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Comments

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Comment on "Atomic structure and ordering in semiconducting alloys"

M. Podgórny*
Institut für Physik, Universität Dortmund, 4600 Dortmund 50, Postfach 500 500, Germany

M. T. Czyżyk
Instytut Fizyki, Uniwersytet Jagiellonski, 30-059 Krakow, Reymonta 4, Poland

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Recently, an *ab initio* total-energy calculation for the ordered ternary phases of a III-V zinc-blende semiconductor was reported [G.P. Srivastava, J. L. Martins, and A. Zunger, Phys. Rev. B **31**, 2561 (1985)]. We compare these results with those of a simple empirical model. Both models are used in a new approach to the calculation of thermodynamic properties of ternary alloys including the calculation of the cation distribution in the mixed sublattice. The applicability of the models is critically discussed.

Recently, Srivastava, Martins, and Zunger[1] (hereafter referred to as SMZ) have reported an *ab initio* self-consistent calculation of the total energy of hypothetic ordered structures of the In-Ga-P system. In the second part of their paper they considered also some properties of pseudobinary alloys under the simplest assumption of a random distribution of atoms in the mixed sublattice. While agreeing with some of the conclusions drawn by SMZ from their calculations, we wish to do the following here: (a) to show how the results of the SMZ calculation for ordered compounds can be used for a description of the thermodynamics of pseudobinary semiconductor alloys on a more quantitative basis, following the approach developed[2] for the analysis of our elastic model of pseudobinary alloys;[3] (b) to show that a simple quasichemical model with a properly included elastic term but which otherwise employs no adjustable parameters describes better the reality, and that the empirically adjusted SMZ results are quantitatively close to the results of the above-mentioned model; and (c) to discuss critically the applicability of the results to real alloys.

In the recently proposed[3] elastic models of pseudobinary alloys as well as in the SMZ paper the basic structural unit considered is a tetrahedron with four atoms of the mixed sublattice at its vertices and one atom of the common sublattice inside. Extended x-ray-absorption fine-structure (EXAFS) experiments[4,3] have revealed a bimodal distribution of the nearest-neighbor distances and suggested a strong distortion of the common sublattice. The total energy per tetrahedron depends strongly on the displacement of the central atom. The energies for five different coordinations around the central atom can be calculated either classically[3,5] or quantum-mechanically.[1] Knowledge of them suffices to calculate the thermodynamic properties of an alloy on a microscopic basis. In our previous papers[2] we have developed a simple thermodynamic model in the spirit of the well-known quasichemical approximation[6] (QCA) including also the elastic energy. An analogous formalism can be now readily applied to the SMZ results.

In a random $A_{1-x}B_xC$ alloy, tetrahedra with $n=0$, 1, 2, 3, and 4 B atoms are distributed according to the Bernoulli formula

$$P_B^{(n)}(x)=\left[\begin{matrix}4\\n\end{matrix}\right]R_B^{(n)}(x)=\left[\begin{matrix}4\\n\end{matrix}\right]x^n(1-x)^{4-n}\ . \tag{1}$$

The different energies of the five possible configurations lead to a rearrangement of the mixed sublattice in such a way that the free energy of the alloy is minimized. Treating the configurational entropy[2] according to the third-order QCA,[6] and using the variational principle with two Lagrange multipliers that assure normalization of the distribution and the proper composition x of the alloy, we arrive at the following expression for the probability distribution of the tetrahedra:

$$P^{(n)}(x,T)=\frac{\left[\begin{matrix}4\\n\end{matrix}\right]\exp(-\beta\Delta E^{(n)})\mathcal{A}^n}{\sum_{n=0}^{4}\left[\begin{matrix}4\\n\end{matrix}\right]\exp(-\beta\Delta E^{(n)})\mathcal{A}^n}\ , \tag{2}$$

where $\mathcal{A}$ is a real, positive solution of the fourth-order polynomial equation at given T:

$$\sum_{n=0}^{4}(n-4x)\begin{bmatrix}4\\n\end{bmatrix}\exp(-\beta\Delta E^{(n)})\mathcal{A}^{n}=0\ . \tag{3}$$

The molar enthalpy, molar entropy, and molar free energy of mixing are given by

$$h^{M}(x,T)=\sum_{n=0}^{4}P^{(n)}(x,T)\Delta E^{(n)}(x)\ , \tag{4}$$

$$s^{M}(x,T)=-R[(1-x)\ln(1-x)+x\ln x] -R\sum_{n=0}^{4}(P^{(n)}\ln R^{(n)}-P_B^{(n)}\ln R_B^{(n)})\ , \tag{5}$$

and

$$g^{M}(x,T)=h^{M}(x,T)-Ts^{M}(x,T)\ , \tag{6}$$

respectively.

The empirical interaction parameter $\Omega(x,T)$ can be formally defined as

$$\Omega(x,T)=g^{E}(x,T)/x(1-x)\ , \tag{7}$$

where excess free energy of mixing $g^{E}(x,T)$ is defined by

$$g^{E}(x,T)=g^{M}(x,T)-RT[(1-x)\ln(1-x)+x\ln(x)]\ . \tag{8}$$

The application of the above formulas (or, as SMZ did, the application of the Bernoulli distribution) to the original SMZ energies for In-Ga-P yields the negative enthalpy and free energy of mixing [Fig. 2(b)], in complete disagreement with the experimental knowledge, and an empirical adjustment is necessary in both cases in order to bring the results into correspondence with experiment. SMZ ascribe the necessity of empirical corrections to the "Brillouin zone effect." They attach much importance to negative values of the adjusted $\Delta E^{(n)}$ functions for $x=0.25$, 0.5, and 0.75. This result is, in our opinion, weakly substantiated. The excess entropy term causes the adjusted $\Delta E^{(2)}$ $(x=0.5)$ to take on an only slightly negative value of -0.08 kcal/mol instead of the -0.3 kcal/mol reported by SMZ (one should note that *any* model allowing for a clustering or an ordering would shift adjusted $\Delta E^{(n)}$ energies upwards). Taking into account the large error of the experimental data[7] that the adjustment is based upon, one cannot say anything definitive about the sign of $\Delta E^{(n)}$.

The available experimental data[7] are derived from solidus-liquidus curves and represent the high-temperature limit. Hence, all the results discussed below, unless otherwise indicated, refer to the temperature $T=1400$ K (slightly above the melting temperature of InP but far below that of GaP). Figure 1 shows the calculated $P^{(n)}$'s compared to the Bernoulli distribution. Even at the elevated temperature of 1400 K, coordinations of $n=1$, 2, and 3 are strongly favored at $x=0.25$, 0.5, and 0.75, respectively, invariably at the expense of the $n=0$ and $n=4$ configurations. Figure 2(a) shows the excess enthalpy and excess free energy of mixing for $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{P}$ at 1400 K compared to the excess enthalpy and free energy for a random alloy.

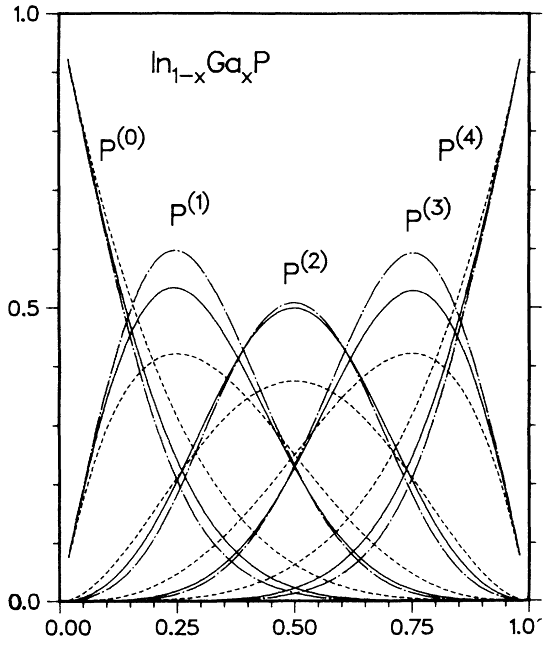

FIG. 1. Probability distribution $P^{(n)}(x)$ of tetrahedra with n Ga atoms in $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{P}$ calculated at 1400 K. Dashed line, the Bernoulli distribution; dash-dotted line, distribution calculated from the original SMZ energies $\Delta E^{(n)}$; solid line, distribution calculated from SMZ energies $\Delta E^{(n)}$ adjusted to give the experimental value (Ref. 10) of Ω interaction parameter (see text).

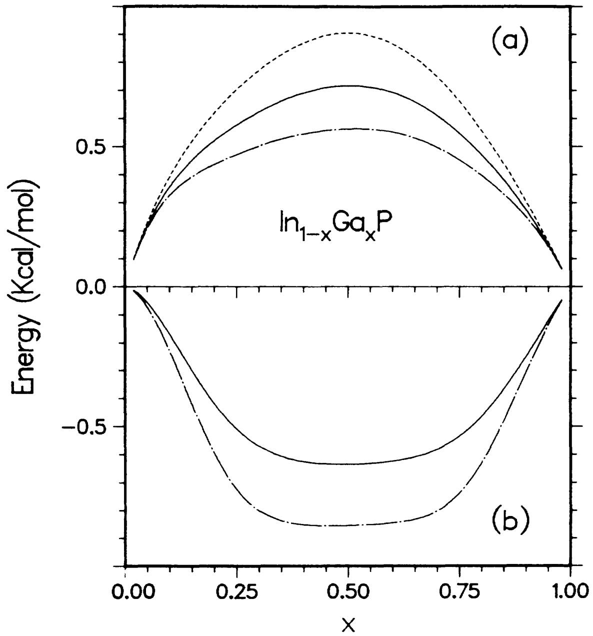

FIG. 2. Enthalpy and excess free energy of mixing for $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{P}$. Solid lines, excess free energy of mixing $g^{E}(x)$; dash-dotted lines, enthalpy of mixing $h^{M}(x)$; dashed line, enthalpy and excess free energy of mixing for a random alloy calculated for (a) $\Delta E^{(n)}$ energies adjusted to reproduce experimental value of Ω interaction parameter, (b) original $\Delta E^{(n)}$ energies.

The free-energy curve $g^M(x,T)$ contains, in principle, all the relevant information needed for calculation of spinodal decomposition and phase-coexistence diagrams. Although approximations inherent to the QCA make this method not particularly suitable for phase-diagram calculation, it is a common practice to use it for this purpose. Figure 3 shows $g^M(x,T)$ for a few temperatures (a) and the spinodal decomposition curve obtained from the mixed-phase stability condition $d^2g^M(x,T)/dx^2>0$ (b). A striking feature of this (for ternary compounds unconventional) diagram is the existence of "channels" around $x=0.25$, 0.5, and 0.75 within which the disordered alloy should be at least metastable even if grown at low temperatures.[8] A discussion of the phase-coexistence diagram is beyond the scope of this paper. We would like to observe only that in some temperature region (slightly below the critical temperature) the disproportionation into *A*- and *B*-rich phases can result in two phases with concentrations bracketing not as usually $x=0.5$ but rather $x=0.125$, 0.375, 0.625, and 0.875, depending on the nominal concentration of the mixture. It follows from this fact that the phase-coexistence curve would possibly possess, in analogy with the spinodal curve, also four well-defined maxima.

Everything said in the previous paragraph supports the general conclusions drawn by SMZ although, as will be discussed later, we do not share their enthusiasm about a possibility of growing ordered phases. Nevertheless, their numerical results can hardly be treated as a sufficient basis for a quantitative thermodynamical analysis due to the necessity of empirical corrections of the $\Delta E^{(n)}$ functions. On the other hand, their adjusted $\Delta E^{(n)}$'s differ only slightly from the results of simple model[2] which brings together the QCA and simplified valence-force-field (VFF) approaches[9] and which approximates experimental results for $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{P}$ with good accuracy calling for no adjustable parameters. In this model, the functions formally equivalent to $\Delta E^{(n)}(x)$ defined by SMZ are[2]

$$\Delta E^{(n)}(x,T)=n(4-n)w+E^{(n)}(x,T)\ , \qquad (9)$$

where $E^{(n)}(x,T)$ are the elastic energies obtained from the VFF minimization with bond-bending terms neglected.[3] The temperature dependence of $E^{(n)}$ is introduced via the temperature dependence of the lattice and elastic constants. w in (9) is (commonly used in QCA) an interaction parameter equal to twice the energy needed to create two *AB* pairs from one *AA* and one *BB* pair. It can take on both positive and negative values. It is of importance that w is more than just an empirical parameter—its value can be measured with use of x-ray diffuse scattering.[10] For $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{P}$ the reported experimental value[10] is 0.4 kcal/mol. Using this value and the temperature-dependent lattice and elastic constants[11] we obtain an excess free energy of mixing in excellent agreement with experiment.[7] Then for the purpose of comparison with SMZ results we dropped the temperature dependence from our model. The w value requires then an adjustment and takes on the value of 0.2 kcal/mol. Figure 4

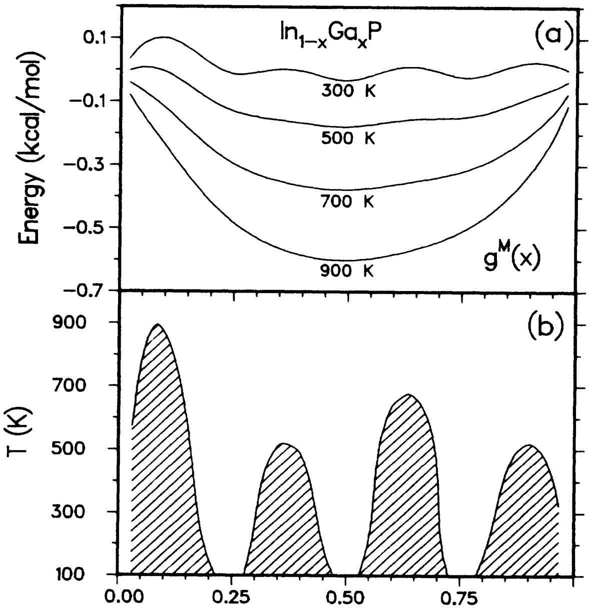

FIG. 3. (a) Free energy of mixing $g^M(x)$ for $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{P}$ at different temperatures, and (b) spinodal decomposition curve. Shaded areas visualize the regions of alloy instability.

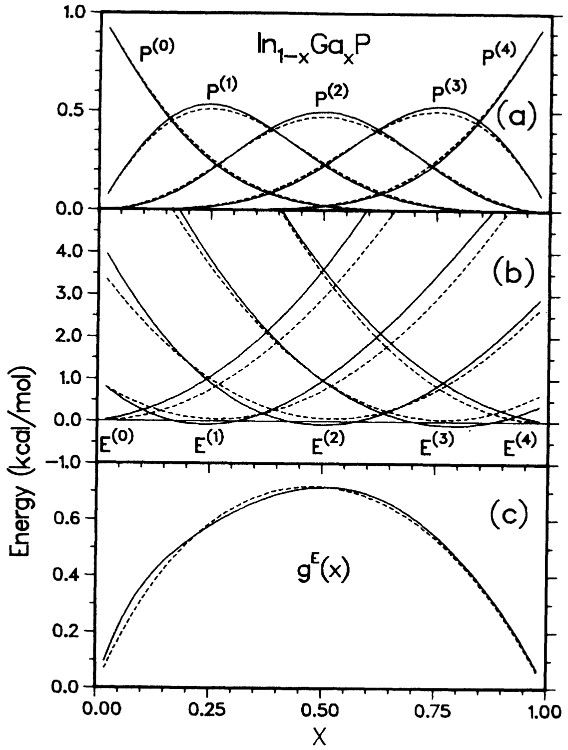

FIG. 4 Comparison of the results based on the adjusted quantum-mechanical energies $\Delta E^{(n)}$ obtained by SMZ (solid lines) with those of our elastic model (dashed lines): (a) probability distribution $P^{(n)}(x)$, (b) energies $\Delta E^{(n)}(x)$, (c) excess free energies of mixing.

displays the detailed comparison of our results with the results based on the empirically adjusted $\Delta E^{(n)}$ of SMZ. It should be noted that both approaches yield the same characteristic asymmetry of the $\Delta E^{(n)}(x)$ curves. This close correspondence between the quantum-mechanical results that take into account all the microscopic effects of the nonmixed-lattice relaxation and the primitive empirical ansatz (9) is surprising and calls for a further comment. The bond-bending terms in VFF are known to be not negligible for III-V compounds and their absence in (9) seems to be disturbing at first glance. However, all the terms in the VFF model are expressed with respect to "equilibrium bond lengths" and "equilibrium bond angles." Now when the lattice constant of an ordered phase is changed, the necessary change of the bond lengths is distributed proportionally between both of them, whereas the bond angles remain constant or change only a little. Hence the bond-bending terms are not necessary in (9). Moreover, the close resemblance of the quantum-mechanical and empirical results suggests that regardless of the large charge redistribution (Fig. 2 in Ref. 1), the bond-stretching force constants do not change much in comparison to those in pure materials.

The present thermodynamic model seems to work at least as well as the other theories[12] developed and used until now. At the same time it is clear that the treatment is highly approximate. Both SMZ's and our calculations of $\Delta E^{(n)}$ are based on the structural model which assumes that the mixed sublattice remains fixed. This model is not able to interpret all the features discovered by EXAFS, i.e., the nearest-neighbor distance distribution widths or the second-neighbor distance distribution.[4] Our recent Monte Carlo computer simulation of the alloy lattice[13] demonstrated that all these features can be consistently and accurately accounted for if the bond-bending terms of the VFF[9] model are included. The results of the simulation yield the estimate of both mixed- and common-sublattice distortions. We have shown[13] that the average atom displacement from the zinc-blende lattice sites for the mixed sublattice is by no means negligible and amounts to one-half of that of the common sublattice and that the chalcopyrite analogy of Mikkelsen and Boyce[4] is not valid. Nevertheless, we have been able to reproduce the EXAFS results only under the assumption that the equilibrium bond angle remains the same as in the zinc-blende lattice. It is still sensible to surmise that hitherto-still-hypothetic ordered intermediate compounds might, when synthesized, possess the structures predicted by SMZ. The real geometry of the disordered alloy lattice seems to be, however, more involved. It is natural to presume that the chemical disorder causes charge transfer between different bonds to be not as complete as in the eventual ordered crystal. As a result, the alloy lattice tends to maintain, on average, both original bond lengths and bond angles. It is possible only if both sublattices are distorted and the correctly interpreted EXAFS data prove that it is really the case. Hence, there are reasons to believe that "Brillouin zone effects"[1] are not a sole source of difficulties when transferring energetic properties of ordered structures to an alloy. These effects are likely to cause only a rigid shift of $\Delta E^{(n)}$ curves for $n=1$, 2, and 3; the structural effects can affect considerably the x dependence of $\Delta E^{(n)}$ and, subsequently, the estimate of the thermodynamic properties of the alloy. In particular, the stability of mixed phases with $x=0.25$, 0.5, and 0.75 and the higher probability of $n=1$, 2, and 3 tetrahedra, respectively, at these concentrations are both due to the deep minima of the $\Delta E^{(n)}$ functions. The corrected probability distribution $P^{(1)}(x)$ calculated in the extreme limit of the VFF model with bond-bending terms included[13] (in which case the charge transfer is completely neglected) deviates only marginally from the Bernoulli distribution. Hence, we consider the foregoing thermodynamic analysis to be the limiting case in a sense that the calculated distribution $P^{(1)}(x)$ constitutes the upper limit for a deviation from randomness in real ternary alloys. On the other hand, even the VFF-based[13] estimate yields the mixed bond probability $y_{12}(x)=P^{(1)}(x)/4+P^{(2)}(x)/3+P^{(3)}(x)/4$ slightly larger than the random value $y_{12}^{R}=x(1-x)$, in apparent contradiction to the results of the standard QCA.[14] The predictions of our model are, therefore, qualitatively different from those of the standard QCA. There, a positive value of the excess free energy of mixing (and, hence, of the parameter w) leads inevitably to phase separation at low temperatures and to tendency of clustering of the like species at any temperature. This can be true for binary alloys; for ternary alloys, however, the elastic energy will drive any such system to become more homogeneous instead of to disproportionate. In any case, a distortion of the mixed sublattice tends to nullify this effect and decreases the relative stability of mixed disordered phases with x close to 0.25, 0.5, and 0.75.

Our second criticism concerns the discussion of the ordering temperature $T_O=(\Delta H_D-E_O)/\Delta S_D$ (this expression contains a misprint in Ref. 1). The authors did not evaluate it but pointed out later that T_O for In-Ga-P should be ~ 200 K lower than conventional growth temperatures. It does not seem to follow from their results. The evaluation of T_O for the case of random distribution used by SMZ yields $T_O=2.2/(1.377\times10^{-3})\cong 1600$ K. Manipulating in an elementary way the definitions of thermodynamic functions of mixing (4)–(6) and (8) one can show that, independently of the approximations used to get the distribution, the ordering temperature T_O will be given by the solution of the nonlinear equation

$$T_O=[g^E(T_O)-E_O]/S^M_{\text{random}} \; . \tag{10}$$

Therefore, any formalism yielding the value of the excess free energy of mixing g^E that agrees with experiment[7] will give a similar estimate. Allowing for even a 50% error in the experimental value we are still left with $T_O>1300$ K. In other words, should the reported value of $\Delta E^{(2)}=-1.48$ kcal/mol be correct, one should have no difficulties at all in synthesizing the chalcopyritelike In-Ga-P phase. Since there is no experimental evidence of such a phase we are tempted to contest the value of $\Delta E^{(2)}$ reported by SMZ.

Finally, we want to point out that high-precision

EXAFS measurements could be used for direct estimation of the deviation from randomness. As was proposed already in Refs. 4 and 3 and as SMZ subsequently calculated, the bond lengths in ordered structures are much the same as in pure compounds (see Fig. 1 in Ref. 1). On the other hand, the bond lengths $R_{BC}[AC:B]$ and $R_{AC}[BC:A]$ in the dilute-alloy limit are determined by the lattice relaxation around an impurity[5] and differ appreciably from bond lengths in pure AC and BC compounds.[5,13] The average AC and BC bond lengths in $A_{1-x}B_xC$ alloy lie on the curves that in the case of the random distribution are merely the linear interpolations between R_{AC} (R_{BC}) and $R_{AC}[BC:A]$ ($R_{BC}[AC:B]$).[3,1] If the probability $P^{(n)}(x)$ of mixed configurations is enhanced, we expect a nonlinear $\bar{R}_{AC}(x)$ and $\bar{R}_{BC}(x)$ dependence with upper (lower) curve bowed upwards (downwards). The effect should be within experimental resolution for alloys with a large lattice mismatch and has been already observed for $Cd_{1-x}Zn_xTe$.[15]

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[*] On leave of absence from the Institute of Physics of the Jagiellonian University, Krakow, Poland.

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