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Consideration of the Verleur model of far-infrared spectroscopy of ternary compounds

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The clustering model proposed by Verleur and Barker [Phys. Rev. **149**, 715 (1966)] to interpret far infrared data for face-centered-cubic ternary compounds is critically analyzed. It is shown that their approach, satisfactory for fitting some ternary compound spectral curves, is too restricted by its one-parameter β model to be able to describe preferences (with respect to a random distribution case) for the five tetrahedron configurations.

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Infrared spectroscopy of lattice vibrations in ternary compounds of $A_{1-x}B_xZ$ (two cations $A,B+$ one anion Z) and AY_yZ_{1-y} (one cation $A+$ two anions Y,Z) types enable us to obtain information about their real crystalline microstructure and interior interactions. To explain the features of vibration spectra in elemental tetrahedra of zinc blende (ZB) structures of ternary compounds, Verleur and Barker[1,2] considered (for GaAs$_y$P$_{1-y}$) the contributions of the *five* basic elemental tetrahedra $\{T_k\}_{k=0,4}$, with an A cation at the center and *four Y,Z* anions at the vertexes: $T_0(A{:}^4Z)$, $T_1(A{:}^3Z+{}^1Y)$, $T_2(A{:}^2Z+{}^2Y)$, $T_3(A{:}^1Z+{}^3Y)$, and $T_4(A{:}^4Y)$.

As is well known, fcc tetrahedron ion coordination is characterized by each *central* ion being surrounded by 4 nearest neighbors (NN's) and 12 next-to-nearest neighbors (NNN's). This is well described by *Bethe's lattice*, also referred to as the *regular tree of coordination number 4* for NN's, introduced by Ziman[3] to describe disordered systems.

In the case of far-infrared (FIR) spectroscopy, each phonon mode observed as an individual line in reflectivity spectra from a ternary AY_yZ_{1-y} (or $A_{1-x}B_xZ$) compound is related to a lattice ion pair, either $A{:}Y$ or $A{:}Z$ (symmetrically for *ABZ* $A{:}Z$ or $B{:}Z$) from each of the five configurations T_k. To avoid verbosity the treatment is limited to *AYZ*: for *ABZ*, the reader has to canonically adjust adequately the letters and use for the relative contents x wherever y appears.

Thus, for *AYZ*, if $N_k^{AY}(y)$ and $N_k^{AZ}(y)$ are the populations of the corresponding pairs *AY* and *AZ*, and f_k^{AY} and f_k^{AZ} the specific elemental oscillator strengths per corresponding ion pair of configuration T_k, the oscillator strengths S_k^{AY} and S_k^{AZ} of each phonon mode are

$$S_k^{AY}(y)=f_k^{AY}N_k^{AY}(y), \quad S_k^{AZ}(y)=f_k^{AZ}N_k^{AZ}(y). \tag{1}$$

Specific elemental oscillator strengths $f_0^{AZ}=f^A$ and $f_4^{BZ}=f^B$ are proper to the two binary constituents, while $\{f_k^{AY}\}_{k=1,3}$ and $\{f_k^{AZ}\}_{k=1,3}$ are proper to the three ternary configurations. For a random distribution of Y and Z ions around cation A and N_{0t}, the total number of tetrahedra (i.e., a total number of ion pairs, $N_{0p}=4N_{0t}$),

$$S_k^{AY}(y)=N_{0t}f_k^{AY}kp_k(y), \quad S_k^{AZ}(y)=N_{0t}f_k^{AZ}(4-k)p_k(y), \tag{2}$$

where $\{p_k(y)\}_{k=0,4}$ are the binomial polynomials $p_k(y)=C_k^4x^k(1-y)^{4-k}$ and $C_k^4=4!/[k!(4-k)!]$ the binomial coefficients.

If we assume that for the five tetrahedron configurations *all* four specific elemental oscillator strengths for a given pair are equal and independent of x, i.e.,

$$\{f_k^{AY}\}_{k=1,4}=f_{AY}, \quad \{f_k^{AZ}\}_{k=0,3}=f^{AZ},$$

we obtain a linear dependence on composition for the total oscillation strength of the respective modes *AY* and *AZ* of AY_yZ_{1-y} solid solutions:

$$\Sigma_{k=0,4}S_k^{AY}(y)=yN_{0p}f^{AY}, \quad \Sigma_{k=0,4}S_k^{AZ}(y)=(1-y)N_{0p}f^{AZ}. \tag{3}$$

In the alloys GaAs$_y$P$_{1-y}$ (Ref. 1) and CdSe$_y$Te$_{1-y}$ (Ref. 2), the deviation of the experimental sum of oscillation strength from linearity with composition has been explained by assuming a nonrandom distribution of anions in the lattice. This is well-documented information about *site occupation preferences* (SOP's) from NNN's for ternary III-V and II-VI alloys. To fit experimental results to the theoretical expression, Verleur and Barker[1] approximated the latter by introducing a *clustering* one-parameter β model. This intrinsically implies a preferential specific cluster segregation of binary cation-anion pairs in elemental tetrahedra. The model leads to individual configuration populations $\{P_k\}_{k=0,4}$,

$$\begin{aligned}P_0(y)&=P_4(1-y)+\beta y(1-y)+p_0(y)+\beta p_1(y)/2)\\&\quad+\beta p_2(y)/6,\\P_1(y)&=P_3(1-y)=(1-\beta)[p_1(y)+2\beta p_2(y)/3],\\P_2(y)&=P_2(1-y)=(1-\beta)^2p_2(y),\end{aligned} \tag{4}$$

and yields satisfactory fits of the experimental spectral curves.

Using this approach, other authors analyzed vibration spectra of CdHgTe (Ref. 4), CdMnTe (Ref. 5), and CdZnTe (Ref. 6) ternary compounds. Perkowitz *et al.*,[7] having investigated CdTe$_y$Se$_{1-y}$ ternary compounds, concluded that the clustering parameter β defined by Verleur and Barker[1] depends on the relative cation-content x approximately as $y(1-y)$. The large value for the clustering parameter β obtained and used

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by Verleur and Barker[1,2] and others[4–7] led to contrasting, segregated fractional distributions of tetrahedron-coordinated ternary compounds that are not confirmed by x-ray microprobe analysis (space resolution $\sim 3\ \mu$m).[1] Auger spectroscopy (resolution ~ 20 Å) (Ref. 8) reveals no such distributions either. Besides lattice vibration analysis, nuclear magnetic resonance studies on CdZnTe, HgCdTe, CdSeTe, and CdMnTe (Ref. 9) yield information on tendencies to SOP's in II-VI ternary materials. Mikkelsen and Boyce,[10,11] using an extended x-ray absorption fine structure (EXAFS) analysis of GaInAs, discussed the clustering problem and concluded that "appreciable clustering on the atomic scale is absent in this zinc-blende solid solution" (Ref. 11, p. 7136). Analyzing EXAFS data for ZnMnSe ternary compounds, Pong *et al.*[12] observed SOP qualitative results. Recent EXAFS data for $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}_y\mathrm{Sb}_{1-y}$ (Ref. 13), $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}_y\mathrm{Te}_{1-y}$ (Refs. 14 and 15), and $\mathrm{Zn}_{0.5}\mathrm{Cd}_{0.5}\mathrm{Se}_{0.5}\mathrm{Te}_{0.5}$ (Ref. 16) quaternary compounds elaborated on the grounds of a statistical approach by Robouch and Kisiel[17] give SOP's for several elemental tetrahedron configurations. Results suggest that in solid solutions certain ions tend to pair preferentially.[13–15,17]

Qualitative NNN results of Pong *et al.*[12] for ZnMnSe were analyzed using a statistical approach.[18] It was shown that ZnMnSe SOP's are described by three weight biasing parameters that differ from the random coefficients of the Bernoulli binomial polynomials taken as eigenfunctions. A complete statistical analysis[19] of eight ternary compounds (ZnMnSe, ZnMnS, GaInAs, GaAsP, CdZnTe, ZnMnTe, CdMnTe, and HgMnTe) yields information on the SOP's obtained from EXAFS-measured average coordination numbers, as well as on interion distances, and the sizes and shapes both of undistorted (binary T_0 and T_4) and of distorted (strictly ternary T_1, T_2, T_3) elemental tetrahedra. The statistical analysis presented and the discussion of results[19] is supported by a tendency of SOP's that correlates both with observed standard enthalpy of creation in ternary and quaternary compounds[19–22] and with transitions from monophase to polyphase structure.[23]

Worth noting is that the EXAFS GaAsP data reported by Wu *et al.*[24] indicate a close to random distribution for the configuration populations, free of any segregation or clustering. This result is clearly in contrast with the high $\beta = 0.75$ value that Verleur and Barker[1] calculated as per their model for the same ternary compound.

The Verleur-Barker[1] model implies (1) Perfect symmetry with respect to $y = 0.5$ [see Figs. 1(a) and 1(b)], (2) $\Sigma_{k=0,4} P_k = 1 + 2\beta(1-\beta)y^2(1-y)^2$ for the populations and $\Sigma_{k=0,4} k P_k = 4y + 4\beta(1-\beta)y^2(1-y)^2$ for the average coordination number, and (3) distributions for (a) $\beta \to 0$ tending to the corresponding random Bernoulli distributions, (b) $\beta = 1$ implies total insolubility ("clustering-segregation") of the two constituent *AY* and *AZ*, with configurations T_1, T_2, and T_3 forbidden, thus populations $P_0(y) = y$, $P_4(y) = 1 - y$, and $P_1(y) \equiv P_2(y) \equiv P_3(y) \equiv 0$, and (c) $\beta \neq 0$ leads to a *symmetric* drift of populations away from $y = 0.5$. This implicitly depletes the strictly ternary configurations (below random) to the benefit of the two binary ones (necessarily above random)—referred to as the "clustering-segregation" effect. In the model, configuration T_2 is implicitly most depressed.

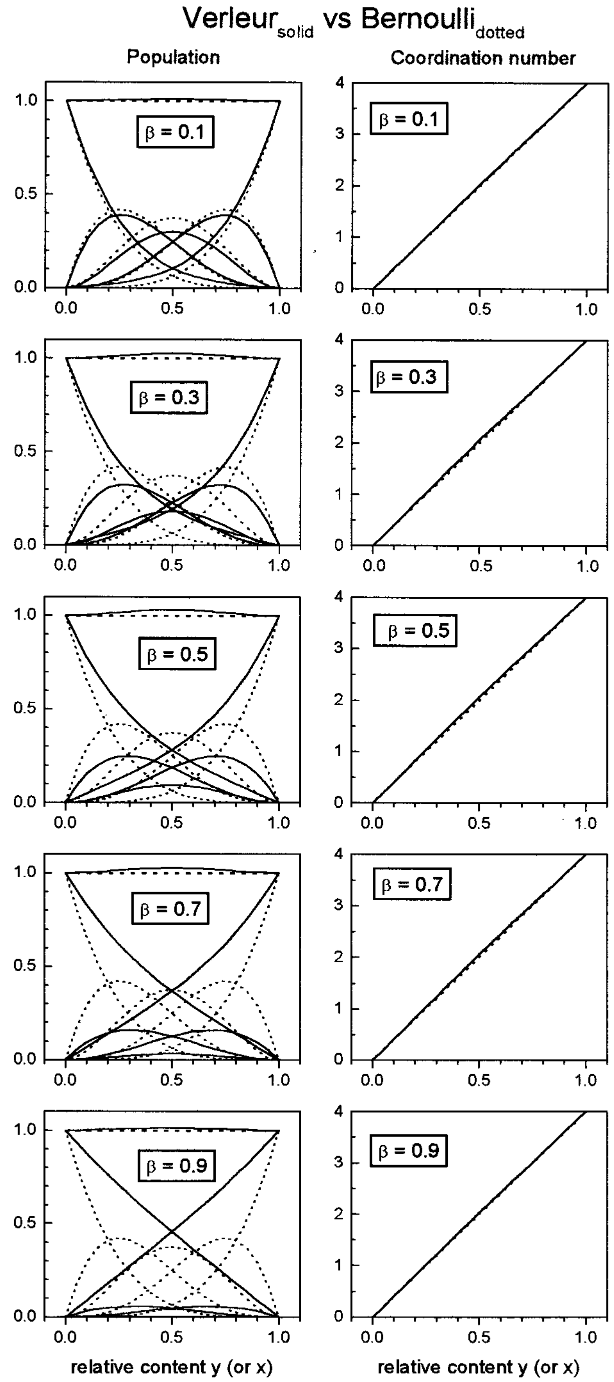

FIG. 1. Verleur functions as a function of y, for $\beta = 0.1, 0.3, 0.5, 0.7, 0.9$. (a) Verleur populations $\{P_k(\beta,y)\}_{k=0,4}$ and $\Sigma_{k=0,4} P_k(\beta,y)$. (b) Coordination numbers $\Sigma_{k=0,4} k P_k(\beta,y)$. All corresponding random ($\beta = 0$) curves are superimposed as dotted lines for comparison.

As a consequence, although Verleur and Barker's simple harmonic force model[1] gives a satisfactory description of experimental spectral curves, it *cannot* describe (a) site occupation preferences observed and reported in the literature,[10–16] (b) asymmetric $\{T_k\}$ populations or (c) ternary configuration populations dominant over binary ones (''anti-segregation'') observed both by EXAFS (Ref. 17) and by FIR spectroscopy (Ref. 25) or (d) nondepressed ternary population P_2 of configuration T_2 [actually predominant in ZnMnSe (Ref. 12) or ZnMnTe and CdMnTe (Ref. 17)].

Verleur and Barker actually warn[1] the reader of a contradiction in GaAsP of the model results with its initial hypothesis—namely, an overclustering or segregation they admit unable to detect, nor did later, higher-resolution Auger spectroscopy.[8]

Worth noting is that in their last article Kosyrev *et al.*,[25] to interpret observed CdHgTe FIR spectra, abandon the concept of clustering and attempt an alternative explanation for the departure of their results from linearity as per Eqs. (3).

We believe that the valid pioneering β model[1,2] is too restrictive with its one parameter to describe configuration populations of FIR data and that an *ad hoc* model for FIR data interpretation, analogous to the one developed for EXAFS,[19] is needed. Indeed, the rich FIR experimental database deserves a thorough SOP-wise reinterpretation.

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[1] H. W. Verleur and A. S. Barker, Phys. Rev. **149**, 715 (1966).

[2] H. W. Verleur and A. S. Barker, Phys. Rev. **155**, 750 (1967).

[3] J. M. Ziman, *Models of Disorder* (Cambridge University Press, Cambridge, England, 1979).

[4] S. P. Kozyrev, L. K. Vodopyanov, and R. Tribulet, Solid State Commun. **45**, 383 (1983).

[5] J. M. Wrobel, B. P. Clayman, P. Becla, R. Sudharsanan, and S. Perkowitz, J. Appl. Phys. **64**, 310 (1988).

[6] S. Perkowitz, L. S. Kim, Z. C. Feng, and P. Becla, Phys. Rev. B **42**, 1455 (1990).

[7] S. Perkowitz, L. S. Kim, and P. Becla, Phys. Rev. B **43**, 6598 (1991).

[8] C. N. Afonso, M. Alonso, J. L. Nerira, M. F. da Salva, A. D. Sequeira, and J. C. Soares, J. Vac. Sci. Technol. A **7**, 3256 (1989).

[9] D. Zamir, K. Beshah, P. Becla, P. A. Wolff, R. G. Griffin, D. Zax, S. Vega, and N. Yellin, J. Vac. Sci. Technol. A **6**, 2612 (1988).

[10] J. C. Mikkelsen and J. B. Boyce, Phys. Rev. Lett. **49**, 1412 (1982).

[11] J. C. Mikkelsen and J. B. Boyce, Phys. Rev. B **28**, 7130 (1983).

[12] W-F. Pong, R. A. Mayanovic, B. A. Bunker, J. K. Furdyna, and U. Debska, Phys. Rev. B **41**, 8440 (1990); B. A. Bunker, J. Vac. Sci. Technol. A **5**, 3003 (1987).

[13] Sh. M. Islam and B. A. Bunker, Phys. Lett. A **156**, 247 (1991).

[14] A. Kisiel, J. Łazewski, M. Zimnal-Starnawska, E. Burattini, and A. Mycielski, Acta Phys. Pol. A **90**, 1032 (1996).

[15] A. Kisiel, J. Łazewski, M. Zimnal-Starnawska, E. Burattini, and A. Mycielski, J. Phys. IV **7**, C2-1197 (1997).

[16] Q. Lu, B. A. Bunker, H. Luo, A. J. Kropf, K. M. Kemner, and J. K. Furdyna, Phys. Rev. B **55**, 9910 (1997).

[17] B. V. Robouch and A. Kisiel, Acta Phys. Pol. A **94**, 497 (1998); J. Alloys Compd. **286**, 80 (1999).

[18] B. V. Robouch and A. Kisiel, in *Proceedings of the 5th Polish National Symposium of Synchrotron Radiation Users*, edited by J. Gronkowski and M. Lefeld-Sosnowska (Warsaw University, Warsaw, 1999), p. 207.

[19] B. V. Robouch and A. Kisiel (unpublished).

[20] *CRC Handbook of Chemistry and Physics*, 7th ed., edited by D. L. Lide (CRC Press, Boca Raton, 1997).

[21] Landolt Bornstein-Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik, edited by J. Bartels, H. Borchers, P. Ten Bruggencate, H. Hausen, K. H. Hellwege, Kl. Schafer, and E. S. Schmidt, Vol. II, Pt. 4 (Springer Verlag, Berlin, 1961), pp. 179–260.

[22] *Lange's Handbook of Chemistry*, 4th ed., edited by J. A. Dean (McGraw Hill, New York, 1992).

[23] R. Juza, A. Rabenau, and G. Pasher, Z. Anorg. Allg. Chem. **285**, 61 (1956).

[24] Z. Wu, K. Lu, X. Wang, J. Dong, H. Li, Ch. Li, and Zh. Fang, Phys. Rev. B **48**, 8694 (1993).

[25] S. P. Kosyrev, L. K. Vodopyanov, and R. Triboulet, Phys. Rev. B **58**, 1374 (1998).