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Self-assembling of 1B4Sb and 4B10Sb clusters in GaAs:(B, As)

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Self-assembling conditions of 1B4Sb and 4B10Sb clusters is discussed. Boron and Sb co-doping transforms GaAs into GaAs-rich $B_xGa_{1-x}Sb_yAs_{1-y}$ quaternary submolecular alloy. The reasons of self-assembling are a decrease of the free energies of the constituent compounds and diminution of the strain energy after formation of clusters.

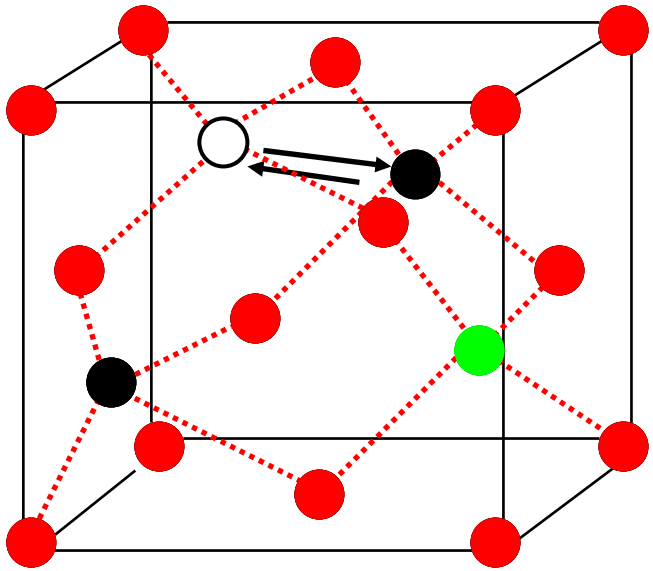
Self-assembling conditions are represented by the minimum condition of the free energy of GaAs-rich $B_xGa_{1-x}Sb_yAs_{1-y}$ quaternary alloy.

If the Sb content is larger than that of boron almost all boron atoms are in 1B4Sb clusters. Other boron impurities are isolated. If the boron content is nearly equal or larger than that of Sb self-assembling of 4B10Sb clusters is strongly preferential.

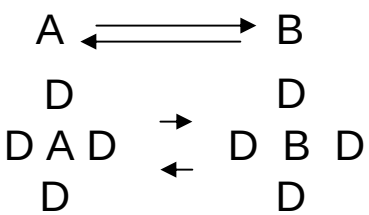
Quaternary supramolecular alloys of binary compounds

$A_xB_yC_{1-x-y}D$ ($In_xAl_yGa_{1-x-y}As$),
$AB_xC_yD_{1-x-y}$ ($CdTe_xSe_yS_{1-x-y}$)

A,B - ○ B,C - ● C,D - ● D,A - ●



Self-diffusion process of A and B cations

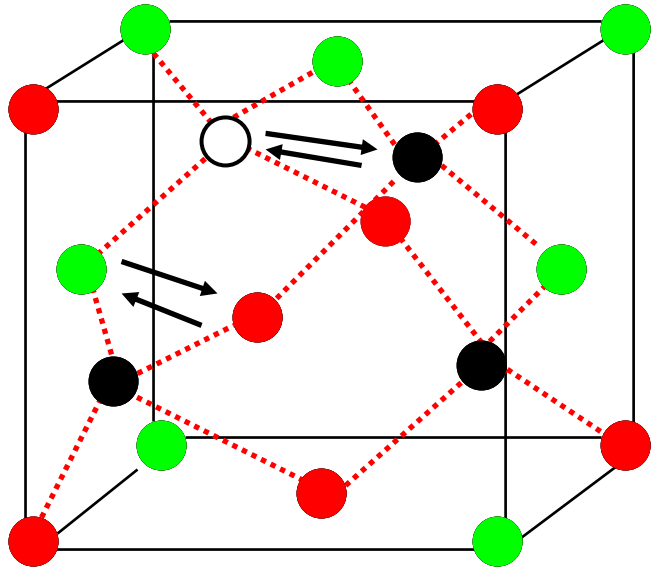


Exchange of the places between the molecules of binary compounds

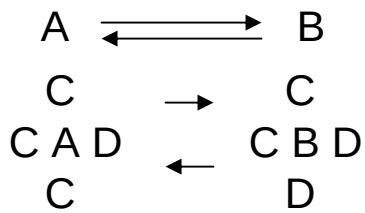
Quaternary submolecular alloys of binary compounds

$A_xB_{1-x}C_yD_{1-y}$
($In_xGa_{1-x}As_yP_{1-y}$, $Zn_xCd_{1-x}Se_yS_{1-y}$)

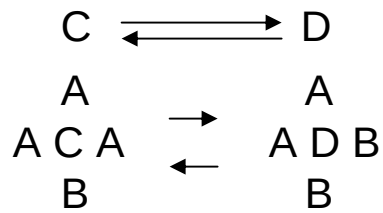
A - ○ B - ● C - ● D - ●



Self-diffusion process of the A and B cations



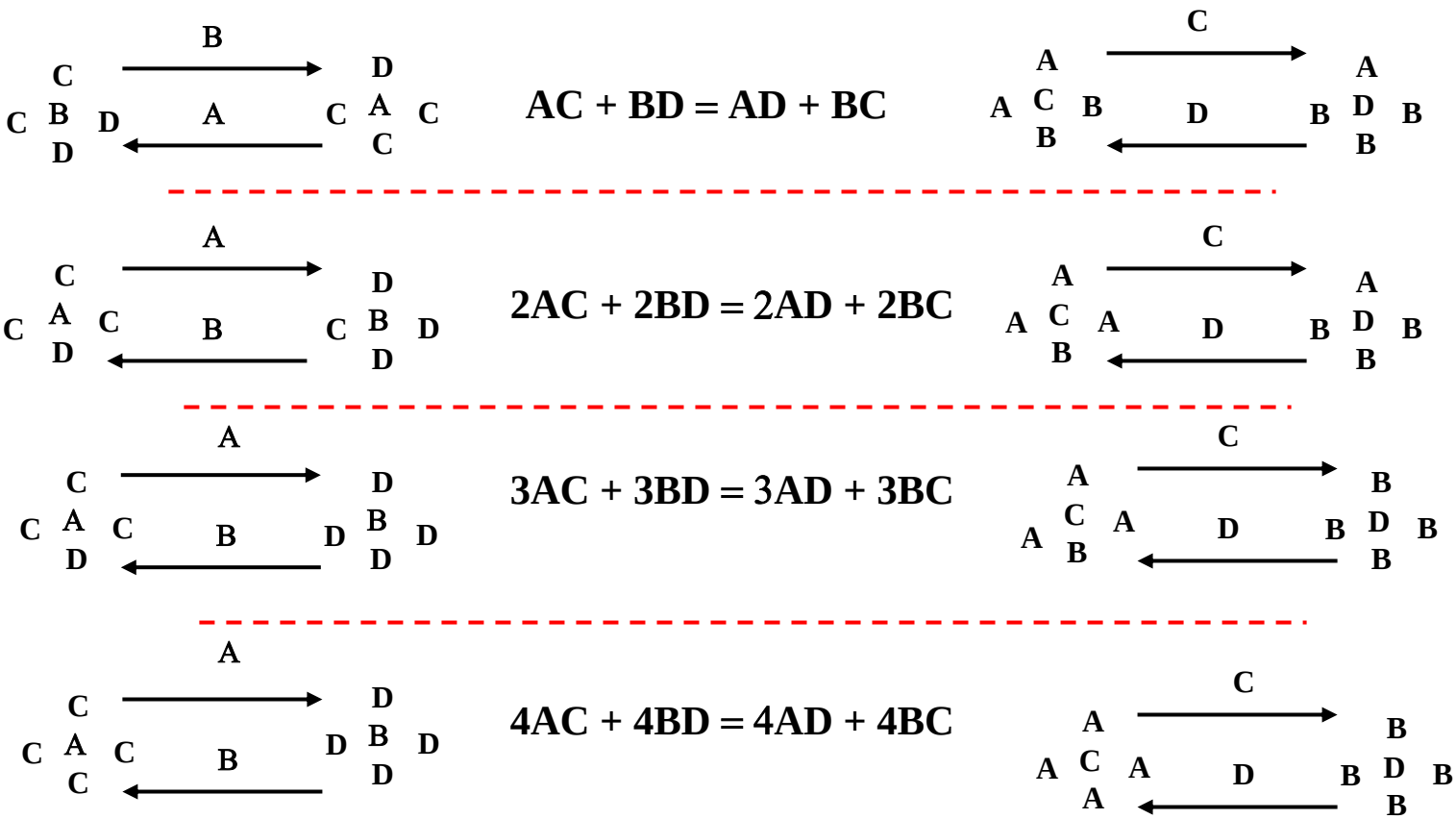
Self-diffusion process of the C and D anions



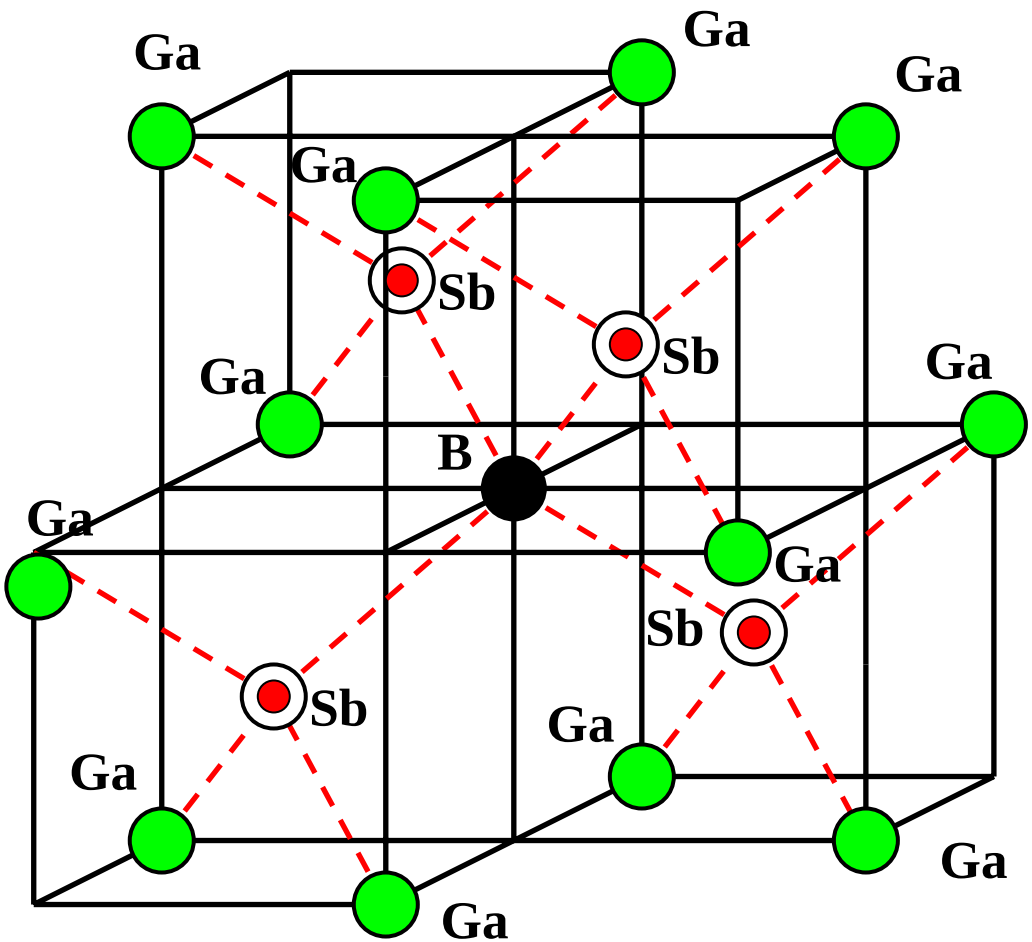
Reaction between the chemical bonds

A-C + B-D A-D + B-C

Solid state reactions in $A_xB_{1-x}C_yD_{1-y}$ submolecular tetrahedrally coordinated alloys



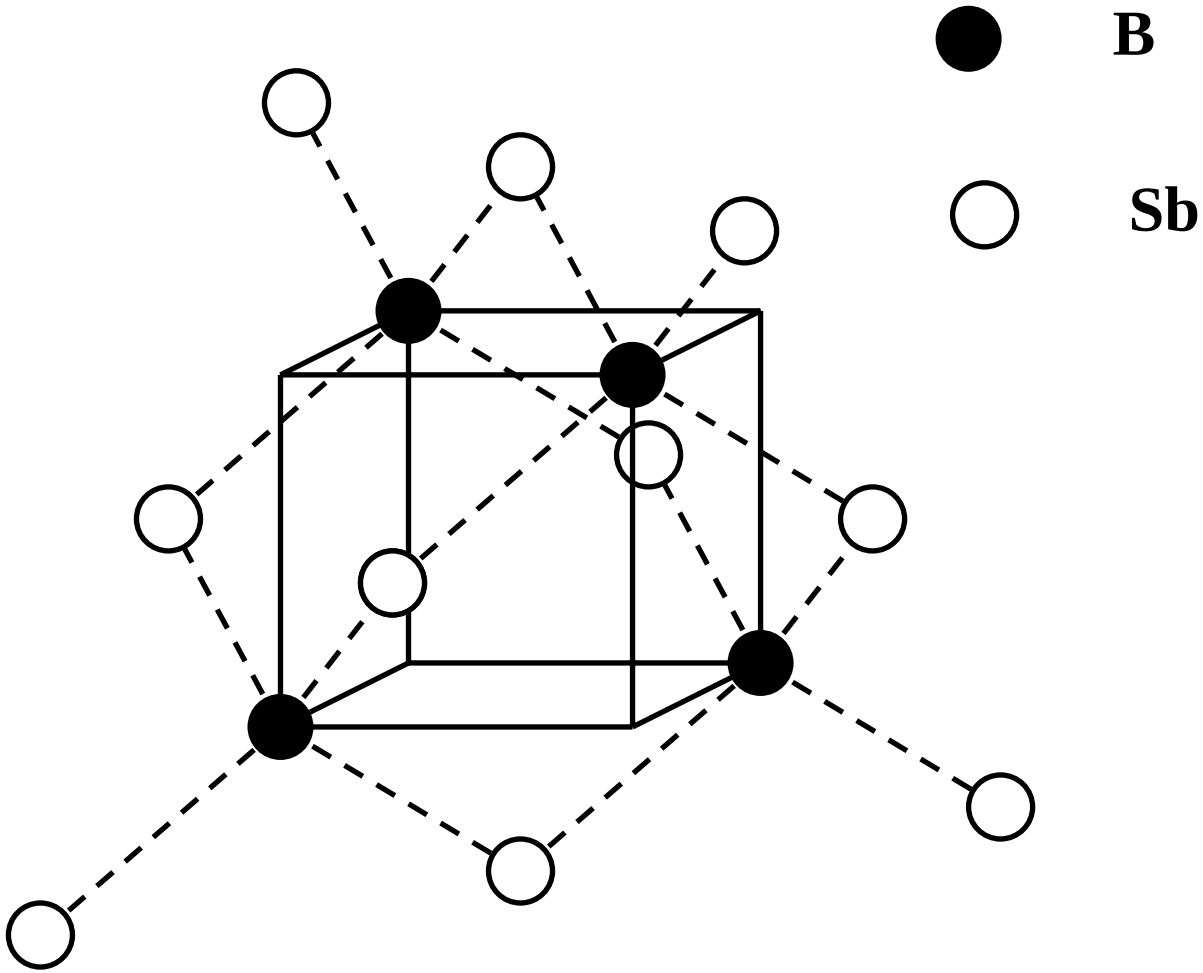
Quadruple of 1B3Ga1Sb tetrahedral cells in GaAs-rich $B_xGa_{1-x}Sb_yAs_{1-y}$ submolecular alloy - GaAs:(B, Sb)



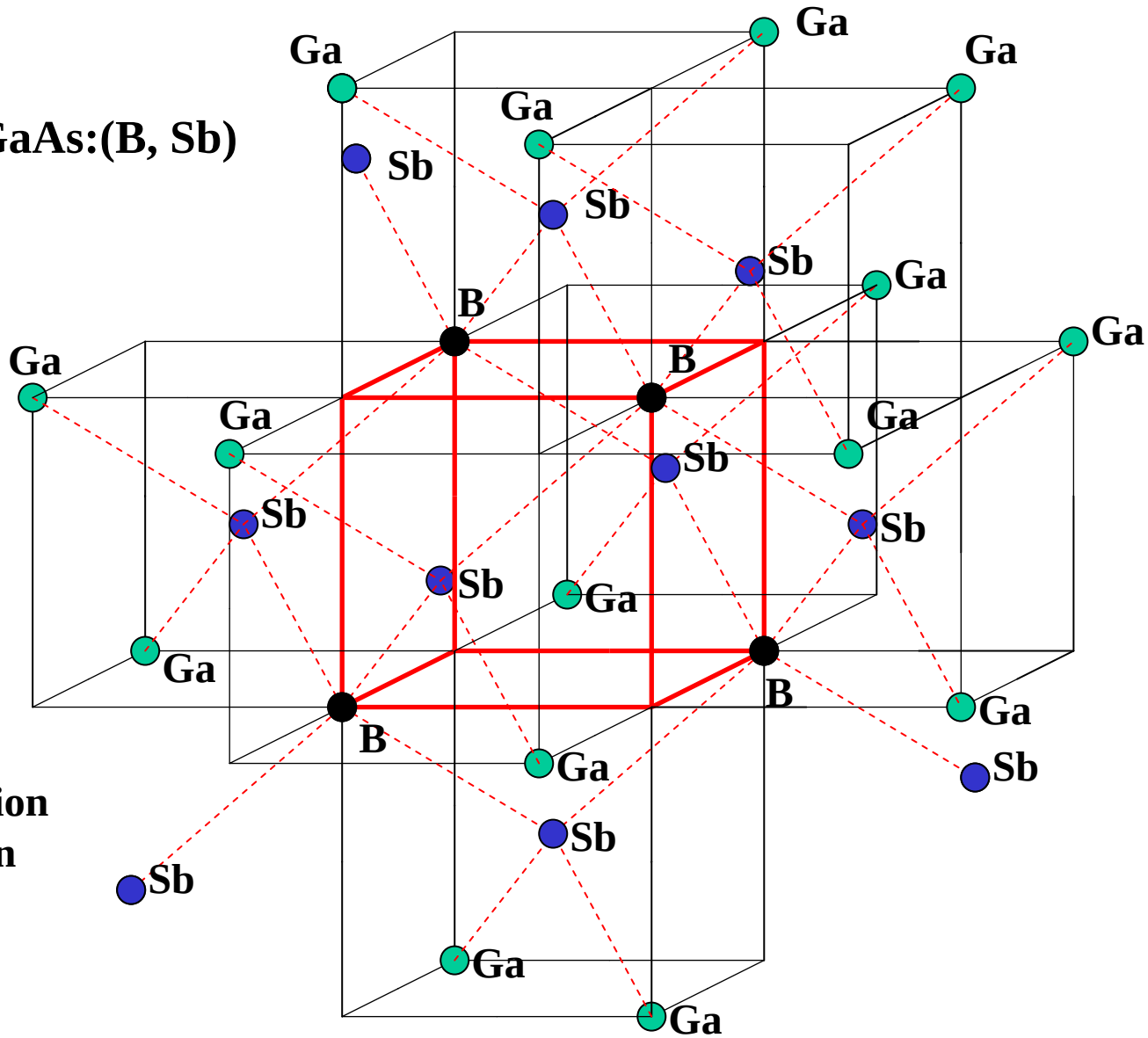
$B_{0.25}Ga_{0.75}Sb$
is chemical composition of 1B4Sb cluster in GaAs:(B, Sb)

$$E^{g}_{BSb} = 0.59eV, E^{g}_{BAs} = 1.46eV, E^{g}_{GaSb} = 0.72eV, E^{g}_{GaAs} = 1.44eV$$

4B10Sb cluster



4B10Sb cluster in GaAs:(B, Sb)



$B_{0.4}Ga_{0.6}Sb$ **is chemical composition of 4B10Sb cluster in GaAs:(B, Sb)**

Free energy of the cluster ordered GaAs-rich $B_xGa_{1x}Sb_yAs_{1-y}$

$$f = h_{Chem} + u_{Mech} - Ts_{Conf}$$

1. Chemical term - enthalpies of the constituent compounds

$$h_{Chem} = \Delta h^0(\alpha+\beta)(1-y)x + h^0_{\mathrm{GaAs}} + \left(h^0_{\mathrm{BSb}} - h^0_{\mathrm{GaSb}}\right)x + \left(h^0_{\mathrm{GaSb}} - h^0_{\mathrm{GaAs}}\right)y$$

$$\Delta h^0 = h^0_{\mathrm{BSb}} - h^0_{\mathrm{BAs}} - h^0_{\mathrm{GaSb}} + h^0_{\mathrm{GaAs}} = -1.86\times10^2\ \mathrm{kJ/mole}$$

2. Mechanical term - strain energy

$$u_{Mech} = u_{\mathrm{B}}(1-\alpha-\beta)x + u_{1\mathrm{B4Sb}}\alpha x + 0.25u_{4\mathrm{B10Sb}}\beta x + u_{\mathrm{Sb}}(y - 4\alpha x - 2.5\beta x)$$

$$\alpha = \frac{N_{1\mathrm{B4Sb}}}{N_{\mathrm{B}} + N_{1\mathrm{B4Sb}} + 4N_{4\mathrm{B10Sb}}} \qquad \beta = \frac{4N_{4\mathrm{B10Sb}}}{N_{\mathrm{B}} + N_{1\mathrm{B4Sb}} + 4N_{4\mathrm{B10Sb}}}$$

$u_{\mathrm{B}} = 8.472\times10^4\ \mathrm{J/mole}$ $\qquad$ $u_{\mathrm{Sb}} = 1.331\times10^4\ \mathrm{J/mole}$

$u_{1\mathrm{B4Sb}} = 4.735\times10^4\ \mathrm{J/mole}$ $\qquad$ $u_{4\mathrm{B10Sb}} = 8.778\times10^4\ \mathrm{J/mole}$

Valence force field model for crystals with the zinc blende structure

There are bond stretching (elastic constants of bonds) and bond bending (elastic constants of angles between bonds) constants

Deformation energies of a bond and an angle are given, respectively, as

$$u_{Bond} = \frac{3\alpha}{8R^2}\left(R^2 - r^2\right)^2$$

$$u_{Angle} = \frac{3\beta}{8R^2}\left(R^2\cos\varphi_0 - r^2\cos\varphi\right)^2$$

where $\alpha = \alpha(C_{11}, C_{12}, C_{44})$ and $\beta = \beta(C_{11}, C_{12}, C_{44})$ are the bond stretching and bond bending elastic constatnts, respectively; R and r are the undistorted and distorted distaces between the nearest atoms, respectively; φ and φ_0 are the undistorted and distorted angles between bonds, respectively.

3. Configurational entropy term

$$-Ts_{Conf} = RT(1-\beta)x\ln\frac{(1-\beta)x}{1-\beta x} + RT(1-x)\ln\frac{1-x}{1-\beta x}$$

$$+ RT(y-4\alpha x-2.5\beta x)\ln\frac{y-4\alpha x-2.5\beta x}{1-4\alpha x-2.5\beta x} + RT(1-y)\ln\frac{1-y}{1-4\alpha x-2.5\beta x}$$

$$+ RT(1-\alpha-\beta)x\ln\frac{1-\alpha-\beta}{1-\beta} + RT\alpha x\ln\frac{\alpha}{1-\beta}$$

$$+ 0.1RT\beta x\ln\frac{0.1\beta x}{0.074} + 0.074RT\ln\frac{0.074-0.1\beta x}{0.074}$$

Self-assembling of 1B4SB and 4B10SB clusters decreases the sum of the enthalpies of the constituent compounds, strain energy and configurational entropy. These diminutions depend on the impurity concentrations, temperature and cluster order parameters.

The transformation of clusters and isolated impurities (4B10Sb) → 2(1B4Sb) + 2(B) + 2(Sb) increases the sum of the enthalpies of the constituent compounds since it increases the B-Sb and Ga-As bond concentrations, decreases the strain energy and increases the configurational entropy.

The transformation (4B10Sb) + 6(Sb) → 4(1B4Sb) does not change the sum of the enthalpies of the constituent compounds, increases the strain energy and decreases the entropy.

Thus, self-assembling of clusters and transformations of clusters are competing processes.

Conclusions

1. GaAs:(B, Sb) is GaAs-rich $B_xGa_{1-x}Sb_yAs_{1-y}$ alloy
in which self-assembling of 1B4Sb and 4B10Sb clusters
reducing the free energy should occur
in the wide temperature and impurity content ranges.

2. If boron is a minority impurity 1B4Sb clusters should form only.

3. If the concentrations of the impurities are nearly equal or Sb is
a minority impurity self-assembling of 4B10Sb clusters
is strongly preferential.