UDC 548.313

A GENERAL QUASICHEMICAL MODEL OF MINERAL DISORDERING*

L. M. Truskinovskiy, Yu. I. Sigalovskaya, E. E. Senderov and V. S. Urusov

Vernadskiy Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences, Moscow

The Yang-Li quasichemical model is extended to examine the details of order-disorder transitions in nonstoichiometric inorganic compounds containing crystallochemically nonequivalent positions. A crystal is represented as a set of atomic groups (quasimolecules or basic clusters), whose interactions are neglected in the free-energy calculation. Statistical calculations of the free energy and entropy involve solving a transcendental-equation system. The parameters are the number of positions in a cluster and two quantities with the dimensions of energy, which characterize the short-range and long-range interactions; the latter distinguishes this model from the analogous one for alloys, where the short-range interaction is decisive and there is no positional preference. The self-consistency condition is formulated as a criterion for cluster selection, with the aid of which numerous mineral and alloy structural types containing two types of cations that are disordered over two types of position have been classified.

Redistribution of atoms by structural positions is characteristic of most rock-forming minerals and is basic to geological thermobarometry [1, 2]. The positioning is completely ordered at low temperatures, with each type of atom occupying its own type of position and forming a sublattice. Disordering occurs as the temperature rises, with mixing of the atoms in a given sublattice; this continues until the proportions become comparable in each sublattice, which corresponds to complete disorder.

There are two types of order-disorder transition. The first occurs when the atoms occupy crystallochemically equivalent positions in a state of disorder, and then ordering splits a single regular point system into two (superlattice formation and crystal symmetry reduction). Examples are provided by disordering in binary alloys [3, 4], which at low temperatures represent superlattices in relation to the metal structures. There are also minerals [2] such as dolomite $(Ca, Mg)CO_3$, columbite-ixiolite $(Nb, Fe)O_2$, and the feldspars for which the cation positions become indistinguishable in a state of complete disorder. The second category includes disordering involving only some of the atoms, which shift between positions that remain distinguishable even with complete disorder; in that case, disordering can occur without symmetry change within a single phase. This is the type found in most minerals and their synthetic analogs: pyroxenes, amphiboles, melilites, olivines, spinels, etc. [1, 2].

In ordering of the first type, the main driving force is the tendency for an atom to surround itself with a maximum number of neighbors of another type. The main role here is played by nearest-neighbor interactions, which reduce to paired ones. On the other hand, in the second type, the cations differ in positional energy preference; this is due to the long-range forces (mean field).

---

*Translated from Geokhimiya, No. 11, pp. 1511-1526, 1987.

ISSN0016-7029/88/0006-0004$7.50/0

As the cations interact over long distances via anion screens, the short-range cation interaction is usually of secondary importance. In addition to semiempirical rules such as Lowenstein's principle [5], local electrical neutrality (bond valence-strength balance) [6], the need to incorporate how the bond lengths in the polyhedra are dependent on the mode of joining (Pauling's rule) [7], and the metal-metal interaction for transition elements in chalcogenide cluster structures [2] (such as millerite NiS or nickeline NiAs) indicate that the short-range interaction energy is often important.

Mineral disordering is usually discussed in terms of ideal or regular mixing models [1, 6, 8]. In that approximation, the cation position preference energies are incorporated, while the cations themselves are essentially considered as noninteracting. The cation distribution in each sublattice is taken as random, which can be interpreted as ignoring the short-range order. There are special methods for calculating the thermodynamic functions that incorporate the short-range order in radical form, i.e., in terms of exclusion principles [6, 9, 10], but these have limited application.

In an ordered alloy, where the position preference can be neglected, while the long-range order is entirely due to nearest-neighbor interaction, more rigorous statistical approaches are used to incorporate the long-range and short-range order. Kikuchi's cluster-variation method [11, 12] is the best, which is in essence an extension of the quasichemical method originally proposed by Bethe and Guggenheim [13, 14] and substantially extended by Yang and Li [15-17].

The zeroth approximation in the Kikuchi scheme amounts to the Bragg-Williams regular mixing model [3, 4], while the first corresponds to the classical quasichemical one.

Here we consider an extended quasichemical model for disordering in minerals having crystallochemically nonequivalent positions. The quasichemical model was first used for disorder in minerals (albite) by Senderov [18, 19], who introduced two energy parameters characterizing the cation-cation interaction (nearest-neighbor interaction energy ε_2) and the cation-crystal interaction (preference energy ε_1). One of the major results in [18] was the demonstration that the order-disorder transition in albite is sudden only for a certain $\varepsilon_2 \neq 0$, i.e., has the observed features; the ideal-mixing model having $\varepsilon_2 \equiv 0$, with short-range order ignored, does not predict the transition type even qualitatively.

Here Senderov's model is extended to two-position disordering in a general structure; as in [18], the Yang-Li method is used [15-17]. Although the convergence in this method considered as a successive-approximation one is somewhat worse than in Kikuchi's general one, the method is much simpler, because there are fewer variables to be determined.

The energy can be calculated more exactly in Kikuchi's method because there is substantial basic-cluster overlap. This refinement was necessary for alloys, but it is less significant for minerals, where the main energy is related to position differences, while nearest-neighbor cation interactions are subordinate.

REGULAR-MIXING MODEL: AVERAGE-FIELD APPROXIMATION

Let us consider a mineral lattice containing N atomic positions, over which the cations or anions are disordered; there are crystallochemically nonequivalent positions of two types α and β in amounts correspondingly of cN and $(1 - c)N$. These positions are taken by A and B cations, which can replace one another, and where the number of B cations is xN and that of A ones is $(1 - x)N$.

The position differences are characterized by the filling energies when the configuration energy is written for the given atomic distribution in the form $E = E_0 + E_1$, where

$$E_0 = N_A^\alpha \varepsilon_A^\alpha + N_A^\beta \varepsilon_A^\beta + N_B^\alpha \varepsilon_B^\alpha + N_B^\beta \varepsilon_B^\beta, \quad (1)$$

$$E_1 = N_{AA} \varepsilon_{AA} + N_{AB} \varepsilon_{AB} + N_{BB} \varepsilon_{BB}. \quad (2)$$

Here N_j^i is the number of atoms of type j in position i, ε_j^i is the energy related to cation j filling position i ($j = A$ or B and $i = \alpha$ or β), and N_{KK} and ε_{KK} are the numbers of corresponding nearest-neighbor pairs and their energies ($K = A$ or B). The E_1 term is due to the disordering-cation pair interactions.

Statistical thermodynamics [20] gives the configurational free energy as

$$F(x, T) = -kT \ln\left(\sum_{\{\sigma\}} e^{-\frac{E\{\sigma\}}{kT}}\right) = -kT \ln Z(x, T), \tag{3}$$

where T is temperature, k Boltzmann's constant, and Z the statistical sum. The summation in (3) is taken over all microstates denoted by $\{\sigma\}$, i.e., over all fillings for the positions by A and B, while $E\{\sigma\}$ is the microstate energy.

The summation in (3) may be carried through in two stages. We introduce the long-range order parameter w*, which is the proportion of B atoms in α positions. Then

$$Z(x, T) = \sum_{|w} \left[\sum_{\{\sigma\}_w} \exp(-E\{\sigma\}_w/kT)\right],$$

where the summation within the brackets is taken over all microstates having the given value for w. We denote the expression in brackets as $\tilde{Z}(w, x, T)$ to get

$$Z(x, T) = \sum_{w} e^{-\frac{\tilde{F}(w,x,T)}{kT}}, \tag{4}$$

where $\tilde{F}(w, x, T) = -kT \ln \tilde{Z}$. Usually, as N is large ($N \sim 10^{23}$) the summation in (4) is replaced by defining the maximal term [20], i.e., by calculating the equilibrium value $\bar{w}(x, T)$ from the condition

$$\partial \tilde{F}(w, x, T)/\partial w = 0, \tag{5}$$

where we put $F(x, T) = \tilde{F}(\bar{w}(x, T), x, T)$.

Regular-solution theory gives a simple approximation for $\tilde{F}(w, x, T)$ [20], where it is assumed that all the terms in

$$\sum_{\{\sigma\}_w} \exp(-E\{\sigma\}_w/kT)$$

are identical, since all states with the given w are equally probable and the distribution over the positions may be taken as random. Then

$$\tilde{F}_R(w, x, T) = -kT \ln\left[g_\infty(w, x, T)\, e^{-\frac{\tilde{E}_R(w,x,T)}{kT}}\right], \tag{6}$$

where

---

*Parameter w can vary over the following ranges:

$$\text{ordering region} \begin{cases} 0 \leqslant w \leqslant c, \text{ for } 0 \leqslant x \leqslant 1-c, \\ \dfrac{x-(1-c)}{x} \leqslant w \leqslant c, \text{ for } 1 \geqslant x > 1-c. \end{cases}$$

$$\text{anti-ordering region} \begin{cases} c \leqslant w \leqslant c/x, \text{ for } c < x \leqslant 1, \\ c \leqslant w \leqslant 1, \text{ for } c \geqslant x \geqslant 0. \end{cases}$$

$$g_\infty(\omega, x, T) = \frac{(N_A^\alpha + N_B^\alpha)!}{N_A^\alpha!\, N_B^\alpha!} \cdot \frac{(N_A^\beta + N_B^\beta)!}{N_A^\beta!\, N_B^\beta!} - \tag{7}$$

is the total number of permutations over the sublattices for a given ω,

$$N_B^\alpha = \omega x N,\ N_B^\beta = (1-\omega)\, xN,\ N_A^\alpha = cN - \omega x N,$$
$$N_A^\beta = (1-c)\, N - (1-\omega)\, xN. \tag{8}$$

From (7) and (8), the expression for the entropy $\hat{S}^{id} = k \ln g_\infty$ can be transformed by means of Stirling's formula to

$$\begin{aligned}\tilde{S}^{id}(\omega, x, T) = kN \{&c \ln c + (1-c) \ln (1-c) - x\omega \ln x\omega - \\ &- (1-\omega)\, x \ln (1-\omega)\, x - (c - \omega x) \ln (c - \omega x) - \\ &- [1 - c - (1-\omega)\, x] \ln [1 - c - (1-\omega)\, x]\}.\end{aligned} \tag{9}$$

To calculate $\tilde{E}_R(\omega, x, T)$ we have to use (1) and (2); we combine (1), (2) and (8) to get

$$\begin{aligned}\tilde{E}_{OR}(\omega, x, T) = {}& \omega x N\, (\varepsilon_B^\alpha - \varepsilon_B^\beta - \varepsilon_A^\alpha + \varepsilon_A^\beta) + xN\, (\varepsilon_B^\beta - \varepsilon_A^\beta) + \\ &+ cN\, (\varepsilon_A^\alpha - \varepsilon_A^\beta) + N\varepsilon_A^\beta,\end{aligned}$$

$$\begin{aligned}\tilde{E}_{1R}(\omega, x, T) = {}& \frac{N}{2} \{[c\, (z_\alpha - z_\beta) + z_\beta]\, \varepsilon_{AA} + x\, [\omega\, (z_\beta - z_\alpha) - \\ &- z_\beta]\, (\varepsilon_{AA} - \varepsilon_{BB})\} + \left[\varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})\right] N_{AB},\end{aligned} \tag{10}$$

where we have used the identities

$$2N_{BB} + N_{AB} = z_\alpha N_B^\alpha + z_\beta N_B^\beta,\ 2N_{AA} + N_{AB} = z_\alpha N_A^\alpha + z_\beta N_A^\beta; \tag{11}$$

with z_α, and z_β the coordination numbers of the corresponding positions*.

Let us assume that out of the z_α nearest neighbors of an α position, $z_{\alpha\alpha}$ correspond to α positions and $z_{\alpha\beta}$ to β ones. We introduce $z_{\beta\beta}$ and $z_{\beta\alpha}$ similarly and assume that there are no correlations to get [21]

$$\begin{aligned}N_{AB}^{id} = {}& N\, (c - \omega x) \left[z_{\alpha\alpha} \frac{\omega x}{c} + z_{\alpha\beta} \frac{(1-\omega)\, x}{1-c}\right] + \\ &+ N\, [1 - c - (1-\omega)\, x] \left[z_{\beta\alpha} \frac{\omega x}{c} + z_{\beta\beta} \frac{(1-\omega)\, x}{1-c}\right].\end{aligned} \tag{12}$$

We combine (10)-(12) to get an expression quadratic in ω for $\tilde{E}_R$, which is characteristic of regular-mixing models [3, 4, 10]. The coefficient to ω^2 is

$$\frac{x^2 N}{c\,(1-c)} [z_{\beta\alpha} - z_{\alpha\alpha} + c\,(z_\alpha - z_\beta)] \left[\varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})\right],$$

and is naturally called the nonideality parameter. This parameter arises because of nearest-neighbor interactions; for

$$\varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB}) = 0$$

the mixing may be considered as ideal.

*We have in mind the nearest neighbors, namely cations participating in the disordering.

Equilibrium equation (5) takes the following form in the regular-mixing approximation:

$$kT \ln \frac{(1-w)(c-wx)}{w[1-c-(1-w)x]} = E_1 + wE_2,$$

where

$$E_1 = \varepsilon_1 + \varepsilon_3 - z_\alpha \varepsilon_2 - x\varepsilon_2 \frac{z_{\beta\beta} - z_{\alpha\beta}}{1-c},$$

$$E_2 = \frac{\varepsilon_2 x}{c(1-c)} [z_{\beta\alpha} - z_{\alpha\alpha} + c(z_\alpha - z_\beta)].$$

The physical meanings of the energy parameters

$$\varepsilon_1 = \varepsilon_B^\alpha + \varepsilon_A^\beta - \varepsilon_A^\alpha - \varepsilon_B^\beta,$$

$$\varepsilon_2 = \varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB},$$

$$\varepsilon_3 = z_\alpha \varepsilon_{BB} + z_\beta \varepsilon_{AA} - (z_\alpha + z_\beta)\varepsilon_{AB}$$

will be defined below, and we merely note that there will be a transition from disorder to order or antiorder (see footnote 1) correspondingly for ($\varepsilon_2 > 0$) as the temperature is reduced:

$$\frac{\varepsilon_1}{\varepsilon_2} + \frac{\varepsilon_3}{\varepsilon_2} \gtrless z_\alpha + \frac{x}{1-c}\left[(1-c)z_\alpha + (1+c)z_\beta + 2\frac{z_{\beta\alpha}}{c}\right].$$

GENERALIZED QUASICHEMICAL MIXING MODEL

The average-field approximation results can be improved on by applying analogous arguments not to a single atom but to a group. To calculate $\tilde{Z}(w, x, T)$ more exactly, we split up the crystal into M identical groups (clusters), each of which contains m positions: there are sm α positions and $(1-s)m$ β ones. Clearly, there are 2^m different fillings with A and B atoms. Each such filling can be characterized by a set of zeros and ones: $(q_1, \ldots, q_m)$ where $q_i = 0$ if an A atom occurs in position i and $q_i = 1$ if a B atom does. Any array is characterized by the set of numbers ξ_a, $a = 1, \ldots, 2^m$, where $\xi_a M$ is the number of groups of a given type characterized by the subscript a, where the numbers q_i^a $(i = 1, \ldots, m)$ specify the group types completely. Then the statistical sum can be put as

$$\tilde{Z}(w, x, T) = \sum_{\{\xi_a\}_w} e^{-\frac{E\{\xi_a\}_w}{kT}} g(\{\xi_a\}_w, w, x, T), \tag{13}$$

where the summation is over all sets $\{\xi_a\}_w$, compatible with the specified w.

This means that the ξ_a should satisfy the constraints

$$\sum_{a=1}^{2^m} \xi_a = 1, \quad \sum_{a=1}^{2^m} q_i^a \xi_a = b_i. \tag{14}$$

Here $b_1, \ldots, b_{sm}$ are the group proportions in which the α positions with numbers $i = 1, \ldots, sm$ are occupied by B atoms (these are equal to the proportions of α positions in the crystal occupied by B atoms), and similarly we have $b_{sm+1}, \ldots, b_m$ for the β positions having $i = sm+1, \ldots, m$. Then

$$b_1 = \ldots = b_{sm} = wx/c, \quad b_{sm+1} = \ldots = b_m = (1-w)x/(1-c).$$

The main assumption that allows us to arrive at (13) is that the energy is the same for all microstates belonging to the class $\{\xi_a\}_w$. The numbers ξ_a act as internal degrees of freedom, which take the values $\tilde{\xi}_a(w, x, T)$ at equilibrium. The function $g(\{\xi_a\}_w, w, x, T)$ characterizes the degeneracy in state class $\{\xi_a\}_w$, being equal to the number of microstates having the given macroparameter set ξ_a.

The $\tilde{\xi}_a$ are defined from the minimum free-energy condition (summation in (13) is replaced by defining the largest term):

$$\tilde{F}(\{\xi_a\}_w, w, x, T) = E\{\xi_a\}_w - kT \ln g(\{\xi_a\}_w) \tag{15}$$

subject to (14); Lagrange multipliers give us an equation family for the functions $\tilde{\xi}_a(w, x, T)$:

$$\partial\Lambda/\partial\xi_a = 0,\ \partial\Lambda/\partial\mu_i = 0,\ \partial\Lambda/\partial\eta = 0, \tag{16}$$

where

$$\Lambda(\xi_a, \mu_i, \eta) = \tilde{F} - \sum_i \mu_i \left(\sum_a \xi_a q_i^a - b_i\right) - \eta\left(\sum_a \xi_a - 1\right)$$

is the Lagrange function, with μ_i $(i=1, \ldots, m)$; and η the Lagrange multipliers, whose number is equal to the number of constraints in (14). We can now determine the equilibrium $\tilde{\xi}_a$ if the functions $g(\{\xi_a\}_w)$, and $E(\{\xi_a\}_w)$ are known.

The classical quasichemical method [13, 14] is based on the assumption that $g(\{\xi_a\}_w)$ is proportional to the total number of permutations for the M groups. Following the Yang-Li method [15-17], we put

$$g(\{\xi_a\}_w) = g_0(w, x, T)\left[\frac{M!}{\prod_a (\xi_a M)!}\right]^{\lambda}. \tag{17}$$

If the groups do not intersect, the coefficients $g_0(w, x, T)$ and λ are one, whereas if there are positions common to several groups, the number of positions in the group set exceeds the number in the structure. As we consider only cation pair interactions, we take λ as equal to the ratio of the number of pairs in the crystal to the number of pairs in the group set. The factor $g_0(w, x, T)$ occurs because we certainly increase the number of microstates corresponding to the given $\{\xi_a\}_w$ set when we enumerate all group permutations: in fact, out of the total group permutations, the only real ones are those in which the cations common to several groups are identical in all of these (Fig. 1). Then $g_0(w, x, T)$ is a normalization, and the value is given by the condition

$$g_0(w, x, T) \sum_{\{\xi_a\}_w} \left[\frac{M!}{\prod_a (\xi_a M)!}\right]^{\lambda} = g_\infty(w, x, T). \tag{18}$$

By e_a we denote the energy of a type a group. The group set energy can be put as

$$E(\{\xi_a\}_w) = M \sum_a \xi_a e_a.$$

We combine (15) and (17) and use Stirling's formula to get the free energy

$$\tilde{F}(\{\xi_a\}_w, w, x, T) = -kT \ln g_0 + \lambda M \left[\sum_a \frac{e_a}{\lambda} \xi_a + kT \sum_a \xi_a \ln \xi_a \right]. \tag{19}$$

As

$$\sum_a \xi_a \left(\frac{e_a}{\lambda} + kT \ln \xi_a \right)$$

is the energy per molecule in an ideal gas mixture consisting of 2^m kinds of molecules having concentrations ξ_a, $\sum_a \xi_a = 1$ and the energies e_a/λ and $a = 1, \ldots, 2^m$, then the equilibrium $\tilde{\xi}_a$ are determined from the equilibrium composition subject to (14), which can be reformulated in terms of the corresponding reactions. If we take q_i^a to be the number of type i particles, conditions (14) correspond to particle conservation for each type in the mixture*.

We substitute (10) into (16), and with (14) (the result of minimizing Λ with respect to η and μ_1) we get

$$kT \ln \tilde{\xi}_a = \left(\frac{\eta}{\lambda M} - kT \right) + \sum_{i=1}^{m} \frac{\mu_i}{\lambda M} q_i^a - \frac{e_a}{\lambda}.$$

We redefine the Lagrange multipliers and retain the old symbols to get finally

$$\tilde{\xi}_a = \eta \prod_{i=1}^{m} \mu_i^{q_i^a} e^{-\frac{e_a}{\lambda kT}}. \tag{20}$$

Let us now calculate $g_0(w, x, T)$. We replace the sum in (18) by the maximum term and determine the functions $\tilde{\xi}_a^*(w, x, T)$, and the condition for a turning point in

$$\left[M! \Big/ \prod_a (\xi_a M)! \right]^{\lambda}$$

is used with (14). This task clearly amounts to the one solved previously subject to the condition that the energies e_a are equated to zero in (20). Then the result can be written at once:

$$\tilde{\xi}_a^* = \eta^* \prod_{i=1}^{m} \mu_i^{*q_i^a}, \tag{21}$$

where the Lagrange multiplers η^*, and μ_i^* are defined by

$$\eta^* \sum_a \prod_i \mu_i^{*q_i^a} = 1, \quad \eta^* \sum_a \prod_i \mu_i^{*q_i^a} \cdot q_j^a = b_j. \tag{22}$$

As in the case $e_a \neq 0$, there is a unique solution, and this time it can be written out explicitly. We introduce

$$\varphi(\mu_1^*, \ldots, \mu_m^*) = \sum_a \prod_i \mu_i^* q_i^a.$$

*This analogy between groups and molecules in a gas mixture is responsible for the term quasichemical approximation.

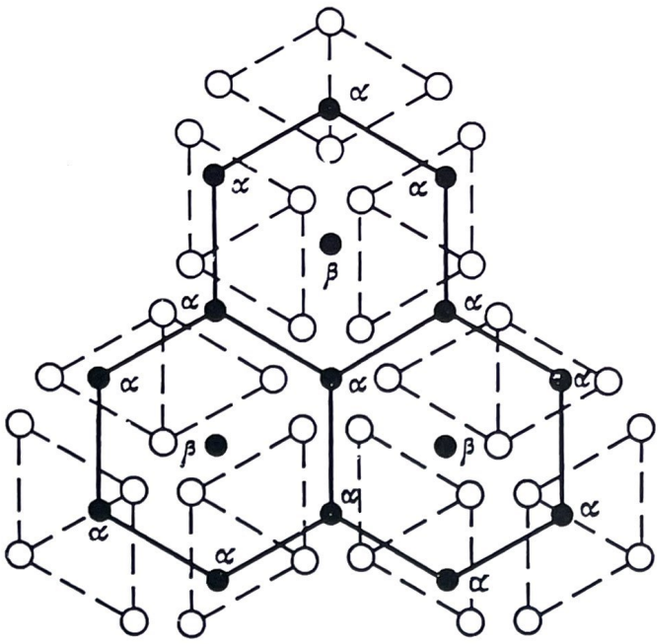

Fig. 1. Representation of a crystal as a group set. One possible decomposition of a hexagonal planar lattice is given (m = 4, c = 1/3, s = 1/4). Each α position belongs to six groups (k_α = 6), and each β position to three (k_β = 3). The number of pairs in the group set is related to the number of pairs in the crystal as 4:3 ($\lambda=3/4$, $M=N$, $z_\alpha=z_\beta=6$, $p=4$).

Then (22) is rewritten as

$$\eta^*\varphi = 1, \quad \eta^* (\partial\varphi/\partial\mu_i^*)\,\mu_i^* = b_i.$$

We note that

$$\varphi = \prod_i (1 + \mu_i^*),$$

so finally

$$\mu_i^* = b_i/(1 - b_i), \quad \eta^* = \prod_i (1 - b_i).$$

We then have everything necessary for calculating $\tilde{Z}(w, x, T)$, $\tilde{F}(w, x, T)$ and $\tilde{S}(w, x, T)$. We substitute (18) and (17) into (13) and restrict ourselves to the maximum term on summation. Then

$$\tilde{Z}(w, x, T) = g_\infty(w, x, T)\left[\prod_a \frac{(\tilde{\xi}_a M)!}{(\tilde{\xi}_a^* M)!}\right]^\lambda \exp\left(-M\sum_a \frac{\tilde{\xi}_a e_a}{kT}\right) =$$
$$= \exp\left(-\frac{\tilde{S}}{k} - M\sum_a \frac{\tilde{\xi}_a e_a}{kT}\right).$$

The crystal entropy S can be represented from Stirling's formula as

$$\tilde{S}(w, x, T) = \tilde{S}^{id} + \tilde{S}^{ex},$$

where $\tilde{S}^{id}$ is given by (9) and

$$\tilde{S}^{ex}(w, x, T) = -\lambda kM \sum_a (\tilde{\xi}_a \ln \tilde{\xi}_a - \tilde{\xi}^*_a \ln \tilde{\xi}^*_a). \tag{23}$$

We combine (9), (21) and (23) to get

$$\tilde{S}(w, x, T) = \tilde{S}^{id}_\alpha \left(1 - \lambda \frac{sMm}{cN}\right) + \tilde{S}^{id}_\beta \left(1 - \lambda \frac{(1-s)Mm}{(1-c)N}\right) - \lambda kM \sum_a \tilde{\xi}_a \ln \tilde{\xi}_a. \tag{24}$$

Here $\tilde{S}^{id}_\alpha$ and $S^{id}_\beta = \tilde{S}^{id} - \tilde{S}^{id}_\alpha$ are the ideal mixing entropies for the A and B cations in the α and β sublattices, which are correspondingly

$$\begin{aligned} \tilde{S}^{id}_\alpha(w, x, T) &= kN\,[c \ln c - wx \ln wx - (c - wx) \ln (c - wx)], \\ \tilde{S}^{id}_\beta(w, x, T) &= kN\,\{(1-c) \ln (1-c) - (1-w)\,x \ln (1-w)\,x - \\ &\quad - [1 - c - (1-w)\,x] \ln [1 - c - (1-w)\,x]\}. \end{aligned} \tag{25}$$

When the ratio of the numbers of α and β positions in the group set is as in the crystal, i.e., when $s = c$, (24) simplifies to

$$\tilde{S}(w, x, T) = (1 - \tilde{\lambda})\,\tilde{S}^{id} - \lambda kM \sum_a \tilde{\xi}_a \ln \tilde{\xi}_a. \tag{26}$$

It follows from (26) that for

$$\tilde{\lambda} = \lambda \frac{sMm}{cN},$$

close to one, the crystal entropy approximates to that of an ideal gas mixture consisting of molecules characterized by the indices $a = 1, \ldots, 2^m$ (the Bethe-Guggenheim hypothesis). In the other limiting case ($\lambda \to 0$), we get the entropy of an ideal distribution over the positions, i.e., the usual ideal or regular mixing approximation.

From (20) we get the final expression for the free energy:

$$\tilde{F}(w, x, T) = -kT \ln g_0 + \lambda kMT \left[\ln \eta + \sum_i b_i \ln \mu_i\right]. \tag{27}$$

Here

$$k \ln g_0 = (1 - \tilde{\lambda})\,\tilde{S}^{id}_\alpha + (1 - \tilde{\lambda}')\,\tilde{S}^{id}_\beta, \quad \tilde{\lambda}' = \lambda \frac{(1-s)Mm}{(1-c)N}.$$

In the particular case $c = s$, (27) with $k \ln g_0 = (1 - \tilde{\lambda})\,\tilde{S}^{id}$ was derived in [16], where a method different from but equivalent to ours was used.

To determine the equilibrium value of $\bar{w}(x, T)$ it is necessary to equate the derivative of (27) with respect to w to zero; by virtue of (14),

$$\frac{\partial}{\partial w} \ln \eta = -\sum_i b_i \frac{\partial}{\partial w} \ln \mu_i,$$

we get

$$\left[\prod_{i=1}^{sm} \mu_i^{1/c} \Big/ \prod_{i=sm+1}^{m} \mu_i^{1/(1-c)}\right] = \left[\frac{c - wx}{wx}\right]^{\left(\frac{1-\tilde{\lambda}}{\lambda}\right)\frac{N}{M}} \left[\frac{(1-w)\,x}{1 - c - (1-w)\,x}\right]^{\left(\frac{1-\tilde{\lambda}'}{\lambda}\right)\frac{N}{M}}. \tag{28}$$

We combine (28) with (14),

$$\frac{\sum_a \exp\left(-\frac{e_a}{kT}\right)\prod_i \mu_i^{q_i^a} q_j^a}{\sum_a \exp\left(-\frac{e_a}{kT}\right)\prod_i \mu_i^{q_i^a}} = \begin{cases} \frac{wx}{c}, & j=1, \ldots, sm \\ \frac{(1-w)x}{1-c}, & j=sm+1, \ldots, m, \end{cases} \tag{29}$$

to get a system composed of $m+1$ nonlinear equations containing the $m+1$ unknowns μ_i $(i=1, \ldots, m)$ and w, which is involved in determining $w(x, T)$ in this approximation.

GROUP ENERGY CALCULATION AND DECOMPOSITION CRITERION

By analogy with (1) and (2), the energy e_a of a group, $a=1, \ldots, 2^m$ can be represented as the sum of two components: e_{0a}, the energy due to the cations taking the position in the lattice and e_{1a}, the energy of the nearest-neighbor cation pair interactions:

$$e_{0a} = {}^{(a)}m_A^\alpha \varepsilon_A^\alpha + {}^{(a)}m_B^\alpha \varepsilon_B^\alpha + {}^{(a)}m_A^\beta \varepsilon_A^\beta + {}^{(a)}m_B^\beta \varepsilon_B^\beta, \tag{30}$$

$$e_{1a} = {}^{(a)}m_{AA}\varepsilon_{AA} + {}^{(a)}m_{AB}\varepsilon_{AB} + {}^{(a)}m_{BB}\varepsilon_{BB}. \tag{31}$$

Here ${}^{(a)}m_j^i$ is the number of j cations in i positions in group a, ${}^{(a)}m_{jk}$ being the number of corresponding pairs in group a $(j, k=A, B;\ i=\alpha, \beta,\ a=1, \ldots, 2^m)$.

There are relations between ${}^{(a)}m_j^i$:

$${}^{(a)}m_A^\alpha + {}^{(a)}m_B^\alpha = sm,\ {}^{(a)}m_A^\beta + {}^{(a)}m_B^\beta = (1-s)m;$$

and

$${}^{(a)}m_B^\alpha = \sum_{i=1}^{sm} q_i^a,\ {}^{(a)}m_B^\beta = \sum_{i=sm+1}^{m} q_i^a.$$

We substitute these into (30) to get

$$e_{0a} = e_{00} + e_{10}\sum_{i=1}^{m} q_i^a + \varepsilon_1 \sum_{i=1}^{sm} q_i^a,$$

where $\varepsilon_1 = \varepsilon_B{}^\alpha + \varepsilon_A{}^\beta - \varepsilon_A{}^\alpha - \varepsilon_B{}^\beta$ is the energy of the exchange reaction

$$A_\alpha + B_\beta \rightleftarrows B_\alpha + A_\beta,$$

$$\varepsilon_{10} = \varepsilon_B^\beta - \varepsilon_A^\beta,\ \varepsilon_0 = m[s\varepsilon_A^\alpha + (1-s)\varepsilon_A^\beta]. \tag{32}$$

Let us now calculate the group-set energy E_0. As each i position belongs simultaneously to k_i groups, we have

$$\tilde{E}_0 = M\sum_a \tilde{\xi}_a \left[\left(\sum_{i=1}^{sm}\frac{1}{k_i}\right)\varepsilon_A^\alpha + \left(\sum_{i=sm+1}^{m}\frac{1}{k_i}\right)\varepsilon_A^\beta + \right.$$
$$\left. + \left(\sum_{i=1}^{sm}\frac{q_i^a}{k_i}\right)\varepsilon_1 + \left(\sum_{i=1}^{m}\frac{q_i^a}{k_i}\right)\varepsilon_{10}\right].$$

We note that

$$M\sum_{i=1}^{sm}(1/k_i)=cN,\ M\sum_{i=sm+1}^{m}(1/k_i)=(1-c)N,$$

which gives $\tilde{E}_0=\tilde{E}_{0R}(w, x, T)$ (see (10)). Then E_0 is independent of $\tilde{\xi}_a$, so we can extract the factor $\exp[-\tilde{E}_0(w, x, T)/kT]$ for the summation in (13) and take the energy

$$E(\{\xi_a\}_w)=M\sum_a \tilde{\xi}_a e_a$$

in (15) as entirely due to the pair cation interactions ($e_a\equiv e_{1a}$).

We now calculate $\tilde{E}_1$. As

$$^{(a)}m_{BB}+{}^{(a)}m_{AB}=\sum_{i=1}^{m}q_i^a z_i,$$

where z_i is the number of nearest cation neighbors of position i in a group (the coordination number), we have

$$e_{1a}={}^{(a)}m_{AA}\varepsilon_2+\sum_{i=1}^{m}q_i^a z_i(\varepsilon_{BB}-\varepsilon_{AB})+p(2\varepsilon_{AB}-\varepsilon_{BB}).$$

Here p is the total number of pairs in a group and $\varepsilon_2=\varepsilon_{AA}+\varepsilon_{BB}-2\varepsilon_{AB}$ is the energy of the reaction between pairs

$$AA+BB\rightleftarrows 2AB. \tag{33}$$

A superlattice tends to arise if $\varepsilon_2>0$. Transferring to the group set*, we have

$$\tilde{E}_1=\lambda M\sum_a\tilde{\xi}_a e_{1a}=\lambda M(\tilde{E}_1'+\tilde{E}_1''),$$

$$\tilde{E}_1'=\left(\sum_a\tilde{\xi}_a^{(a)}m_{AA}\right)\varepsilon_2,$$

$$\tilde{E}_1''=\left(\sum_i b_i z_i\right)(\varepsilon_{BB}-\varepsilon_{AB})+p(2\varepsilon_{AB}-\varepsilon_{BB}).$$

As $\tilde{E}_1''$ is independent of $\tilde{\xi}_a$, we can extract $\exp(-\tilde{E}_1''\lambda M/kT)$ as a factor from the sum in (13). The groups' energy can thus be taken as $\tilde{E}_1'$, which is dependent only on ε_2, and one can put $e_a=\lambda^{(a)}m_{AA}\varepsilon_2$ in (29).

The formula for the crystal free energy F can now be put as

$$\begin{aligned}\tilde{F}(w, x, T)=N\Bigg\{&c\varepsilon_A^{\alpha}+(1-c)\varepsilon_A^{\beta}+x(\varepsilon_B^{\beta}-\varepsilon_A^{\beta})+\\&+\lambda\frac{M}{N}\left[p(2\varepsilon_{AB}-\varepsilon_{BB})+\sum_{i=sm+1}^{m}z_i\frac{\varepsilon_{BB}-\varepsilon_{AB}}{1-c}\right]+\\&+wx\left[\varepsilon_1+\lambda\frac{M}{N}(\varepsilon_{BB}-\varepsilon_{AB}\left(\frac{\sum_{i=1}^{sm}z_i}{c}-\frac{\sum_{i=sm+1}^{m}z_i}{1-c}\right)\right]\Bigg\}-\\&-T(1-\tilde{\lambda})\tilde{S}_{\alpha}^{id}-T(1-\tilde{\lambda}')\tilde{S}_{\beta}^{id}+\lambda kMT\left(\ln\eta+\sum_{i=1}^{m}b_i\ln\mu_i\right).\end{aligned} \tag{34}$$

*We have incorporated the fact that the number of pairs in the group set exceeds the number of pairs in the crystal by a factor $1/\lambda$.

The expression in braces contains a term independent of ω that defines the energy-reference level and does not influence $\bar{w}(x, T)$. The term proportional to ω is important. It may be dependent on the unsymmetrical combination of the energy constants $\varepsilon_{BB}-\varepsilon_{AB}$. To elucidate what energy-constant combinations may affect the equilibrium order, we note that any microstate (atomic configuration) can be derived from some specified cation-position redistribution. Let us therefore consider the simplest permutation of this type (see (32)) and calculate the corresponding energy change.

We assume that the z_α nearest neighbors of a given cation α position include x_α A cations and $(z_\alpha-x_\alpha)$ B cations, while the immediate environment of a β position includes x_β A cations and $z_\beta-x_\beta$ B ones. Then the energy of (32) is

$$\Delta E=\varepsilon_1+\varepsilon_3+\varepsilon_2(x_\beta-x_\alpha-z_\beta), \tag{35}$$

where $\varepsilon_3=z_\alpha\varepsilon_{BB}+z_\beta\varepsilon_{AA}-(z_\alpha+z_\beta)\varepsilon_{AB}$; with $z_\alpha=z_\beta=z$, the energy ε_3 amounts to $z\varepsilon_2$. Then (35) shows that $\tilde{F}(w, x, T)$ may be dependent on the energy parameters ε_j^i, ε_{jk} ($i=\alpha$, or β; $j, k=A$, or B) apart from an additive constant only via combinations* of the form $\varepsilon_1+\varepsilon_3$ and ε_2.

This conflicts with (34), because we have calculated the energy while neglecting many of the bonds in the crystal, so the calculation in principle can produce a substantial dependence of $\tilde{F}$ on the nonphysical combinations of the basic energy constants. The detailed form of the corresponding relationship, which leads to model inadequacy, is related to basic-cluster choice.

We thus have to devise a criterion for splitting up the crystal into groups, which restricts the choice to groups whose incorporation does not lead to the expression for F containing major energy parameters differing from $\varepsilon_1+\varepsilon_3$ and ε_2. That criterion is readily formulated from (34). We rewrite the factor to wx in (34) as

$$\varepsilon_1+\lambda\frac{M}{N}\left[\frac{\sum_{i=1}^{sm} z_i}{c}-\frac{\sum_{i=sm+1}^{m} z_i}{1-c}\right]\frac{\varepsilon_3-z_\beta\varepsilon_2}{z_\alpha-z_\beta}.$$

This expression can be written in terms of $\varepsilon_1+\varepsilon_3$ and ε_2 if**

$$\frac{\sum_{i=1}^{sm} z_i}{c}-\frac{\sum_{i=sm+1}^{m} z_i}{1-c}=\frac{(z_\alpha-z_\beta)\,2p}{z_\beta+c\,(z_\alpha-z_\beta)}, \tag{36}$$

where we have used $\lambda=(N/M)[c(z_\alpha-z_\beta)/2p+z_\beta/2p]$. When (36) is obeyed, (34) simplifies substantially. Then (28) with (36) may be rewritten as

$$\frac{\prod_{i=1}^{sm}\mu_i^{1/c}}{\prod_{i=sm+1}^{m}\mu_i^{1/(1-c)}}\,e^{\frac{(\varepsilon_1+\varepsilon_3)-z_\beta\varepsilon_2}{kT}\cdot\frac{N}{\lambda M}}=\left(\frac{c-wx}{wx}\right)^{\frac{1-\tilde{\lambda}}{\lambda}\frac{N}{M}}\left(\frac{(1-w)\,x}{1-c-(1-w)\,x}\right)^{\frac{1-\tilde{\lambda}'}{\lambda}\frac{N}{M}}. \tag{37}$$

*For example, the expression $wx(z_\beta-z_\alpha)(\varepsilon_{AA}-\varepsilon_{BB})$ in (11) can be put in the form $wx[2\varepsilon_3-\varepsilon_2(z_\alpha+z_\beta)]$.

**Criterion (36) has remained overlooked in previous papers, which is explicable, for (36) is obeyed for any decomposition into groups in AB alloy having a primitive or body-centered lattice (and in the usual model planar grids) as considered by Bethe [13], Guggenheim [14], Yang [15], and Li [17], as well as for the tetrahedral groups in AB_3 alloy examined by Yang and Li [16] and Senderov's group choice in the albite model [18]. On the other hand, most nontrivial structures for minerals and alloys show (36) imposing very stringent constraints on the basal-cluster choice (Table 1).

Table 1

Classification of Structures of Some Disordered Alloys and Minerals Based on (36)

Structure type and position kinds	Superlattice description*	Coordination		Relation between z_α and z_β**	Criterion	Examples
		α positions	β positions			
CsCl αβ	BCC lattice, α positions at cube centers, β at vertices	8β Cube	8α Cube	I *a*	Always obeyed, any decomposition	CuZn, CuPd, AgCd, AgZn, CoFe
NiAs αβ	HCP composed of β positions, all octahedral cavities occupied by α positions	6β Trigonal prism	6α Octahedron	I *a*	Ditto	PtZn, PtPb, AuSn, IrSn, IrPb
CuAu αβ	CCP lattice, α and β positions alternately occupied by layers parallel to [001]	4α+8β Cube-octahedron	8α+4β Cube-octahedron	I b	Constraint $\sum_{i=1}^{sm} z_i = \sum_{i=sm+1}^{m} z_i$	CuAu, FePb, CoPt, NiMn, NiPt
NaTl αβ	BCC lat., with α or β posit. at the cent., and α and β ones form. tetrahedra at the vert.	4α+4β Cube	4α+4β Cube	I b	Ditto	δ″-LiZn, γ-LiCd, β-LiAl, LiGa
PtCu αβ	CCP lattice, α and β positions occupying alternately layers perpendicular to [111]	6α+6β Cube-octahedron	6α+6β Cube-octahedron	I b	»	PtCu, $(Ca, Mg)CO_3$
Cu_3Au $\alpha_3\beta$	CCP lattice, α positions at face centers, β positions at cell vertices	8α+4β Cube-octahedron	12α Cube-octahedron	I b	Constraint $\frac{1}{3}\sum_{i=1}^{sm} z_i = \sum_{i=sm+1}^{m} z_i$	Pt_3Ti, Ni_3Mn, Au_3Pt, Cd_3Au
Al_3Ti $\alpha_3\beta$	CCP lattice, three layers parallel to [111]: in the first layer, the β positions are at the face centers and the α positions at the vertices, while in the second layer there are only α posit., and in the third layer there are α positions at the face centers and β ones at the vertices	8α+4β	12α	I b	Ditto	Fe_3Ti, Ga_3Ti, Au_3Zn, Ga_3Zr

centers and β ones at the vertices						
Clinopyroxenes αβ	Chains of $[Si_2O_6]_\infty^{4-}$ silicon-oxygen tetrahedra, α and β positions are oxygen octahedra linking the chains	2α+3β	3α+2β	I b	Constraint $\sum_{i=1}^{sm} z_i = \sum_{i=sm+1}^{m} z_i$	$(Mg, Fe)_2Si_2O_6$
Melilites, *M* posit. αβ	Layers linked by the edges and faces of distorted Thomson cubes parallel to [001]	2α+3β	3α+2β	I b	Ditto	Leucophanite, meliphanite
Biotites $\alpha_2\alpha$	Tetrahedral $[AlSi_3O_{12}]_\infty^{5-}$ layers perp. to [001], α and β positions between layers	3α+3β	6α	I b	Constraint $\frac{1}{2}\sum_{i=1}^{sm} z_i = \sum_{i=sm+1}^{m} z_i$	Biotite $K(Mg, Fe)_3(OH)_2AlSi_3O_{10}$
Spinels $\alpha_2\beta$	CCP O^{2-} anions, α posit. 1/2 of octahedral cavit., β posit. 1/4 of tetrahedral cavities	6α+6β Cube-octahedron	12α Cube-octahedron	I b	Ditto	Al_2MgO_4, Fe_3O_4
Plagioclase $\alpha_3\beta$	Framework of four-member tetrahedral rings	3α+β	4β	I b	Constraint $\frac{1}{3}\sum_{i=1}^{sm} z_i = \sum_{i=sm+1}^{m} z_i$	$NaAlSi_3O_8$—$CaAl_2Si_2O_8$
CaF_2 $\alpha_2\beta$	CCP of β positions, with α positions occupying all tetrahedral cavities	4β Tetrahedron	8α Cube	II *a*	Always obeyed, any decomposition	Sn_2Ir, Al_2Pt, Ga_2Pt, In_2Pt
CdI_2 $\alpha_2\beta$	HCP of α positions, layer-wise filling by β positions in half of the octahedral cavities, pattern: layer filled then layer empty	3β Triangle	6α Octahedron	II *a*	Ditto	Te_2Ni
β-W	BCC lattice composed of β positions, α positions at faces in pairs	8α+6β	12α Icosahedron	II b ***	Constraint $\frac{1}{3}\sum_{i=1}^{sm} z_i - \sum_{i=sm+1}^{m} z_i = \frac{2p}{27}$	Ti_3Pt, V_3Co, Mo_3Zr, Ti_3Au

Table 1 (continued)

Structure type and positions kinds	Superlattice description*	Coordination		Relation between z_α and z_β**	Criterion	Examples
		α positions	β positions			
Olivines $\alpha\beta$	Single $[SiO_4]^{4-}$ tetrahedra, octahedral α and β positions	$2\alpha+2\beta$	2α	II *б*	Constraint $\sum_{l=1}^{sm} z_l - \sum_{l=sm+1}^{m} z_l = \frac{2p}{3}$	Mg_2SiO_4—Fe_2SiO_4
Ortho-pyroxenes $\alpha\beta$	$[Si_2O_6]_\infty^{4-}$ chains, α and β positions link chains	$2\alpha+3\beta$	3α	II *б*	Constraint $\sum_{l=1}^{sm} z_l - \sum_{l=sm+1}^{m} z_l = \frac{p}{2}$	$(Mg, Fe)_2Si_2O_6$
Melilites, T positions $\alpha\beta_2$	Layers of five-membered rings composed of single α positions and duplicated β positions	$\alpha+2\beta$ Triangle	4α Square	II *б*	Constraint $\sum_{l=1}^{sm} z_l - \frac{1}{2}\sum_{l=sm+1}^{m} z_l = \frac{p}{5}$	$Ca_2Al_2SiO_7$

*Ordered phase described.

**The structure types are divided into the following classes on the relation between z_α and z_β: $z_\alpha = z_\beta$ I*a*, all α positions coordinated only to β positions and vice versa I*b*, $z_\alpha \neq x_\beta$, II*a* analogous to I*a*, II*b* analogous to I*b*.

***Extensive alloy set in subclass II*b* omitted, see [22] for details.

If there is no short-range order, when $\varepsilon_2 \equiv 0$, (37) takes the form of the classical equilibrium equation for a crystal showing ideal mixing:

$$\exp \frac{\varepsilon_1 + \varepsilon_3}{kT} = \frac{(c - \omega x)(1 - \omega)}{\omega [1 - c - (1 - \omega) x]} .$$

CONCLUSIONS

An extension of the Yang-Li quasichemical model is provided for examining order-disorder transitions in many inorganic compounds containing crystallochemically nonequivalent positions. Disordering in such a structure is specific because of competition between the cations on the one hand tending to take up preferred positions and on the other their tendency to surround themselves by atoms of another type in the first coordination sphere. Consequently, an adequate model requires us to incorporate not only the preference energies due to long-range forces but also the short-range energies, which provide the short-range cation order.

The model is a cluster one, for which it is characteristic that the energy is calculated precisely within a certain group (cluster), while the groups themselves are taken as noninteracting. The method enables us to construct an approximation sequence, the result being closer to the exact one, the larger the cluster is.

An equation system has been derived whose solution enables us to recover the explicit thermodynamic functions such as the internal energy, free energy, and entropy. The parameters are the cluster size and the energies characterizing the short-range and long-range forces. An important stage in the procedure is choosing the basal cluster. A self-consistent criterion has been given, which when applied to simple structures enables us to choose the group arbitrarily, but which in the general case restricts the freedom of choice considerably.

This method will be used in a series of forthcoming papers dealing with disorder in particular rock-forming minerals (melilites, spinels, etc.).

REFERENCES

1. Saxena, S., 1975. Thermodynamics of Rock-Forming Mineral Solid Solutions [Russian translation], Mir, Moscow, 205 pp.
2. Urusov, V. S., 1977. Teoriya izomorfnoy smesimosti [Isomorphous-Miscibility Theory], Nauka, Moscow, 251 pp.
3. Nix, F. C. and W. Shockley, 1938. Usp. Fiz. Nauk, v. 20, No. 3, p. 344.
4. Ziman, J., 1982. Disorder Models: the Theoretical Physics of Homogeneously Disordered Systems [Russian translation], Mir, Moscow, 592 pp.
5. Loewenstein, W., 1954. Amer. Miner., v. 39, p. 92.
6. Kurepin, V. A., 1981. Termodinamika mineralov peremennogo sostava i geologicheskaya termobarometriya [Variable-Composition Mineral Thermodynamics and Geological Thermobarometry], Naukova Dumka, Kiev, 160 pp.
7. Pauling, L., 1960. The Nature of the Chemical Bond, Cornell Univ. Press.
8. Urusov, V. S., 1983. Phys. Chem. Miner., v. 9, p. 1.
9. Men', A. I., et al., 1977. Sostav - defektnost' - svoystvo tverdykh faz. Metod klasternykh komponentov [The Cluster-Component Method in Relation to Solid-Phase Compositions, Defectiveness, and Properties], Nauka, Moscow.
10. Mazo, R. M., 1977. Amer. Miner., v. 62, p. 1232.
11. Kikuchi, R., 1951. Phys. Rev., v. 81, p. 988.
12. Burton, B. and R. Kikuchi, 1984. Amer. Miner., v. 69, p. 165.
13. Bethe, H. A., 1935. Proc. Royal Soc. Ser. A, v. 150, No. 871, p. 552.
14. Guggenheim, E. A., 1935. Proc. Royal Soc. Ser. A, v. 148, p. 304.
15. Yang, C. N., 1945. J. Chem. Phys., v. 13, No. 3, p. 66.
16. Yang, C. N. and Y. Y. Li Chin, 1947. J. Phys., v. 7, p. 59.
17. Li, Y. Y., 1949. J. Chem. Phys., v. 17, No. 4, p. 447.
18. Senderov, E. E., 1980. Phys. Chem. Miner., v. 6, No. 4, p. 251.
19. Senderov, E. E. and A. V. Korovin, 1987. Geokhimiya, No. 6, p. 766.
20. Fowler, F. and E. A. Guggenheim, 1949. Statistical Thermodynamics [Russian translation], Izd. Inostr. Lit., Moscow.
21. Smirnov, A. A., 1985. Metallofizika, v. 7, No. 3, p. 12.
22. Bokiy, G. B., 1954. Vvedeniye v kristallokhimiyu [Introduction of Crystal Chemistry], Izd. MGU, Moscow, 490 pp.