlap with literature values within reference-uncertainty bars (Tab.6). Such a satisfactory reproduction validates the model assumptions, and gives confidence the model is useful in giving deeper understanding of FIR results.

Equations, tables and figures are taken from our previous publications (as referenced) documented in greater detail.

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TAB.5: Individual unfolding of $GaAs_yP_{1-y}$ spectra for each spectrum parameters $\{^{iGa}W_k, {}^{iGa}\Gamma_k\}_{i=As,P,k=0,4}$ and $\{^{GaAs}s, {}^{GaP}s\}$ taken free. $\{W_1=0.975, W_2=1.0715, W_3=1.034,$ as per Wu & al data}: table of best fit parameter values for dipoles GaAs k= 1,4 and for GaP k=0,3. Amplitudes are given to two decimals.

phonon dipole configuration =		GaAs				GaP			
		$^4As^0P$	$^3As^1P$	$^2As^2P$	$^1As^3P$	$^0As^4P$	$^1As^3P$	$^2As^2P$	$^3As^1P$
		k= 4	3	2	1	0	1	2	3
	y_{As}								
ω [cm^{-1}]	1%	257.8	261.9	264.3	268.4	363.5	365.5	377.0	379.0
	15%	259.6	261.6	263.6	271.2	362.9	364.9	366.9	381.0
	44%	265.1	269.2	271.2	273.2	350.7	352.7	363.6	373.9
	72%	269.7	271.7	273.7	279.6	342.8	344.8	350.9	360.6
	94%	269.5	271.5	278.5	280.5	345.8	347.8	349.8	351.8
Γ [cm^{-1}]	1%	8.64				4.06			
	15%	10.04				6.58			
	44%	10.74				11.52			
	72%	6.00				9.24			
	94%	3.99				11.50			
A	1%	0.00	0.00	0.00	0.04	1.84	0.05	0.00	0.00
(given	15%	0.02	0.01	0.08	0.17	1.05	0.55	0.09	0.01
to two	44%	0.13	0.21	0.28	0.12	0.26	0.57	0.42	0.11
decimals)	72%	0.52	0.46	0.18	0.02	0.02	0.13	0.31	0.26
	94%	1.63	0.28	0.02	0.00	0.00	0.00	0.03	0.17

TAB. 6: Individual unfolding of $GaAs_yP_{1-y}$ spectra, $\{W_1=0.975, W_2=1.0715, W_3=1.034\}$: table of best fit values $\{^{GaAs}s_y, {}^{GaP}s_y\}$, their average values, and comparison to values in literature.* indicates low signal unreliable values

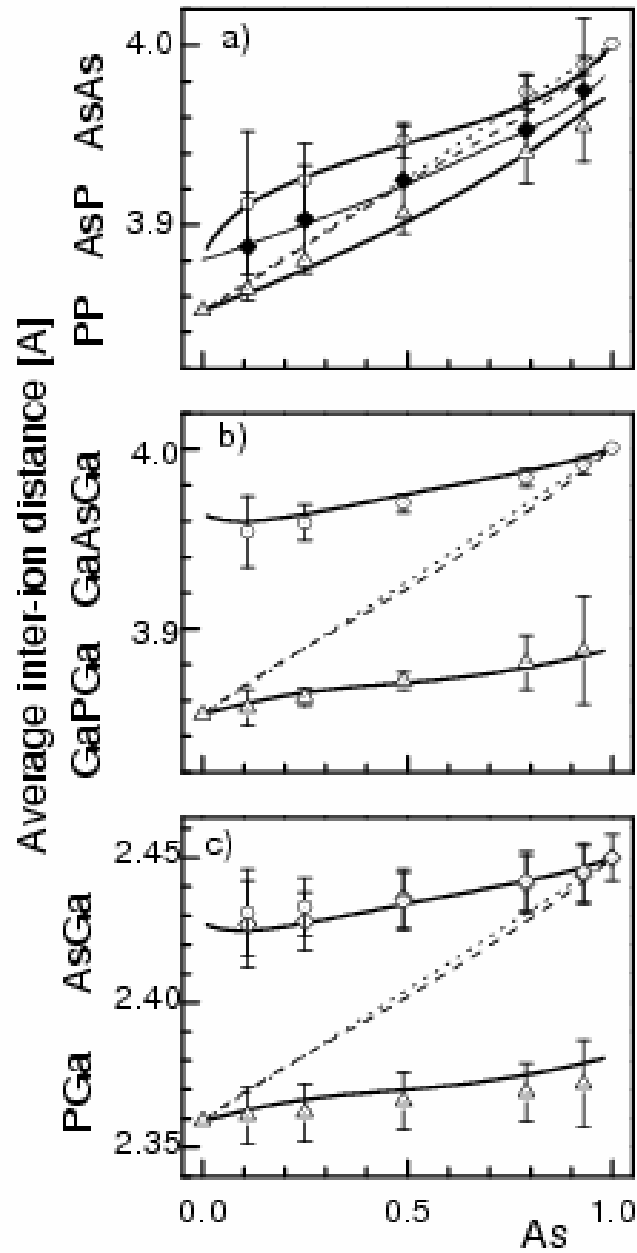| y_{As}	GaAs	GaP
1%	*	1.97
15%	2.18	1.98
44%	1.68	2.49
72%	1.58	2.77
94%	2.00	*
All 5 together (global values)	1.75	1.98
Aver. experimental	1.84±0.11	2.24±0.17
Aver. Literature	1.815±0.21	2.06±0.16
ratio	0.90±0.14	1.15±0.17

FIG.2: Average inter-ion distances [Å] as a function of relative content x for $GaAs_xP_{1-x}$ [12]: comparison of model best fit curves vs. reported experimental data. Points are (circles) for As-related (top curves), (triangles) for P-related (bottom curves), and (diamond) for mixed AsP-ion distances. *Linear combination of weighted average distances* (LCWAD) curves (thin dashed) and corresponding reference Vegard Law lines (thin dotted) are all reported [9].
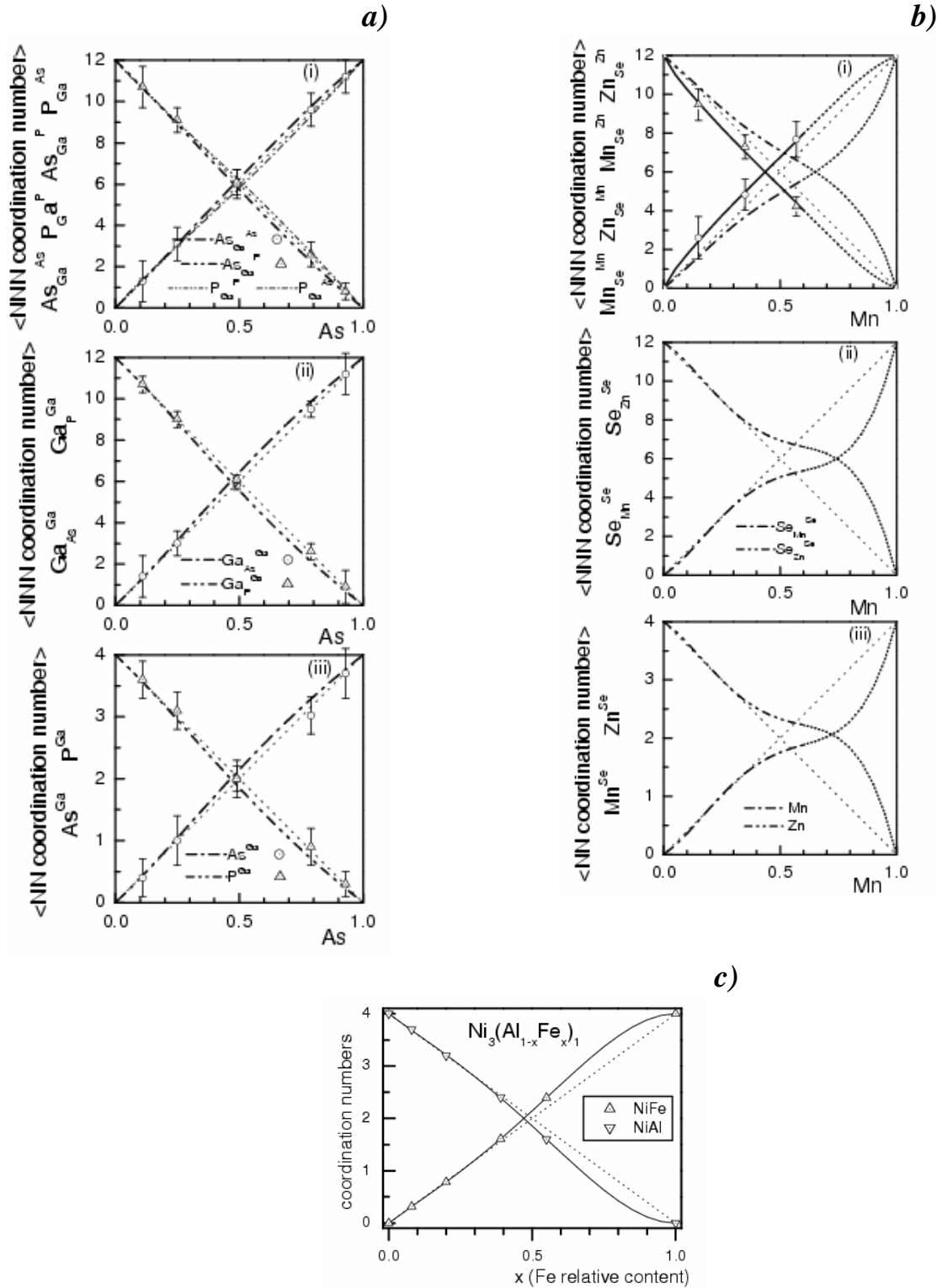
a)

b)

c)

FIG. 3: Average *co-ordination numbers* as a function of relative content x: comparison of model best fit curves using SOP values deduced from distance measurements [**a)** {0.98,1.07,1.03} $GaAs_xP_{1-x}$ [9]; **b)** {0.62,1.67,0} $ZnMn_xSe_{1-x}$ [10]; **c)** {1.01,0.86,1.33} $Ni_3(Al_{1-x}Fe_x)_1$ [11]] vs. independently measured *co-ordination number* data.
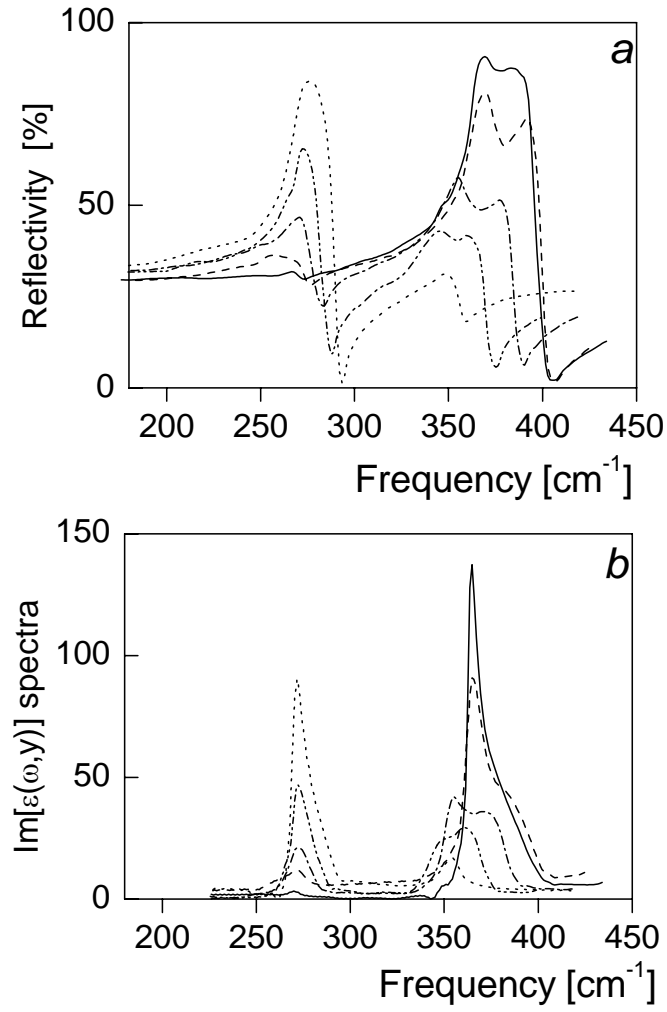
FIG. 4: GaAs$_y$P$_{1-y}$: **a)** reflectivity [%] spectra [13]; **b)** corresponding normalized Im[$\varepsilon(\omega,y)$] Kramers-Kronig derived spectra. Curves: y=0.1 (solid), 0.15 (dashed), 0.44 (dotted), 0.79 (dash-dotted), 0.94 (dash-dot-dotted).
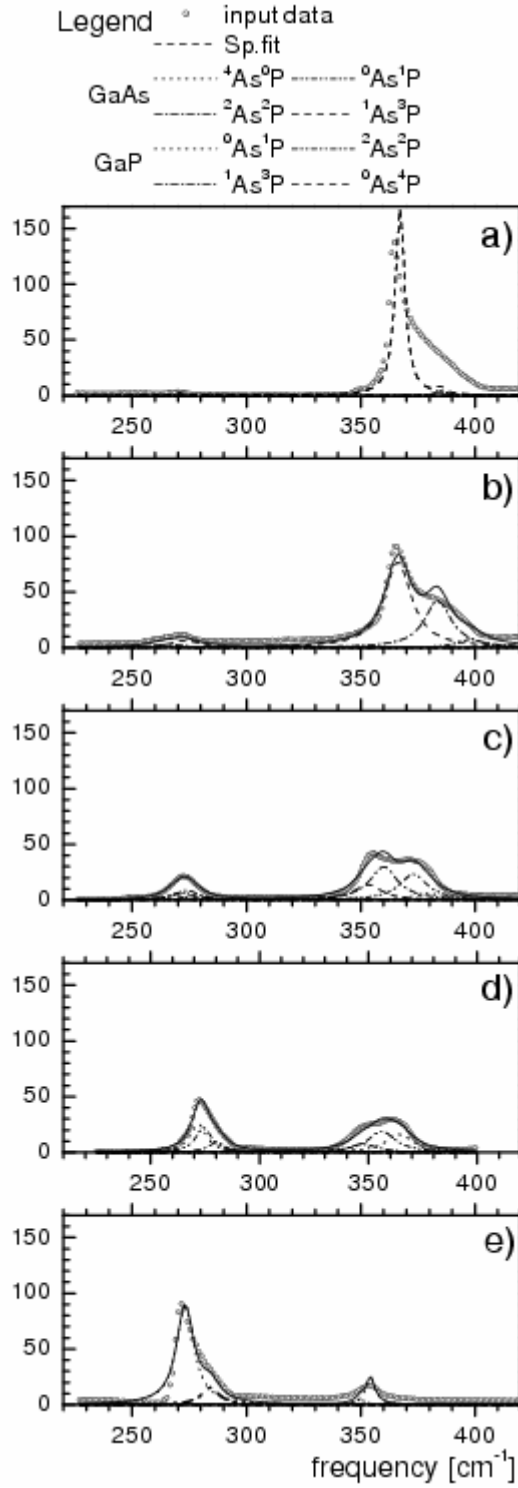
FIG.5: Model best fit unfolding of GaAs$_y$P$_{1-y}$ Im[$\varepsilon(\omega,y)$]] spectrum for SOP coefficients {W_1=0.98, W_2=1.07, W_3=1.03}, and **a)** y=0.01, **b)** y=0.15, **c)** y=0.44, **d)** y=0.72, **e)** y=0.94. The four line bands of {$^{GaAs}\omega_k$}$_{k=1,4}$ and of {$^{GaP}\omega_k$}$_{k=0,3}$ are seen distinct below and above ω=300cm^{-1} respectively; experimental points (circles), best-fit (solid lines), unfold lines (various discontinuous lines); obtained frequencies and intensities given in Table-5