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SHORT-RANGE FORCES IN MINERAL DISORDERING: MELILITE-TYPE STRUCTURES*

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Cation disordering in a mineral structure having two nonequivalent positions is described by a regular-mixing model. The atomic-configuration energy calculations incorporate not only the long-range interaction (average field) but also the interactions between nearest neighbors. The short-range interaction contributes to the long-range energy if the positions are unequally coordinated, and the crystalline-field effect can be accentuated or balanced out as far as order inversion. The general trends are demonstrated in the example of cation disordering in the tetrahedral positions in a structure of melilite type.

The tightening of the need for accuracy in calculations of mineral thermodynamic functions is reflected in more complicated mixing models. The ideal-mixing model, which until recently was the basic approximation for high-temperature disordering, has been recognized as inadequate in many cases [1-6].

The main shortcoming in that model is neglect of the short-range interaction between the disordering atoms when one calculates the configurational energy

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It seems clear that one needs to incorporate such pair interactions, which can usually be reduced to nearest-neighbor ones.

The simplest way of incorporating the short-range order is in terms of a regular-mixing model, which was devised originally for disordering (mixing) in alloys [7-9] and has been applied as a purely phenomenological model to minerals [2, 3, 10]. In [11], the basic formulas were derived for the fairly general case of two-position disordering, including differences in coordination between positions. A statistical model gave a relation between the phenomenological ordering coefficients on the one hand and the basic geometrical characteristics (composition and coordination) and energy characteristics (elementary-volume energies) on the other.

Here we examine qualitative features of disordering in minerals arising from the assumption of regular mixing; the main attention is given to the relative importance of the short-range and long-range interactions. The model is applied to disordering in melilite-type structures. It is found that incorporating the interaction of cations in adjacent polyhedra explains the observed antiordering in boron gehlenites.

CATION REGULAR-MIXING MODEL

Let us consider a $A_{1-x}B_x[Y]$ solid solution in which $N(1-x)$ cations of type A and Nx ones of type B are distributed over two crystallochemically nonequivalent positions α and β; the disposition of the Y atoms is fixed. Let the structure contain Nc α positions and $N(1-c)$ β ones.

The complete-order state or normal state is that of a cation array in which the maximum possible number of A atoms occupy α positions, while complete disorder is a uniform distribution over the cations, and complete antiorder (or inverse state) is a distribution where the maximum possible number of b atoms are in α positions.

We define the long-range order characteristic w as the proportion of B atoms in α positions; the cation distribution is described by

$$(A_{c-wx}B_{wx})^{\alpha}(A_{1-c-(1-w)x}B_{(1-w)x})^{\beta}[Y].$$

Here w may vary over the following ranges: preferential ordering corresponds to $w_0 \leqslant w < c$; preferential antiordering to $c < w \leqslant w_1$ and complete disorder for $w = c$. The values of w in complete ordering (w_0) and antiordering (w_1) are

$$w_0 = \begin{cases} 0, & 0 \leqslant x \leqslant 1-c, \\ \dfrac{x-(1-c)}{x}, & 1 \geqslant x > 1-c, \end{cases}$$

$$w_1 = \begin{cases} c/x, & c < x \leqslant 1, \\ 1, & c \geqslant x \geqslant 0. \end{cases}$$

The model is based on random mixing within independent sublattices, which is an extension of the ideal-mixing model, and it includes not only the long-range interaction (average field), which amounts to the position preference, but also pair interaction of cations (nearest neighbors).

The energy of the crystal U is the sum of two terms [11]:

$$U_1 = \varepsilon_A^{\alpha}N_A^{\alpha} + \varepsilon_B^{\alpha}N_B^{\alpha} + \varepsilon_A^{\beta}N_A^{\beta} + \varepsilon_B^{\beta}N_B^{\beta},$$

$$U_2 = N_{AA}^{\alpha\alpha}\varepsilon_{AA}^{\alpha\alpha} + N_{AB}^{\alpha\alpha}\varepsilon_{AB}^{\alpha\alpha} + N_{BB}^{\alpha\alpha}\varepsilon_{BB}^{\alpha\alpha} + N_{AA}^{\alpha\beta}\varepsilon_{AA}^{\alpha\beta} + N_{AB}^{\alpha\beta}\varepsilon_{AB}^{\alpha\beta} + N_{BB}^{\alpha\beta}\varepsilon_{BB}^{\alpha\beta} + N_{AB}^{\beta\alpha}\varepsilon_{AB}^{\beta\alpha} + N_{AA}^{\beta\beta}\varepsilon_{AA}^{\beta\beta} + N_{AB}^{\beta\beta}\varepsilon_{AB}^{\beta\beta} + N_{BB}^{\beta\beta}\varepsilon_{BB}^{\beta\beta}.$$

Here ε_k^i and N_k^i are the energies and numbers of atoms of type k (k = A or B) in the i positions ($i=\alpha, \beta$), while $\varepsilon_{kl}^{ij}, N_{kl}^{ij}$ ($i, j=\alpha, \beta$; $k, l=A, B$) are the energies and numbers of kl pairs in the i-j positions. By energy of a pair of adjacent

atoms ε_{jk}^{ij} one means the excess energy of the pair by comparison with $\varepsilon_k^i+\varepsilon_l^j$ for atoms k and l in positions i and j. Atoms at the centers of adjacent polyhedra do not usually form bonds one to the other, and the excess energy is due to the lattice deformation and/or changes in the local valencies of the bridge anions when cations that differ in size and charge enter adjacent polyhdedra. There may be an additional contribution from the direct interaction between the electron shells of transition elements in a polyhedra joined by their faces, as for example in nickel arsenide structures. The assumption of randomness gives $N_B^\alpha = wxN$, $N_B^\beta=(1-w)xN$, $N_A^\alpha=N(c-wx)$, $N_A^\beta=[1-c-(1-w)x]N$. The number of atoms N_k^i and the number of pairs N_{kl}^{ij} are related by

$$z_{ii}N_k^i = 2N_{kk}^{ii} + N_{AB}^{ii}\ (i=\alpha,\beta,\ k=A,B),$$
$$z_{ij}N_k^i = N_{kk}^{ij} + N_{AB}^{ij}\ (i,j=\alpha,\beta,\ i\neq j,\ k=A,B).$$

Here we have retained the symbols of [11]: z_α and z_β are the position coordination numbers, which are the numbers of nearest cation positions around α and β positions correspondingly, while z_{ij} is the number of type j positions in the immediate cation environment of an i position (i, j = α, β). The following relations between z_i and z_{ij} (i, j = α, β) follow from the geometry: $z_\alpha = z_{\alpha\beta}+z_{\alpha\alpha}$, $z_\beta=z_{\beta\alpha}+z_{\beta\beta}$, $cz_{\alpha\beta}=(1-c)z_{\beta\alpha}$.

Then U can be written as

$$U = Nwx(\varepsilon_1+\varepsilon_3) - \frac{1}{2}\frac{Nx^2w^2}{c(1-c)}\{c[z_{\alpha\alpha}\varepsilon_2^{\alpha\alpha} + z_{\alpha\beta}\varepsilon_2^{\alpha\beta} - z_{\beta\alpha}\varepsilon_2^{\beta\alpha} - z_{\beta\beta}\varepsilon_2^{\beta\beta}] + z_{\beta\alpha}\varepsilon_2^{\beta\alpha} - z_{\alpha\alpha}\varepsilon_2^{\alpha\alpha}\} - \frac{1}{2}Nwx\left\{\frac{x}{1-c}[2z_{\beta\beta}\varepsilon_2^{\beta\beta} - z_{\alpha\beta}(\varepsilon_2^{\alpha\beta}+\varepsilon_2^{\beta\alpha})] + 2z_{\alpha\alpha}\varepsilon_2^{\alpha\alpha} + z_{\alpha\beta}(\varepsilon_2^{\alpha\beta}+\varepsilon_2^{\beta\alpha}) + z_{\beta\alpha}(\varepsilon_2^{\beta\alpha}-\varepsilon_2^{\alpha\beta})\right\} + C,$$

$$\varepsilon_1 = \varepsilon_A^\beta - \varepsilon_A^\alpha + \varepsilon_B^\alpha - \varepsilon_B^\beta,\ \varepsilon_2^{ij} = \varepsilon_{AA}^{ij} + \varepsilon_{BB}^{ij} - 2\varepsilon_{AB}^{ij},\ i,j=\alpha,\beta,$$

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

where C is a term independent of w.

In a mineral structure, the ε_{kl}^{ij} (i, j=α, β, k, l=A, B) are determined on the one hand by the types of A and B in adjacent polyhedra* and on the other by the types of polyhedron and the mode of their junction. If the types around the α and β positions are the same, as are the modes of joining, the bond energy will be determined only by the type of cation. For example, in albite or gehlenite, one gets Al-Si disordering over two types of tetrahedron joined by their vertices. For such compounds, differences such as $\varepsilon_{kk}^{ij} - \varepsilon_{kl}^{ij}$ are independent of the type of ij position; there are three energy parameters in the expression for the internal energy:

$$\varepsilon_1 = \varepsilon_A^\beta - \varepsilon_A^\alpha + \varepsilon_B^\alpha - \varepsilon_B^\beta, \qquad (1)$$
$$\varepsilon_2 = \varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB},\ \varepsilon_3 = z_\alpha\varepsilon_{BB} + z_\beta\varepsilon_{AA} - (z_\alpha+z_\beta)\varepsilon_{AB}.$$

In what follows, let us restrict consideration of structures for which such energy-parameter substitution is possible.

*Here we are speaking of the true coordination polyhedra, the anion environments of cations A and B.

The free (configurational) energy in that approximation is $F=U-TS^{id}$, where

$$S^{id}=Nk\{c\ln c+(1-c)\ln(1-c)-xw\ln xw-$$
$$-x(1-w)\ln x(1-w)-(c-wx)\ln(c-wx)-$$
$$-[1-c-(1-w)x]\ln[1-c-(1-w)x]\}.$$

When the free energy is minimized with respect to w, we get an equation for the equilibrium w as a function of temperature [11]:

$$kT\ln K=E_1+wE_2, \tag{2}$$

in which

$$K=\frac{(1-w)(c-wx)}{w[1-c-(1-w)x]},$$
$$E_1=\varepsilon_1+\varepsilon_3-\varepsilon_2 p,\ E_2=-\varepsilon_2 q,$$
$$p=z_\alpha+\frac{x}{1-c}(z_{\beta\beta}-z_{\alpha\beta}), \tag{3}$$
$$q=\frac{x}{c(1-c)}[z_{\beta\alpha}-z_{\alpha\alpha}+c(z_\alpha-z_\beta)].$$

In (2), we have the energy parameters ε_1, ε_2 and ε_3 in addition to the temperature and structural characteristics; these characterize the various types of interaction. Here ε_1 corresponds to a cation interacting with the crystalline field and is equal to the energy resulting from the elementary exchange

$$A(\alpha)+B(\beta)\xrightarrow{\varepsilon_1}A(\beta)+B(\alpha). \tag{4}$$

The sign choice for ε_1 is equivalent to defining the normal and inverse states. We will subsequently take $\varepsilon_1\geqslant 0$ and use symbols for the cations and positions such that (4) consumes energy.

Cations in adjacent polyhedra show a pair interaction characterized by ε_2, the energy arising from the formation of two pairs of like cations from two pairs of unlike ones [12, 13]:

$$2AB\xrightarrow{\varepsilon_2}AA+BB.$$

It follows from (3) that incorporating short-range cation interaction results in an additional contribution to the long-range energy, so the latter is $\varepsilon_1+\varepsilon_3$.

Nearest-neighbor interactions are responsible for ε_2 and ε_3; ε_2 varies in association with isostructural changes in composition. For example, ε_2 characterizes the Al-Si, Si-Mg, Si-B, and other such interactions for the melilites: gehlenite, åkermanite, borian gehlenite, and so on, where one gets discrete changes in ε_2. One can get continuous ε_2 variation in solid-solution series, e.g., from gehlenite to B-gehlenite, if Si is taken as one of the cations and the other is taken as $(Al_{1-x}B_x)$, where x represents the composition.

As ε_2 and ε_3 have the same nature, one naturally expects that the two vary proportionally, so as a simplification, we take $\varepsilon_3=\zeta\varepsilon_2$, where ζ characterizes the effects of the interaction between a cation and the immediate coordination sphere on the long-range interaction energy. If the positions are equally coordinated, $z_\alpha=z_\beta=z$), (1) implies $\zeta=z$; any deviation of ζ from z characterizes the difference between the α and β positions. For given z_α and z_β, ζ is dependent according to (1) on the relation between the energies $\varepsilon_a=\varepsilon_{AA}-\varepsilon_{AB}$ and $\varepsilon_b=\varepsilon_{BB}-\varepsilon_{AB}$.

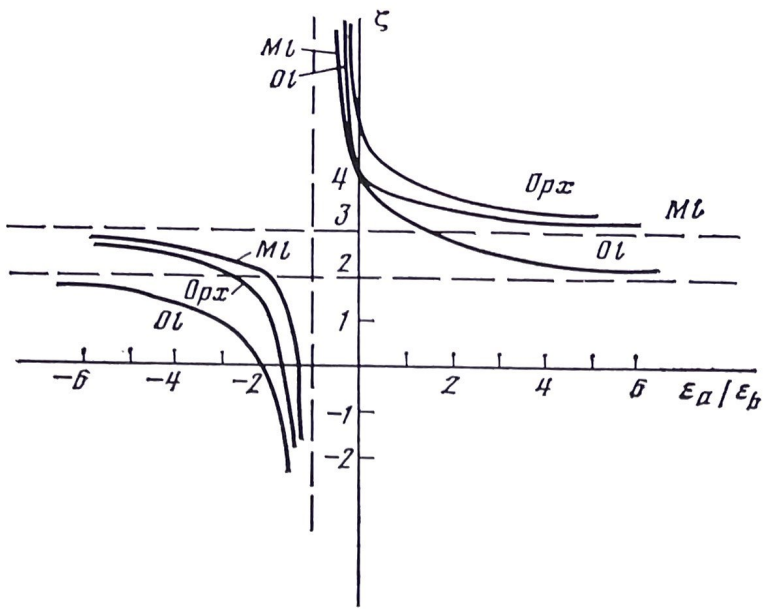

Fig. 1. Parameter $\zeta=\varepsilon_3/\varepsilon_2$ as a function of $\varepsilon_a/\varepsilon_b=(\varepsilon_{AA}-\varepsilon_{AB})/(\varepsilon_{BB}-\varepsilon_{AB})$ for minerals having unsymmetrical ($z_\alpha \neq z_\beta$): *Ml* melilites (*T* positions), *Ol* olivines, *Opx* orthopyroxenes.

The $\varepsilon_a/\varepsilon_b$ dependence of ζ is governed by the relation between z_α and z_β (Fig. 1):

$$\zeta=\frac{z_\beta\frac{\varepsilon_a}{\varepsilon_b}+z_\alpha}{\frac{\varepsilon_a}{\varepsilon_b}+1}.$$

Positive ζ correspond to strengthened short-range interaction strengthening the long-range, which applies in particular for equally coordinated positions, where $\zeta=z_\alpha=z_\beta=z$. In a close-packed structure having high cation coordination numbers such as in a spinel, where $z = 12$, one naturally expects that there will be a considerable contribution to the long-range energy from the interactions between nearest-neighbor cations.

Near-zero ζ correspond to open structures with unequally coordinated positions (olivines), while structures having $\zeta<0$ are interesting, as the short-range interaction weakens the long-range one. The short-range interaction there may weaken or eliminate the ordering effect from the average field and also cause antiordering.

CATION DISORDERING IN MELILITES

There is an extensive group of minerals and synthetic compounds having the general formula $M_2T_3O_7$, in which M is a large cation having a low charge and T is a smaller tetrahedral cation having the same charge or a higher one; the structure here is of melilite type [14].

There are nonequivalent positions here, and the scope for isomorphous replacement is extensive, so the compounds are of interest as geothermometers; the most notable are the widely occurring natural melilites in the series from gehlenite $Ca_2Al_2SiO_7$ to åkermanite $Ca_2MgSi_2O_7$.

Such a structure (tetragonal, space group $P\bar{4}2_1m$) is formed by layers of large figures with eight vertices linked on their edges and faces and alternating with mixed anion layers composed of *T* tetrahedra (Fig. 2). The tetrahedral

layers have a 1:2 ratio between the crystallochemically distinct tetrahedron types (T_1 and T_2) over which the T cations are distributed. In the smaller of the T positions (T2), there is in each case a free vertex (an uncompleted O^{2-} anion), which leads to the T2 positions being filled preferentially by the smaller and more highly charged cations, so the larger low-charge T cations are displaced to the T1 positions.

In a gehlenite-type melilite, $M_2T_2^{3+}T^{4+}O_7$ the cation distribution corresponding to bond valency balance [15] is ordered, $M_2(T^{3+})^{T1}(T^{3+}T^{4+})^{T2}O_7$; disordering may occur as the temperature rises, i.e., some of the T^{4+} may enter T1 $M_2(T^{3+}_{1-w}T^{4+}_{w})^{T1}(T^{3+}_{1+w}T^{4+}_{1-w})^{T2}O_7$ cation distribution.

An åkermanite-type melilite corresponds to $M_2(T^{2+}_{1-w}T^{4+}_{w})^{T1}(T^{2+}_{w}T^{4+}_{2-w})^{T2}O_7$, but it is unlikely that T^{2+} will enter T2 because of the marked valency unsaturation in the free oxygen vertex, so it seems that such melilites are always ordered ($w = 0$).

Gehlenite probably becomes disordered as the temperature increases because there is a spread in the lattice parameters for gehlenite synthesized at various temperatures [15]. Structure refinements for natural and synthetic gehlenites [16-18] however leave the extent of this disordering open. A structure refinement has been given for high-temperature gehlenite [18] based on the bond lengths in the T1 and T2 polyhedra, which gave w as 0.014. However, there is no temperature assignment for the [18] estimated disorder, so there is only a limited possibility of using it.

Melilite cation distributions have been simulated [14, 15], and the lattice parameters allow one to estimate $w(T)$; estimates from [19, 20] for gehlenite give $w(1400°C) = 0.12(1)$ (Table 1). Such simulation has been applied to the series from gehlenite to borian gehlenite $Ca_2B_2SiO_7$ [21] with the [22] lattice parameters, which showed order inversion: it is likely that there is antiordering in the essentially borian varieties.

A thermodynamic explanation can be given for the disordering in melilite. In [23, 24], the cation distributions were described using an ideal-mixing model; antiordering can be attained only if one assumes a negative preference energy (long-range interaction energy). At the same time, the valency balance [15] indicates that highly charged cations prefer T2 positions, so that energy would be positive. Thus the ideal-mixing model does not adequately describe disordering in melilite.

REGULAR MODEL OF CATION DISORDERING IN MELILITE

The general regular-model formulas obtained earlier are used to describe disordering here.

The following parameters characterize a gehlenite-type melilite structure:

x	$1/3$	w_0	0
c	$1/3$	w_1	1
z_α	4	K	$\frac{(1-w)^2}{w(1+w)}$
z_β	3	p	2.5
$z_{\alpha\alpha}$	0	q	3.5
$z_{\alpha\beta}$	4	E_1	$\varepsilon_1+\varepsilon_2-2.5\varepsilon_2$
$z_{\beta\alpha}$	2	E_2	$-3.5\varepsilon_2$
$z_{\beta\beta}$	1		

These features mean that small highly charged cations prefer T2 positions; we subsequently denote them as B, and the T2 positions are taken as β ones. Then $\varepsilon_1 \geqslant 0$, and as we do not consider the clustering case, we have $\varepsilon_2 \geqslant 0$ and $\varepsilon_1/\varepsilon_2 \geqslant 0$. A zero value for ε_2 clearly corresponds to ideal mixing. The corresponding $w(T)$ is

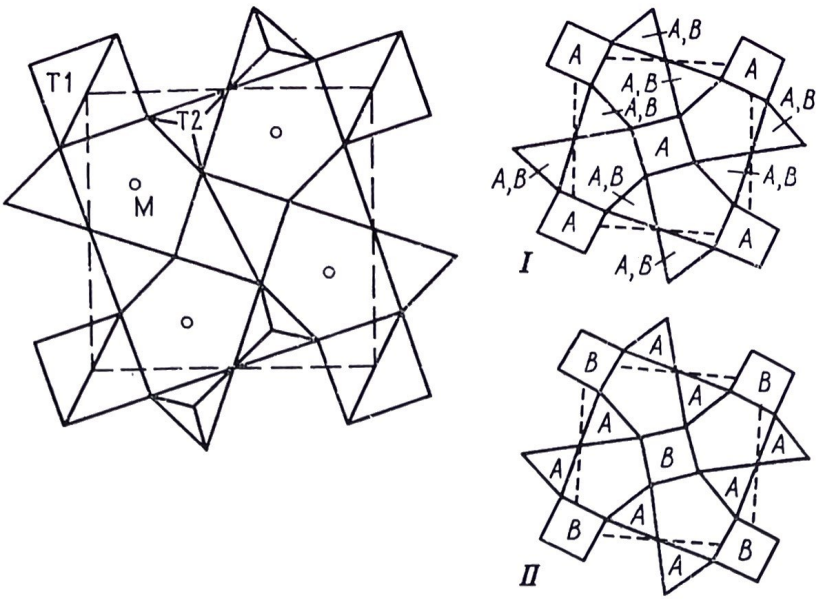

Fig. 2. Melilite-type structure, complex-anion layer, (001) projection. The insets show the normal cation array (ordered I) and the inverse one (antiordered II).

Table 1

Long-Range Order in Gehlenites Synthesized at 620-1440°C (Structure Simulation [20])

T, K	w	$\ln K$	$T \ln K$
		[19]	
913	0	—	—
1173	0,015	4,157	4876
1323	0,037	3,18	4207
1423	0,067	2,50	3558
1567	0,074	2,37	3714
1623	0,097	2,04	3311
1673	0,097	2,04	3413
1733	0,119	1,77	3067
		[20]	
943	0	—	—
1293	0,048	2,89	3802
1593	0,071	2,43	3870
1693	0,116	1,80	3044

$$w(T) = \frac{-1-2u+\sqrt{1+8u^2}}{2(1-u)}, \quad u = \exp(-\varepsilon_1/kT).$$

The normal state occurs for $\varepsilon_1 > 0$; order inversion is impossible for positive ε_1.

If $\varepsilon_2 \neq 0$ (2) describes the disordering. The form of $w = w(\theta)$, in which ($\theta = kT/\varepsilon_1$ is the reduced temperature, is governed by the relation between the dimensionless energy parameters $\zeta = \varepsilon_3/\varepsilon_2$ and $\chi = \varepsilon_2/\varepsilon_1$ (Fig. 3).

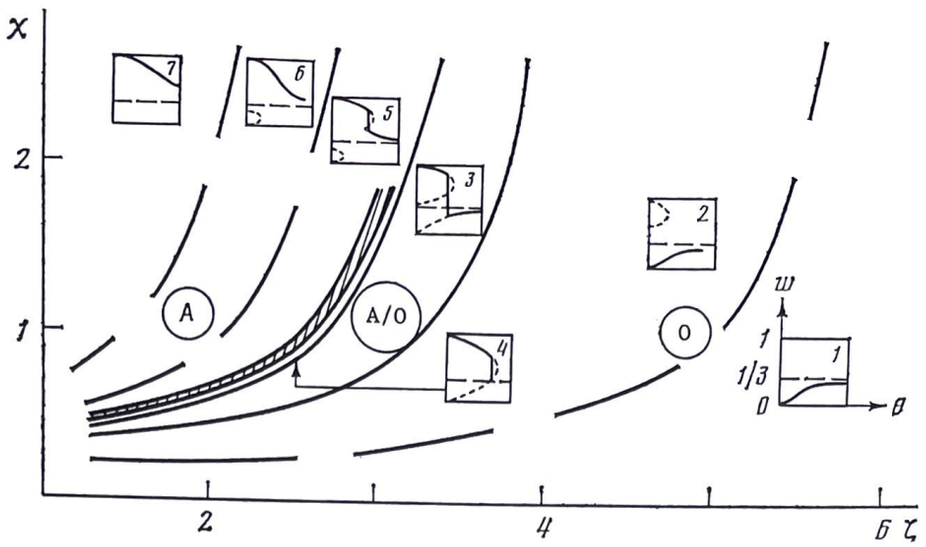

Fig. 3. Regions showing order O and antiorder A in the space of the energy parameters $\chi=\varepsilon_2/\varepsilon_1$ and $\zeta=\varepsilon_3/\varepsilon_2$. The intermediate A/O region lies between the curves $\chi=1/(11/3-\zeta)$ and $\chi=1/(4.25-\zeta)$; the insets show topographically distinct solutions to (2). The solid lines represent the stable states and the dashed ones the metastable and unstable ones. The hatched region in χ and ζ has been derived by measurement for gehlenite (Table 1).

The following conditions governs the existence of a θ-unbounded branch of $w(\theta)$ in the ordered (antiordered) range of values of w:

$$\chi<(>)\,1/(11/3-\zeta).$$

As χ is positive, ζ larger than the critical 11/3 mean that this branch cannot go over to the antiordered range in w (inversion order) for any χ; for $\zeta<11/3$, there is $\chi_{cr}=1/(11/3-\zeta)$.

The regular model thus explains the order inversion for positive ε_1 found in B-gehlenites and the marked effect of the short-range forces. This conclusion can be derived qualitatively by counting the like and unlike pairs in the gehlenite structure in the ordered and antiordered states per cell (Fig. 2). If there is a marked short-range effect, antiorder is preferred, since then the cell contains eight unlike and two like pairs, whereas the ordered state leads to a reduction in the number of unlike pairs to five and an increase in the number of like ones to five. The regular model allows one to evaluate this quantitatively, namely to state what strength the short-range interaction should have.

For sufficiently small and sufficiently large χ,

$$\chi<1/(2.5-\zeta),\ \chi>1/(6-\zeta)$$

and (2) has a single root correspondingly in the antiordered and ordered ranges of w (curves 1 and 7 in Fig. 3). For intermediate χ and low T, (2) has three solutions: one (intermediate w) corresponds to maximum free energy, while the other two correspond to minima, with deeper minimum corresponding to the stable state and the less deep one to the metastable state. Calculation of the free energy for $\theta = 0$ and $w = 0$ and shows that $w = 1$ is the stable root for $\chi > 1/(4.25 - \zeta)$ (curves 3-7 in Fig. 3), while $w = 0$ is stable for $\chi < 1/(4.25 - \zeta)$ (curves 1 and 2 in Fig. 3).

Thus in χ-ζ space there are three major regions with differences in behavior of the stable solution to (2); two correspond to the partially ordered state ($0\leqslant w\leqslant 1/3$, $w(\theta=0)=0$; region O in Fig. 3) and the antiordered state ($1/3<w\leqslant 1$,

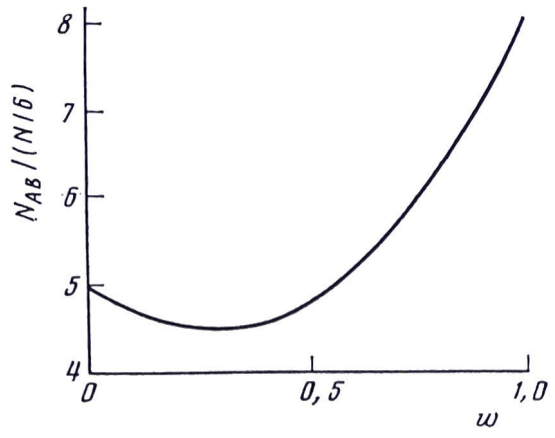

Fig. 4. Normalized number of unlike cation pairs (nearest neighbors) as a function of the disorder parameter.

$w(\theta=0)=1$, region A in Fig. 3), while the third is transitional ($1/(11/3-\zeta)\leqslant \chi\leqslant 1/(4{,}25-\zeta)$ A/O region, Fig. 3), where the behavior of $w(\theta)$ is mixed: at low temperatures ($\theta<\theta_I$), there is antiordering, while at ($\theta>\theta_I$) there is ordering. In the last, there are first-order phase transitions from antiorder to order (curve 3, Fig. 3), and the transition temperature θ_I is defined by

$$\begin{cases} E_1(w'-w'')+\frac{1}{2}E_2[(w')^2-(w'')^2]-\theta_I[S(w')-S(w'')]=0 \\ E_1+E_2w'-\theta_I\ln K(w')=0 \\ E_1+E_2w''-\theta_I\ln K(w'')=0, \end{cases} \tag{5}$$

in which w' and w'' are the order parameters corresponding to the coexisting phases,

$$S(w)=R[2\ln 2-w\ln w-2(1-w)\ln(1-w)-(1+w)\ln(1+w)] \tag{6}$$

being the ideal configuration entropy. The transition temperature θ_I can vary from 0 (for $\chi=1/(4{,}25-\zeta)$) to θ_I', the temperature for the antiorder → disorder type of transition, which occurs at $\chi_{cr}(\zeta)$ (curve 4, Fig. 3), where θ_I' is defined by (5) with $w'=1/3$. Then $1/(3.1-\zeta)>\chi>1/(11/3-\zeta)$ defines a region in χ-ζ space characterized by first-order transitions of antiorder-antiorder type (curve 5, Fig. 3), for which the temperature is $0.18/(3.1-\zeta)>\theta_I''>\theta_I'$. The configuration entropy in this model is given by (6). For $\theta\to\infty$ the entropy approaches $S_b = R(3\ln 3 - 2\ln 2) = 3.742$ eu asymptotically. As w varies with temperature, $S(\theta)$ is governed by the relation between the energy parameters. In the O and A ranges, $S(\theta)$ decreases monotonically with temperature to $S_O = 2R\ln 2 = 2.753$ eu and $S_A = 0$ correspondingly. In the phase-transition range,

$$1/(3.1-\zeta)<\chi<1/(4.25-\zeta)$$

$S(\theta)$ has a discontinuity at $\theta=\theta_I$. The transitions are accompanied by thermal effects [25] $T_I\Delta S$, where $T_I=\theta_I\varepsilon_1/k$, $\Delta S=S(w')-S(w'')$; (5) defines w' and w''.

Another major characteristic of a disordered mineral is the short-range order [7]

$$\sigma = \frac{N_{AB} - N_{AB_{\min}}}{N_{AB_{\max}} - N_{AB_{\min}}}.$$

Here N_{AB} is the number of AB pairs for the given w, while $N_{AB_{\max}}$ and $N_{AB_{\min}}$ are the largest and least possible values of N_{AB}. If the structure contains positions surrounded only by positions of another type, disordering reduces the number of AB pairs, so $N_{AB_{\max}}$ and $N_{AB_{\min}}$ are the numbers of AB pairs in the states of complete order and disorder correspondingly. If the structure contains pairs of $\alpha-\alpha$ or $\beta-\beta$ type, disordering not only reduces the number of AB pairs but also reduces the number of corresponding like pairs. The balance between these results in a minimum on the curve of the dependence of w on N_{AB} at an intermediate value of w. The number of AB pairs in a melilite is [11]

$$N_{AB} = N(c - wx)\left[z_{\alpha\alpha}\frac{wx}{c} + z_{\alpha\beta}\frac{(1-w)x}{1-c}\right] +$$
$$+ N[1 - c - (1-w)x]\left[z_{\beta\alpha}\frac{wx}{c} + z_{\beta\beta}\frac{(1-w)x}{1-c}\right] = \frac{N}{6}(7w^2 - 4w + 5).$$

Here N_{AB} is minimal at 4.439 for w = 4/14 (Fig. 4). There is also a minimum on the curve of the equilibrium σ as a function of T; the temperature representing σ = 0 is

$$T(\sigma=0) = 3.04[\varepsilon_1/k + \varepsilon_2/k(\zeta - 1.5)].$$

For complete disorder σ = 0.028, and $\sigma(T)$ approaches this asymptotically as $T\to\infty$.

Al, Si DISORDERING IN GEHLENITE

Although the regular model describes a qualitative effect (order inversion is B-gehlenites), no detailed fit to the existing measurements on disorder in gehlenite is attained. It is readily seen that the $w(T)$ curves in the O region (Fig. 3) give the correct qualitative picture, but the theoretical and empirical lines differ in curvature, as is most readily demonstrated in plots of $T \ln K$ against w. The regular model gives a straight line with a negative slope, while the empirical $T \ln K$ decrease as w increases (Table 1), so one could choose the energy parameters to fit theory and experiment. However, least-squares fitting to the measurements gives $E_1 \simeq (4840 \pm 140)$ K and $E_2 \simeq (15500 \pm 1700)$ K, which define in χ-ζ space a zone $\chi \simeq 1/[3.59 \pm 0.04) - \zeta]$ that is entirely in the A region (Fig. 3), which shows that the theoretical $w(T)$ corresponds to the metastable branch in (2), while the antiordered state is the stable one at the corresponding χ and ζ.

That inadequacy is due to the regular model being illogical; although cation pair interactions are incorporated in the internal energy, they are not for the entropy, since $\Delta S = \Delta S^{id}$. The near-linear $1/T$ dependence of $\ln K$ indicated nonideal entropy, since least-squares fitting to Table 1 gives

$$\ln K = \frac{8380\ (\pm 660)}{T} - 3.1\ (\pm 0.5).$$

This may be due to more complicated behavior of the configurational entropy on account of the short-range cation ordering or to nonconfigurational entropy dependent on changes in the vibrational spectra on disordering. The model needs to be improved on that basis to determine the nature of the nonideal entropy terms $S^* \simeq (3.1 \pm 0.5)R$.

CONCLUSIONS

A regular-mixing cation model has been proposed for a disordering mineral containing nonequivalent positions, where there are interactions of two types: long-range interaction between the cation and the entire crystal ($\varepsilon_1+\varepsilon_3$) and short-range interaction between cations in adjacent polyhedra ε_2. One component of the long-range energy, ε_1, is determined by the cation position, where the main contributions to ε_1 come from the cations and anions not participating in the disordering, while ε_3 describes the contribution from the short-range interaction to the crystalline field. If the positions are equally coordinated and have z nearest neighbors, $\varepsilon_3=z\varepsilon_2$; while if the disordering positions are unequally coordinated, ε_3 is an independent parameter. The relation between the energy parameters is governed not only by the types of atom but also by the geometry: the numbers and modes of linkage of the coordination polyhedra. The long-range and short-range interactions may be unidirectional or have different directions, as the space of ε_1, ε_2, and ε_3 contains a region in which there is order inversion, where the mean field is balanced by the short-range forces.

The model is applied to melilite disordering and explains the order inversion in the B-gehlenites for positive ε_1.

On the other hand, the model does not give a detailed fit between the observed and theoretical $w(T)$ curves for gehlenite; the observed $1/T$ dependence of ln K shows that the entropy is nonideal. The model must therefore be improved to incorporate more detailed structure symmetry features.

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DIOPSIDE-WATER LIQUIDUS SURFACE DETERMINATION*

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The diopside-water liquidus surface has been examined in detail up to 30 kbar. New measurements have been made at 10, 15, 20 and 25 kbar, and a formal treatment of an ideal two-component solution model gives $\Delta H(Di)$ 18.5 ± 1 kcal, $\Delta V(Di)$ $0.142025 - 0.1095 \times 10^{-5}P - 0.25498 \times 10^{-11}P^2$ cal/bar. With these values, Schröder's equation describes the liquidus surface satisfactorily (including the water-saturated range) in the $CaMgSi_2O_6$-H_2O system; $\Delta H(Di)$ and $\Delta V(Di)$ do not correspond to the actual enthalpy and volume effects in diopside melting [1]. Therefore, liquid models have been devised concerned with the dissolution of water in the liquid and applied to estimating the energy and steric factors required for the coexistence of OH*, H_2O*, and $CaMgSi_2O_6$ groups in diopside-H_2O liquids at various pressures [2].

Eggler [3] was the first to examine the diopside-water system on the 20 kbar isobar at temperatures up to 1430°C; Hodges [4] made measurements at 20 kbar up to 1500°C. Then Rosenhauer and Eggler [5] repeated Hodges' experiments and found a large discrepancy in the solubility of water at the invariant point (Table 1), and two years later [8] they adhered to those results. Eggler and Burnham [6] gave diopside-water liquidus data recorded with a gas vessel at 2 kbar. Table 1 collects the published data for the water-saturated liquidus. Detailed measurements have been made on diopside melting under dry conditions [1]. Analysis of the published evidence for this system indicates that the data are not only very limited but also conflicting. There are no unambiguous results on latent heats of fusion determined by calorimetry, as the range is 18.5-34.1 kcal/mol. The thermodynamics of dry melting of diopside have been examined repeatedly (Table 2), and substantial differences have been found in the enthalpies of the crystal-liquid and crystal-glass transitions. Figure 1 is from [17] and illustrates the relation between the latent heats of melting and vitrification of diopside.

Theoretical analysis [6, 18] shows that the heat and volume change in melting of the mineral alone do not allow one to reproduce measurements satisfactorily from Henry's law or Schröder's equation as applied to ideal solutions. One

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