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An Extended Version of the Regular Solution Model for Stoichiometric Phases and Ionic Melts

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Following the principles outlined in a recent work by Hillert and Staffansson general formulas for the integral and partial free energies are developed for ionic melts and stoichiometric phases of the type $(A_1, A_2 \cdots A_i \cdots A_n)_a$ $(C_1, C_2 \cdots C_i \cdots C_m)_c$. A detailed derivation is carried out for a phase $(A_1, A_2, A_3)_a$ $(C_1, C_2)_c$ and applied to the case where C_2 represents vacant sites in one of the sublattices.

Recently Hillert and Staffansson worked out a regular solution model for stoichiometric phases and ionic melts holding for two elements in one sublattice and two in the other. As there is a need for a model holding for a greater number of elements in the lattices, equations for the integral and partial free energies are derived for such cases using the principles outlined in the work of Hillert and Staffansson.[1]

1. Representation of composition. The coefficients a and c in a stoichiometric phase $(A_1, A_2 \cdots A_i \cdots A_n)_a$ $(C_1, C_2 \cdots C_j \cdots C_m)_c$ express the number of sites in each sublattice and for convenience one usually chooses $a + c = 1$. The number of moles n_{Ai} and n_{Cj} are related by the equation:

$$n_e = \frac{\sum n_{Ai}}{a} = \frac{\sum n_{Cj}}{c} \tag{1}$$

where n_e represents the size of the system.

In ionic melts the requirement of electroneutrality yields a similar relation:

$$n_e = \sum \frac{n_{Ai}}{a_i} = \sum \frac{n_{Cj}}{c_j} \tag{2}$$

where the quantities $1/a_i$ represent the valences of the A_i-atoms (*e.g.* cations) and $1/c_j$ represents the valences of the C_j-atoms (*e.g.* anions) and n_e is the number of equivalents.

It is usual to express the concentration of a certain element by its mol fraction:

$$X_{Ai} = \frac{n_{Ai}}{\sum n_{Ai} + \sum n_{Cj}}, \quad X_{Cj} = \frac{n_{Cj}}{\sum n_{Ai} + \sum n_{Cj}} \tag{3}$$

For an ionic melt the mol fractions often are defined separately for the cations and the anions:

$$Y_{A_i} = n_{A_i}/\sum n_{A_i},\ Y_{C_j} = n_{C_j}/\sum n_{C_j} \tag{4}$$

Alternatively, one may take into account the valences of the ions, thus obtaining:

$$Z_{A_i} = \frac{n_{A_i}/a_i}{\sum n_{A_i}/a_i} = \frac{n_{A_i}/a_i}{n_e},\ Z_{C_j} = \frac{n_{C_j}/c_j}{\sum n_{C_j}/c_j} = \frac{n_{C_j}/c_j}{n_e} \tag{5}$$

All these concentration parameters can be applied to the case of a stoichiometric phase by putting all a_i equal to a and all c_j equal to c. The following relationships are then obtained:

$$Z_{A_i} = Y_{A_i} = X_{A_i}\frac{a+c}{a} \tag{6}$$

$$Z_{C_j} = Y_{C_j} = X_{C_j}\frac{a+c}{c} \tag{7}$$

2. Ideal entropy of mixing. The model proposed by Temkin [2] gives:

$$-S^{ideal}/R = \sum n_{A_i} \ln Y_{A_j} + \sum n_{C_j} \ln Y_{C_j} \tag{8}$$

or by dividing with the size of the system n_e from eqn. (2):

$$-S_m^{ideal}/R = \sum a_i Z_{A_i} \ln Y_{A_i} + \sum c_j Z_{C_j} \ln Y_{C_j} \tag{9}$$

3. States of reference. In our system

$$(A_1)_{a_1}(A_2)_{a_2}\cdots(A_i)_{a_i}\cdots(A_n)_{a_n}(C_1)_{c_1}(C_2)_{c_2}\cdots(C_j)_{c_j}\cdots(C_m)_{c_m}$$

there is a natural reference state for each of the compounds $(A_i)_{a_i}(C_j)_{c_j}$ forming the system. The surface of the reference for the whole system thus cannot be of a simple planar type. The surface of reference is instead chosen as follows:

$$G_m^{ref} = \sum^{n} Z_{A_i} \sum^{m} Z_{C_j}\, {}^{\circ}G_{(A_i)_{a_i}(C_j)_{c_j}} \tag{10}$$

4. Power series representation of the excess free energy. According to a simple regular solution model, the expression for the excess free energy should depend upon the interaction between the various elements in each sublattice

$${}^{E}G_m = \sum_{1}^{n-1} Z_{A_i} \sum_{k=1}^{n-i} Z_{A_{i+k}} K_{A_iA_{i+k}} + \sum_{1}^{m-1} Z_{C_j} \sum_{l=1}^{m-j} Z_{C_{j+l}} K_{C_jC_{j+l}} \tag{11}$$

for $i+k \leq n$ and $j+l \leq m$.

The possible effect between the two sublattices may be described by the following concentration dependence of the K-values:

$$K_{A_iA_{i+k}} = \sum^{m} Z_{C_j} L_{A_iA_{i+k}}{}^{C_j} \tag{12}$$

$$K_{C_jC_{j+l}} = \sum^{n} Z_{A_i} L_{C_jC_{j+l}}{}^{A_i} \tag{13}$$

The partial quantities of the free energy now can be derived from eqns. (9), (10), and (11) using the fundamental relation:

$$\overline{G}_{(A_p)a_p(C_q)c_q} = G_m + \left(\frac{\partial G_m}{\partial Z_{A_p}}\right)_{Z_k} + \left(\frac{\partial G_m}{\partial Z_{C_q}}\right)_{Z_k} - \\ - \sum^{n} Z_{A_i}\left(\frac{\partial G_m}{\partial Z_{A_i}}\right)_{Z_k} - \sum^{m} Z_{C_j}\left(\frac{\partial G_m}{\partial Z_{C_j}}\right)_{Z_k} \quad (14)$$

where the subscript Z_k indicates that the contents of all the other components are kept constant. The remainder of this paper will be limited to the case where $n = 3$ and $m = 2$.

5. The integral and partial molar free energies in a phase consisting of three cations and two anions. For the case of $n = 3$ and $m = 2$ the following expression is obtained for the free energy by combining eqns. (9), (10), and (11):

$$G_m = \sum^{3} Z_{A_i} \sum^{2} Z_{C_j} {}^{\circ}G_{(A_i)a_i(C_j)c_j} + \sum^{2} Z_{A_i} \sum_{k=1}^{3-i} Z_{A_{i+k}} \sum^{2} Z_{C_j} L_{A_iA_{i+k}}{}^{C_j} \\ + \sum^{1} Z_{C_j} \sum_{l=1}^{2-j} Z_{C_{j+l}} \sum^{3} Z_{A_i} L_{C_jC_{j+l}}{}^{A_i} + \\ RT\left[\sum^{3} a_i Z_{A_i} \ln Y_{A_i} + \sum^{2} c_j Z_{C_j} \ln Y_{C_j}\right] = \\ Z_{A_1}Z_{C_1}{}^{\circ}G_{(A_1)a_1(C_1)c_1} + Z_{A_1}Z_{C_2}{}^{\circ}G_{(A_1)a_1(C_2)c_2} + Z_{A_2}Z_{C_1}{}^{\circ}G_{(A_2)a_2(C_1)c_1} \\ + Z_{A_2}Z_{C_2}{}^{\circ}G_{(A_2)a_2(C_2)c_2} + Z_{A_3}Z_{C_1}{}^{\circ}G_{(A_3)a_3(C_1)c_1} + \\ Z_{A_3}Z_{C_2}{}^{\circ}G_{(A_3)a_3(C_2)c_2} + Z_{A_1}Z_{A_2}Z_{C_1}L_{A_1A_2}{}^{C_1} + Z_{A_1}Z_{A_3}Z_{C_1}L_{A_1A_3}{}^{C_1} + Z_{A_2}Z_{A_3}Z_{C_1}L_{A_2A_3}{}^{C_1} \\ + Z_{A_1}Z_{A_2}Z_{C_2}L_{A_1A_2}{}^{C_2} + Z_{A_1}Z_{A_3}Z_{C_2}L_{A_1A_3}{}^{C_2} + Z_{A_2}Z_{A_3}Z_{C_2}L_{A_2A_3}{}^{C_2} \\ + Z_{C_1}Z_{C_2}Z_{A_1}L_{C_1C_2}{}^{A_1} + Z_{C_1}Z_{C_2}Z_{A_2}L_{C_1C_2}{}^{A_2} + Z_{C_1}Z_{C_2}Z_{A_3}L_{C_1C_2}{}^{A_3} \\ + RT(a_1Z_{A_1}\ln Y_{A_1} + a_2Z_{A_2}\ln Y_{A_2} + a_3Z_{A_3}\ln Y_{A_3} + \\ c_1Z_{C_1}\ln Y_{C_1} + c_2Z_{C_2}\ln Y_{C_2}) \quad (15)$$

Eqn. (14) now gives the expressions for the partial free energies:

$$\overline{G}_{(A_1)a_1(C_1)c_1} = {}^{\circ}G_{(A_1)a_1(C_1)c_1} + Z_{A_2}Z_{C_1}(\Delta G_{A_1} - \Delta G_{A_2}) + \\ Z_{A_3}Z_{C_2}(\Delta G_{A_1} - \Delta G_{A_3}) + RT[a_1\ln Y_{A_1} + c_1\ln Y_{C_1}] + \\ {}^{E}G_{(A_1)a_1(C_1)c_1} \quad (16)$$

where

$${}^{E}G_{(A_1)a_1(C_1)c_1} = Z_{A_2}Z_{C_2}[L_{A_1A_2}{}^{C_1} - L_{A_1A_2}{}^{C_2} + L_{C_1C_2}{}^{A_1} - L_{C_1C_2}{}^{A_2}] + \\ Z_{A_3}Z_{C_2}[L_{A_1A_3}{}^{C_1} - L_{A_1A_3}{}^{C_2} + L_{C_1C_2}{}^{A_1} - L_{C_1C_2}{}^{A_3}] + Z_{A_2}{}^{2}L_{A_1A_2}{}^{C_1} + \\ Z_{C_2}{}^{2}L_{C_1C_2}{}^{A_1} + Z_{A_3}{}^{2}L_{A_1A_3}{}^{C_1} + Z_{A_2}{}^{2}Z_{C_2}2[L_{A_1A_3}{}^{C_2} - L_{A_1A_3}{}^{C_1}] + \\ Z_{A_3}{}^{2}Z_{C_2}2[L_{A_1A_3}{}^{C_2} - L_{A_1A_3}{}^{C_1}] + Z_{A_3}Z_{C_2}{}^{2}2[L_{C_1C_2}{}^{A_3} - L_{C_1C_2}{}^{A_1}] + \\ Z_{A_3}Z_{C_2}{}^{2}2[L_{C_1C_2}{}^{A_3} - L_{C_1C_2}{}^{A_1}] + Z_{A_3}Z_{A_3}[L_{A_1A_2}{}^{C_1} + L_{A_1A_3}{}^{C_1} - L_{A_2A_3}{}^{C_1}] \\ + Z_{A_2}Z_{A_3}Z_{C_2}2[L_{A_2A_3}{}^{C_1} - L_{A_2A_3}{}^{C_2} - L_{A_1A_3}{}^{C_1} - L_{A_1A_2}{}^{C_1} + L_{A_1A_2}{}^{C_2} + L_{A_1A_3}{}^{C_2}] \quad (17)$$

ΔG_{A_1}, ΔG_{A_2} and ΔG_{A_3} are defined as follows:

$$\Delta G_{A_1} = {}^{\circ}G_{(A_1)_{a_1}(C_2)_{c_2}} - {}^{\circ}G_{(A_1)_{a_1}(C_1)_{c_1}} \tag{18}$$

$$\Delta G_{A_2} = {}^{\circ}G_{(A_2)_{a_2}(C_2)_{c_2}} - {}^{\circ}G_{(A_2)_{a_2}(C_1)_{c_1}} \tag{19}$$

$$\Delta G_{A_3} = {}^{\circ}G_{(A_3)_{a_3}(C_2)_{c_2}} - {}^{\circ}G_{(A_3)_{a_3}(C_1)_{c_1}} \tag{20}$$

The corresponding expressions for the partial free energies of the other five possible compounds are obtained by replacing the coefficients of eqn. (16) with those of interest.

6. Application to an interstitial and substitutional solution with three elements in the substitutional and one element and vacancies in the interstitial lattice. As shown in the preceding paper,[1] an interstitial solution can be treated as a stoichiometric phase if the vacant interstitial sites are treated as a component. We shall here consider the case where there are three components in the other sublattice. The phase may thus be denoted as $(A_1, A_2, A_3)_a(C, V)_c$. The partial free energies of such a phase can be obtained from eqn. (16) by the insertion of $a = a_1 = a_2 = a_3'$ and $c = c_1 = c_2$. However, it should be remembered that mol fractions are usually calculated without regarding the vacancies as a component. The relation between the mol fractions and the other concentration parameters will not be given by eqns. (6) and (7). Instead the following relations hold

$$Z_{A_i} = Y_{A_i} = \frac{X_{A_i}}{1 - X_C} \tag{21}$$

$$Z_C = Y_C = \frac{a}{c}\frac{X_C}{1 - X_C} \tag{22}$$

$$Z_V = Y_V = 1 - \frac{a}{c}\frac{X_C}{1 - X_C} \tag{23}$$

Furthermore, in order to make the free energy expressions hold for one mole of real material, they must be multiplied with $(1 - X_C)/a$. The quantity $(\bar{G}_{(A_i)_aV_c})/a$ is the partial free energy of a compound composed of A_i in the substitutional sublattice which in fact means the partial free energy of pure A_i. In order to obtain the partial free energy for the interstitial element we can consider the addition of $(A_i)_aC_c/c$ and the simultaneous removal of $(A_i)_aV_c/c$, thus obtaining

$$\bar{G}_C = \frac{1}{c}(\bar{G}_{(A_i)_aC_c} - \bar{G}_{(A_i)_aV_c}) \tag{24}$$

Three alternative expressions of this kind are obtained for $i = 1$, 2, and 3, respectively. The reference state of C thus could be defined as the corresponding difference between the reference states of the compounds, $({}^{\circ}G_{(A_i)_aC_c} - {}^{\circ}G_{(A_i)_aV_c})/c$. However, for convenience, we choose as the reference state this difference plus the constant $L_{CV}^{A_i}$ describing the interaction between C and vacancies in the interstitial sublattice when there is only A_i in the other sublattice. The reference state for C then will be:

$$({}^{\circ}G_{(A_i)aC_c} - {}^{\circ}G_{(A_i)aV_c})/c + L_{CV}{}^{A_i}/c \tag{25}$$

Principally, we can choose any value of i in defining the reference state for C but it is most suitable to choose the alternative corresponding to the base element (A_1). The following expressions for the integral and partial quantities are now obtained:

$$G_m = X_{A_1}\frac{{}^{\circ}G_{(A_1)aV_c}}{a} + X_{A_2}\frac{{}^{\circ}G_{(A_2)aV_c}}{a} + X_{A_3}\frac{{}^{\circ}G_{(A_3)aV_c}}{a} +$$

$$X_C\frac{{}^{\circ}G_{(A_1)aC_c} - {}^{\circ}G_{(A_1)aV_c}}{c} + \frac{X_{A_2}X_C}{(1-X_C)c}[\Delta G_{A_1} - \Delta G_{A_2}] +$$

$$\frac{X_{A_3}X_C}{(1-X_C)c}[\Delta G_{A_1} - \Delta G_{A_3}] + RT[X_{A_1}\ln Y_{A_1} + X_{A_2}\ln Y_{A_2} + X_{A_3}\ln Y_{A_3}] +$$

$$RT[X_C\ln Y_C + \left(\frac{c}{a} - X_C\frac{c+a}{a}\right)\ln(1-Y_C] + {}^{E}G_m \tag{26}$$

where

$$\begin{aligned}
{}^{a}{}^{E}G_m = {} & X_{A_1}Y_CY_{A_2}L_{A_1A_2}{}^{C} + X_{A_1}Y_CY_{A_3}L_{A_1A_3}{}^{C} + X_{A_1}(1-Y_C)Y_{A_2}L_{A_1A_2}{}^{V} + \\
& + X_{A_1}(1-Y_C)Y_{A_3}L_{A_1A_3}{}^{V} + X_{A_2}Y_CY_{A_2}L_{A_2A_3}{}^{C} + X_{A_2}(1-Y_C)Y_{A_3}L_{A_2A_3}{}^{V} \\
& + X_{A_1}Y_C(1-Y_C)L_{CV}{}^{A_1} + X_{A_2}Y_C(1-Y_C)L_{CV}{}^{A_2} + X_{A_3}Y_C(1-Y_C)L_{CV}{}^{A_3}
\end{aligned} \tag{27}$$

$$\begin{aligned}
\bar{G}_{A_1} = {} & {}^{\circ}G_{A_1} + RT\ln Y_{A_1} + RT\frac{c}{a}\ln(1-Y_C) + \\
& \frac{1}{a}\{Y_{A_2}Y_C(\Delta G_{A_2} - \Delta G_{A_1} + L_{A_1A_2}{}^{V} - L_{A_1A_3}{}^{C} + L_{CV}{}^{A_1} - L_{CV}{}^{A_2}) \\
& + Y_{A_3}Y_C(\Delta G_{A_3} - \Delta G_{A_1} + L_{A_1A_3}{}^{V} - L_{A_1A_3}{}^{C} + L_{CV}{}^{A_1} - L_{CV}{}^{A_3}) \\
& + Y_{A_2}{}^{2}L_{A_1A_2}{}^{V} + Y_{A_3}{}^{2}L_{A_1A_3}{}^{V} + Y_C{}^{2}L_{CV}{}^{A_1} + \\
& + Y_{A_2}{}^{2}Y_C2[L_{A_1A_3}{}^{C} - L_{A_1A_2}{}^{V}] + Y_{A_3}{}^{2}Y_C2[L_{A_1A_3}{}^{C} - L_{A_1A_3}{}^{V}] \\
& + Y_{A_2}Y_C{}^{2}2[L_{CV}{}^{A_2} - L_{CV}{}^{A_1}] + Y_{A_3}Y_C{}^{2}2[L_{CV}{}^{A_3} - L_{CV}{}^{A_1}] + \\
& Y_{A_2}Y_{A_3}[L_{A_1A_3}{}^{V} + L_{A_1A_2}{}^{V} - L_{A_2A_3}{}^{V}] + Y_{A_2}Y_{A_3}Y_C2[L_{A_2A_3}{}^{V} - L_{A_2A_3}{}^{C} - \\
& L_{A_1A_3}{}^{V} - L_{A_1A_2}{}^{V} + L_{A_1A_3}{}^{C} + L_{A_1A_3}{}^{C}]\}
\end{aligned} \tag{28}$$

$$\begin{aligned}
\bar{G}_{A_2} = {} & {}^{\circ}G_{A_2} + RT\ln Y_{A_2} + RT\frac{c}{a}\ln(1-Y_C) + \\
& \frac{1}{a}\{Y_{A_1}Y_C(\Delta G_{A_1} - \Delta G_{A_2} + L_{A_1A_2}{}^{V} - L_{A_1A_2}{}^{C} + L_{CV}{}^{A_2} - L_{CV}{}^{A_1}) + \\
& Y_{A_3}Y_C(\Delta G_{A_3} - \Delta G_{A_2} + L_{A_2A_3}{}^{V} - L_{A_2A_3}{}^{C} + L_{CV}{}^{A_2} - L_{CV}{}^{A_3}) + \\
& Y_{A_1}{}^{2}L_{A_1A_2}{}^{V} + Y_{A_2}{}^{2}L_{A_2A_3}{}^{V} + Y_C{}^{2}L_{CV}{}^{A_2} + \\
& Y_{A_1}{}^{2}Y_C2[L_{A_1A_3}{}^{C} - L_{A_1A_2}{}^{V}] + Y_{A_2}{}^{2}Y_C2[L_{A_2A_3}{}^{C} - L_{A_2A_3}{}^{V}] + \\
& Y_{A_1}Y_C{}^{2}2[L_{CV}{}^{A_1} - L_{CV}{}^{A_2}] + Y_{A_3}Y_C{}^{2}2[L_{CV}{}^{A_3} - L_{CV}{}^{A_2}] + \\
& Y_{A_1}Y_{A_3}[L_{A_1A_3}{}^{V} + L_{A_2A_3}{}^{V} - L_{A_1A_2}{}^{V}] + Y_{A_1}Y_{A_3}Y_C2[L_{A_1A_3}{}^{V} - \\
& - L_{A_1A_3}{}^{C} - L_{A_2A_3}{}^{V} - L_{A_1A_3}{}^{V} + L_{A_1A_3}{}^{C} + L_{A_2A_3}{}^{C}
\end{aligned} \tag{29}$$

$$\bar{G}_{A_3} = {}^{\circ}G_{A_3} + RT \ln Y_{A_3} + RT \frac{c}{a} \ln (1 - Y_C) +$$

$$\frac{1}{a}\{ Y_{A_1} Y_C (\Delta G_{A_1} - \Delta G_{A_3} + L_{A_1A_3}{}^{V} - L_{A_1A_3}{}^{C} + L_{CV}{}^{A_3} - L_{CV}{}^{A_1}) +$$

$$Y_{A_2} Y_C (\Delta G_{A_2} - \Delta G_{A_3} + L_{A_2A_3}{}^{V} - L_{A_2A_3}{}^{C} + L_{CV}{}^{A_3} - L_{CV}{}^{A_2}) +$$
$$+ Y_{A_2}{}^2 L_{A_2A_3}{}^{V} + Y_{A_1}{}^2 L_{A_1A_3}{}^{V} + Y_C{}^2 L_{CV}{}^{A_3} + Y_{A_2}{}^2 Y_C 2[L_{A_2A_3}{}^{C} - L_{A_2A_3}{}^{V}]$$
$$+ Y_{A_1}{}^2 Y_C 2[L_{A_1A_3}{}^{C} - L_{A_1A_3}{}^{V}] + Y_{A_2} Y_C{}^2 2[L_{CV}{}^{A_3} - L_{CV}{}^{A_2}] +$$
$$+ Y_{A_1} Y_C{}^2 2[L_{CV}{}^{A_1} - L_{CV}{}^{A_3}] + Y_{A_1} Y_{A_2}[L_{A_2A_3}{}^{V} + L_{A_1A_3}{}^{V} - L_{A_1A_2}{}^{V}] +$$
$$+ Y_{A_1A_2} Y_C 2[L_{A_1A_3}{}^{V} - L_{A_1A_3}{}^{C} - L_{A_1A_3}{}^{V} - L_{A_2A_3}{}^{V} + L_{A_2A_3}{}^{C} + L_{A_1A_3}{}^{C}]\} \quad (30)$$

$$\bar{G}_C = {}^{\circ}G_C + RT \ln \left[\frac{Y_C}{1 - Y_C} \right] +$$

$$\frac{1}{c}\{ -2 Y_C L_{CV}{}^{A_3} + Y_{A_2}(\Delta G_{A_1} - \Delta G_{A_3} + L_{A_1A_3}{}^{C} - L_{A_1A_2}{}^{V} + L_{CV}{}^{A_3} - L_{CV}{}^{A_1}) +$$

$$Y_{A_2}(\Delta G_{A_1} - \Delta G_{A_3} + L_{A_1A_3}{}^{C} - L_{A_1A_2}{}^{V} + L_{CV}{}^{A_3} - L_{CV}{}^{A_1}) +$$
$$2 Y_{A_2} Y_C [L_{CV}{}^{A_1} - L_{CV}{}^{A_3}] + 2 Y_{A_2} Y_C [L_{CV}{}^{A_1} - L_{CV}{}^{A_3}] +$$
$$Y_{A_2}{}^2 [L_{A_1A_3}{}^{V} - L_{A_1A_2}{}^{C}] + Y_{A_2}{}^2 [L_{A_1A_3}{}^{V} - L_{A_1A_3}{}^{C}] +$$
$$Y_{A_2} Y_{A_3} [L_{A_1A_3}{}^{V} + L_{A_2A_1}{}^{V} - L_{A_2A_3}{}^{V} + L_{A_2A_3}{}^{C} - L_{A_1A_3}{}^{C} - L_{A_1A_3}{}^{C}]\} \quad (31)$$

The reference state for C is chosen as

$${}^{\circ}G_C = \frac{1}{c}({}^{\circ}G_{(A_1)_a C_c} - {}^{\circ}G_{(A_1)_a V_c} + L_{CV}{}^{A_3}) \quad (32)$$

These equations will be used when studying equilibria where phases are involved containing one base element plus two more elements in the same sublattice and one in the other sublattice, for instance alloyed austenites, ferrites or non-stoichiometric carbides.

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