DISORDERING EFFECTS IN MANTLE MINERALS: THE FERROMAGNESIAN SPINEL $(Mg, Fe)_2SiO_4$*

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Thermodynamic simulation has been applied to disordering in $(Mg, Fe)_2SiO_2$, whose stability region covers much of the transitional zone in the mantle. The ideal-mixing model requires two order parameters, whose equilibrium values have been calculated for wide pressure and temperature ranges; the degree of disorder and the thermodynamic parameters have been related to the preference energies. Values have been calculated of the configurational entropy, which are of the nature of reference data and are required in calculating heterophase equilibria involving the partially disordered spinel. The effects of disordering in the spinel on the position of the divariant olivine-spinel equilibrium in the solid-solution series have been investigated. Formulas are derived to express the adiabatic gradient in P-T coordinates for disordered spinels, and numerical estimates have been made of the parameter range corresponding to the transition mantle in the zone.

Recently, much effort has been devoted to research on the structure of the region showing anomalous seismic-wave velocities at depths of 400-700 km [1-3]. The seismic features of that zone in the mantle (the transitional zone) are related to physicochemical transformations in the rocks as a result of the high pressures and temperatures. Numerous studies give nonconflicting models for the chemical and phase states of that zone; a basic feature of these is that there is an assemblage of multicomponent solid solutions that undergo solid-state transformations [4-8]. The position and extent of the anomalies are related to the relevant phase diagram. The $MgO-FeO-CaO-Al_2O_3-SiO_2$ multisystem is reasonably representative; it includes dozens of solid phases.

One of the most interesting features of these systems is the possible disordering. At low temperatures, the atoms occupy preferred positions, and disordering is accompanied by increase in the energy, but the entropy also increases. The entropy term becomes strictly more important in the free energy as the temperature increases, so the equilibrium degree of disorder increases, and that degree can be considered as an internal degree of freedom. The disordering is accompanied by heat and volume effects, which alter for example the positions of the phase boundaries corresponding to univariant reactions involving the disordering phases. Also, the slope of the adiabat, which closely represents the mantle temperature profile on concepts involving convecting mantle, is changed [1, 5-8]. Barsukov and Urusov [4] considered the transition zone as a zone of disordering solid solutions on this basis.

Here we evaluate the effects of disordering on the phase boundaries and adiabatic gradient for the mantle with references to the spinels in the Mg_2SiO_4-Fe_2SiO_4 solid-solution series. This system is of particular interest because ferromagnesian spinel is evidently stable in much of the transition zone. For
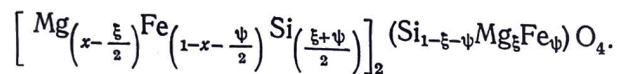
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example, the density discontinuity of the upper boundary of the transitional zone (400 km) is usually ascribed to the transition olivine → β,γ spinel, while the seismic feature at the lower boundary (700 km) is ascribed to γ spinel decomposing either into a mixture of oxides or into $MgSiO_3$ (with a perovskite structure) + periclase. The extent of the stability region for disordered spinel has been examined previously only for the end-members of this series [9-12].

In order to obtain analytic expressions, we restrict ourselves to a simple model with ideal cation mixing between the sublattices, i.e., we neglect the energy of interaction between nearest neighbors, while the distribution over positions nonequivalent in energy is taken as random. However, the expression for the Gibbs energy of $(Mg_xFe_{1-x})_2SiO_4$ derived from this model after eliminating the internal disorder parameters cannot be characterized in terms of an ideal-solution model. The more general model for regular mixing proposed for stoichiometric spinels [11-13] requires the introduction of additional parameters and leads to low degrees of disorder, such as are only observed in this system at the T and P of the transition zone, where the results are hardly different from those from the ideal-mixing model.

ORDERING IN SPINEL SOLID SOLUTIONS

Let us consider the continuous series Mg_2SiO_4-Fe_2SiO_4, where x denotes the molar fraction of Mg_2SiO_4 in the solution, $[Mg_xFe_{(1-x)}]_2(Si)O_4$. The Mg^{2+} and Fe^{2+} are localized in the octahedral positions in the ordered spinel, these being indicated by the square brackets, while the Si^{4+} are in tetrahedral positions denoted by the parentheses. Let ξ be the proportion of tetrahedral positions occupied by Mg^{2+} and ψ the proportion of them taken by Fe^{2+}. The parameter $\lambda = \xi + \psi$ is called the spinel inversion. This is a measure of the disorder: it is zero in an ordered spinel, while in a completely inversed one (disordered) it is 2/3. Thus the formula for a partially inverse spinel is

$$\left[Mg_{\left(x-\frac{\xi}{2}\right)} Fe_{\left(1-x-\frac{\psi}{2}\right)} Si_{\left(\frac{\xi+\psi}{2}\right)} \right]_2 (Si_{1-\xi-\psi}Mg_\xi Fe_\psi) O_4.$$

The Gibbs energy of a partially disordered spinel is

$$G^{Sp} = xG^{Sp}_{Mg}(P, T) + (1-x) G^{Sp}_{Fe}(P, T) + \Delta G^{Sp}(\xi, \psi, x, P, T), \tag{1}$$

shere G^{Sp}_{Mg}, and G^{Sp}_{Fe} are the standard Gibbs energies corresponding to the completely ordered pure phases, and $\Delta G^{sp} = \Delta E^{sp} + P\Delta V^{sp} - T\Delta S^{sp}$ is the Gibbs mixing energy, and ΔE^{sp}, ΔS^{sp}, and ΔV^{sp} are the mixing energy, entropy, and volume. The ideal-solution model gives

$$\Delta E^{Sp} = \xi \Delta E^{Sp}_{Mg} + \psi \Delta E^{Sp}_{Fe}, \quad \Delta V^{Sp} = \xi \Delta V^{Sp}_{Mg} + \psi \Delta V^{Sp}_{Fe}. \tag{2}$$

The exchange energies ΔE^{Sp}_{Mg} and ΔE^{Sp}_{Fe} (see (5) and (6)) characterize the differences in the energy levels of the Mg^{2+} and Fe^{2+} between the tetrahedral and octahedral positions. As $\Delta E^{Sp}_{Mg,Fe} > 0$, the degree of inversion is close to zero at low temperatures. Estimates [10] give $\Delta V^{So}_{Mg,Fe} < 0$, i.e., the volume decreases on disordering and pressure favors disordering.

The expression for the configurational mixing entropy corresponding to a random distribution over the positions can be derived from the formula for the number of microstates corresponding to given values of x, ξ and ψ:

$$g = \frac{N(T)!}{N_{Mg}(T)! \, N_{Fe}(T)! \, N_{Si}(T)!} \cdot \frac{N(M)!}{N_{Mg}(M)! \, N_{Fe}(M)! \, N_{Si}(M)!}, \tag{3}$$

where $N(T) = N_{Mg}(T) + N_{Fe}(T) + N_{Si}(T)$ is the total number of tetrahedral positions T, while $N(M) = N_{Mg}(M) + N_{Fe}(M) + N_{Si}(M)$ is the total number of octahedral ones M

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in the gram formula, where clearly $2N(T) = N(M)$. The numbers of cations in the positions are expressed by ξ and ψ, together with x:

$$N_{Mg}(T) = \xi N(T), \quad N_{Fe}(T) = \psi N(T), \quad N_{Si}(T) = (1 - \xi - \psi) N(T),$$

$$N_{Mg}(M) = \left(x - \frac{\xi}{2}\right) N(M), \quad N_{Fe}(M) = \left(1 - x - \frac{\psi}{2}\right) N(M), \quad N_{Si}(M) = \left(\frac{\xi + \psi}{2}\right) N(M).$$
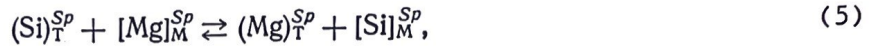
From (3), the mixing entropy can be put as

$$\Delta S^{Sp} = -R\left\{[(1 - \xi - \psi)\ln(1 - \xi - \psi) + \xi\ln\xi + \psi\ln\psi] + \right.$$
$$\left. + 2\left[\left(\frac{\xi + \psi}{2}\right)\ln\left(\frac{\xi + \psi}{2}\right) + \left(\frac{2x - \xi}{2}\right)\ln\left(\frac{2x - \xi}{2}\right) + \left(\frac{2 - 2x - \psi}{2}\right)\ln\left(\frac{2 - 2x - \psi}{2}\right)\right]\right\}, \tag{4}$$

where we neglect the nonconfigurational thermal entropy in accordance with the ideal-mixing model [11-13].

Disordering can be represented as two reactions:

$$(Si)_T^{Sp} + [Mg]_M^{Sp} \rightleftarrows (Mg)_T^{Sp} + [Si]_M^{Sp}, \tag{5}$$

$$(Si)_T^{Sp} + [Fe]_M^{Sp} \rightleftarrows (Fe)_T^{Sp} + [Si]_T^{Sp}. \tag{6}$$

We introduce the corresponding equilibrium constants $K_{Mg}^{Sp} = \exp(\Delta H_{Mg}^{Sp}/RT)$, and $K_{Fe}^{Sp} = \exp(\Delta H_{Fe}^{Sp}/RT)$, where $\Delta H_{Mg,Fe}^{Sp} = \Delta E_{Mg,Fe}^{Sp} + P\Delta V_{Mg,Fe}^{Sp}$ is the disordering enthalpy, to get [13]

$$\frac{(2x - \xi)(1 - \xi - \psi)}{\xi(\xi + \psi)} = K_{Mg}^{Sp}(P, T), \tag{7}$$

$$\frac{(2 - 2x - \psi)(1 - \xi - \psi)}{\psi(\xi + \psi)} = K_{Fe}^{Sp}(P, T). \tag{8}$$

It is readily checked that these two equations can be represented as $\partial G^{Sp}/\partial\xi = 0$, and $\partial G^{Sp}/\partial\psi = 0$, i.e., as equilibrium conditions in relation to ξ and ψ. They contain the enthalpies instead of the Gibbs energies because we have neglected the nonconfigurational entropy, and their solution enables us to determine the equilibrium parameters $\xi = \tilde{\xi}(P, T, x)$ and $\psi = \tilde{\psi}(P, T, x)$.

Let us now examine (7) and (8). To determine the equilibrium $\lambda(P, T, x)$, we have to solve the cubic equation

$$\lambda^3 - \lambda^2 \frac{2x(K_{Fe}^{Sp} - K_{Mg}^{Sp}) + 3K_{Mg}^{Sp} + K_{Fe}^{Sp} - 4}{(1 - K_{Mg}^{Sp})(1 - K_{Fe}^{Sp})} +$$
$$+ \lambda\frac{5 - 2K_{Mg}^{Sp} - 2x(K_{Fe}^{Sp} - K_{Mg}^{Sp})}{(1 - K_{Mg}^{Sp})(1 - K_{Fe}^{Sp})} - \frac{2}{(1 - K_{Mg}^{Sp})(1 - K_{Fe}^{Sp})} = 0, \tag{9}$$

when ξ and ψ are defined by

$$\xi = 2x(1 - \lambda)/[1 - \lambda(1 - K_{Mg}^{Sp})], \quad \psi = 2(1 - x)(1 - \lambda)/[1 - \lambda(1 - K_{Fe}^{Sp})]$$

with $K^{Sp} \equiv K_{Fe}^{Sp}/K_{Mg}^{Sp} = 1$, (9) amounts to the quadratic equation derived in [10] for disordering in the pure (stoichiometric) spinels, and the solution is written explicitly as

$$\lambda = \frac{4}{3 + \sqrt{1 + 8K_{Mg,Fe}^{Sp}}}, \quad \xi = \frac{4x}{3 + \sqrt{1 + 8K_{Mg,Fe}^{Sp}}}, \quad \psi = \frac{4(1 - x)}{3 + \sqrt{1 + 8K_{Mg,Fe}^{Sp}}}. \tag{10}$$

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Then with $K^{sp}=1$, λ ceases to be dependent on composition. For $T \to \infty$, we have $K^{Sp}_{Mg,Fe} \to 1, \xi \to 2x/3$, $\psi \to 2(1-x)/3$, $\lambda \to 2/3$, so the limiting state is that of complete disorder, which corresponds to the maximum configurational entropy, which is $S_{max}= -R\{2x \ln x + 2(1-x)\ln(1-x) + 2\ln 2 - 3 \ln 3\}$. The same asymptote applies for $K^{Sp}_{Mg} \neq K^{Sp}_{Fe}$. With real spinels, the values of K^{Sp}_{Mg} and K^{Sp}_{Fe} are similar [9-14]. We introduced the small parameter $\varepsilon = (K^{Sp}_{Mg} - K^{Sp}_{Fe})/K^{Sp}_{Mg}$. From (9) we have up to terms of the order ε^2

$$\lambda = \frac{-3 + \sqrt{1 + 8K^{Sp}_{Mg}}}{2(K^{Sp}_{Mg} - 1)} - \varepsilon \frac{K^{Sp}_{Mg}(x-1)}{2(K^{Sp}_{Mg} - 1)}\left(3 - \frac{4K^{Sp}_{Mg} + 5}{\sqrt{1 + 8K^{Sp}_{Mg}}}\right). \tag{11}$$

For a given ε, the accuracy of (11) is dependent on x; for $x = 1$, the formula is exact, and the maximum error for $x = 0$ is

$$\Delta \lambda = \varepsilon^2 \frac{2K^{Sp}_{Mg}}{(K^{Sp}_{Mg} - 1)^2} \frac{1}{\sqrt{1 + 8K^{Sp}_{Mg}}}.$$

We can use (11) to derive explicit expressions for the activities of Mg_2SiO_4 and Fe_2SiO_4 in the disordered solution. The chemical potentials of the components

$$\mu^{Sp}_{Mg} = G^{Sp} + (1-x)\partial G^{Sp}/\partial x, \quad \mu^{Sp}_{Fe} = G^{Sp} - x\partial G^{Sp}/\partial x$$

are put as follows on the basis of (1)-(4)

$$\mu^{Sp}_{Mg} = G^{Sp}_{Mg} + RT \ln [(1 - \xi - \psi)(x - \xi/2)^2],$$
$$\mu^{Sp}_{Fe} = G^{Sp}_{Fe} + RT \ln\left[(1 - \xi - \psi)\left(1 - x - \frac{\psi}{2}\right)^2\right].$$

The above expressions for the equilibrium ξ and ψ in terms of λ give

$$\mu^{Sp}_{Mg} = G^{Sp}_{Mg} + RT \ln a^{Sp}_{Mg}(x, P, T), \quad \mu^{Sp}_{Fe} = G^{Sp}_{Fe} + RT \ln a^{Sp}_{Fe}(x, P, T),$$

where

$$a^{Sp}_{Mg} = x^2(1-\lambda)\left[\frac{\lambda K^{Sp}_{Mg}}{1 - \lambda(1 - K^{Sp}_{Mg})}\right]^2; \quad a^{Sp}_{Fe} = (1-x)^2(1-\lambda)\left[\frac{\lambda K^{Sp}_{Fe}}{1 - \lambda(1 - K^{Sp}_{Fe})}\right]^2$$

are the activities of Mg_2SiO_4 and Fe_2SiO_4 in the solid solution. If we take the standard states as those of the disordered end-members, a difference from (1) is that we get the definitions

$$\mu^{Sp}_{Mg} = \hat{G}^{Sp}_{Mg}(P, T) + RT \ln \hat{a}^{Sp}_{Mg}(x, P, T), \quad \mu^{Sp}_{Fe} = \hat{G}^{Sp}_{Fe}(P, T) + RT \ln \hat{a}^{Sp}_{Fe}(x, P, T),$$

where

$$\hat{G}^{Sp}_{Mg} = G^{Sp}_{Mg} + RT \ln\left[(1 - \hat{\xi})\left(1 - \frac{\hat{\xi}}{2}\right)^2\right],$$

$$\hat{G}^{Sp}_{Fe} = G^{Sp}_{Fe} + RT \ln\left[(1 - \hat{\psi})\left(1 - \frac{\hat{\psi}}{2}\right)^2\right],$$

$$\hat{\xi}(P, T) = \frac{4}{3 + \sqrt{1 + 8K^{Sp}_{Mg}}}, \quad \hat{\psi}(P, T) = \frac{4}{3 + \sqrt{1 + 8K^{Sp}_{Fe}}},$$

so

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Activities of the Components $MgSi_{0.5}O_2$ and $FeSi_{0.5}O_2$ in Spinel $(Mg, Fe)_2$ SiO_4 as Functions of Composition at 200 kbar, $\Delta E_{Mg}^{Sp} = 10$ kcal/mol, $\Delta E_{Fe}^{Sp} = 15$ and 30 kcal/mol, and $\Delta V_{Mg,Fe}^{Sp} = -0.5$ cm^3/mol

x	λ	$\hat{a}^{Sp}_{MgSi_{0.5}O_2}$	$\hat{a}^{Sp}_{FeSi_{0.5}O_2}$
		1000 K	
0,1	0,078/0,055	0,093/0,086	0,897/0,876
0,3	0,110/0,099	0,292/0,289	0,690/0,665
0,5	0,134/0,128	0,495/0,494	0,488/0,467
0,7	0,155/0,152	0,698/0,698	0,290/0,277
0,9	0,172/0,171	0,900/0,900	0,096/0,091
		2000 K	
0,1	0,256/0,118	0,095/0,070	0,899/0,876
0,3	0,290/0,215	0,293/0,272	0,695/0,645
0,5	0,320/0,279	0,495/0,484	0,492/0,442
0,7	0,347/0,327	0,698/0,694	0,292/0,257
0,9	0,372/0,366	0,900/0,900	0,096/0,083
		3000 K	
0,1	0,371/0,185	0,097/0,073	0,900/0,890
0,3	0,396/0,283	0,295/0,269	0,698/0,661
0,5	0,420/0,354	0,496/0,481	0,496/0,451
0,7	0,443/0,410	0,698/0,693	0,295/0,260
0,9	0,464/0,454	0,900/0,900	0,098/0,083

Note: The top line is the value for $\Delta E_{Fe}^{Sp} = 15$ and the bottom for 30 kcal/mol.

$$\hat{a}_{Mg}^{Sp} = \left(\frac{1-\lambda}{1-\hat{\xi}}\right)\left[\frac{\lambda x K_{Mg}^{Sp}}{[1-\lambda(1-K_{Mg}^{Sp})](1-\hat{\xi}/2)}\right]^2,$$

$$\hat{a}_{Fe}^{Sp} = \left(\frac{1-\lambda}{1-\hat{\psi}}\right)\left[\frac{\lambda(1-x)K_{Fe}^{Sp}}{[1-\lambda(1-K_{Fe}^{Sp})](1-\hat{\psi}/2)}\right]^2.$$

The form of $\lambda(P, T, x)$ is defined inexplicitly by (9); for $\varepsilon = 0$, $(K_{Mg}^{Sp} = K_{Fe}^{Sp})$, the solution remains ideal, and incorporating the disordering amounts to redefining the standard functions $G_{Mg}^{Sp}(P, T)$ and $G_{Fe}^{Sp}(P, T)$. This is not so for $\varepsilon \neq 0$; the explicit asymptotic expressions for the activities for small ε can be derived from (11). This demonstration of nonideal behavior of the solution for disordered spinels is a consequence of excluding the parameters characterizing the equilibrium disorder. At the same time, the model for mixing of Mg^{2+} and Fe^{2+} in the octahedral positions and for disordering of Mg^{2+}, $Fe^{2\beta}$, and Si^{4+} over the octahedral and tetrahedral ones in the oxygen framework is taken as ideal. An interesting point is that these activity coefficients cannot in general be described by polynomial functions of the composition.

There are large uncertainties over the values of $\Delta E_{Mg,Fe}^{Sp}$ and $\Delta V_{Mg,Fe}^{Sp}$ so it is best to examine how the equilibrium order parameters change when the thermodynamic functions vary. The parameters can be rendered dimensionless; for example, choosing a value for ΔH_{Mg}^{Sp} (or ΔH_{Fe}^{Sp}) is equivalent to choosing the temperature scale, and substantial changes in the degree of inversion will occur when the
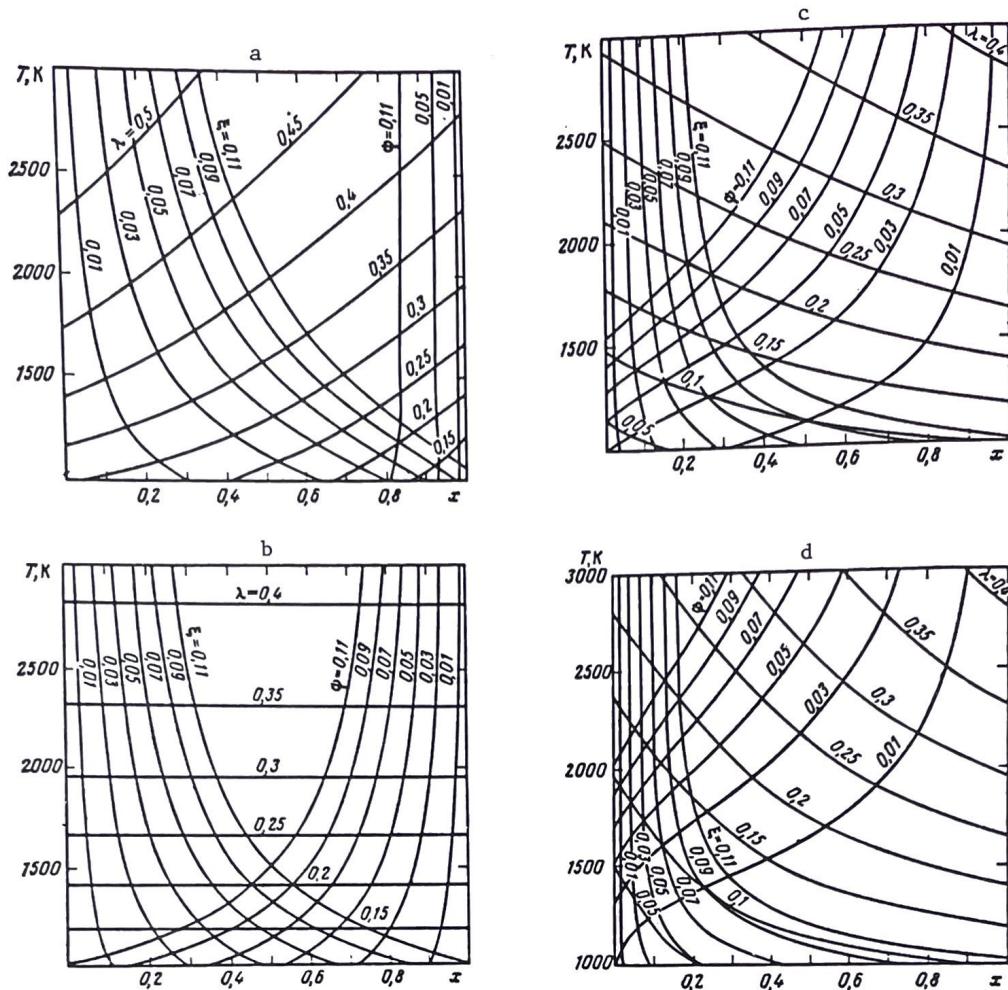
Fig. 1. Level lines for the following functions: $\lambda(P, T, x)$ the degree of inversion, $\xi(P, T, x)$ the proportion of tetrahedral positions occupied by Mg^{2+}, and $\psi(P, T, x)$ the proportion of tetrahedral positions taken by Fe^{2+} for a fixed pressure of 100 kbar with $\Delta V^{Sp}_{Mg,Fe} = -0.5$ cm^3/mol: a) ΔE^{Sp}_{Mg} 10, $\Delta E^{Sp}_{Fe} = 5$; b) $\Delta E^{Sp}_{Mg} = 10$, $\Delta E^{Sp}_{Fe} = 10$; c) $\Delta E^{Sp}_{Mg} = 10$, $\Delta E^{Sp}_{Fe} = 15$; d) $\Delta E^{Sp}_{Mg} = 10$, $\Delta E^{Sp}_{Fe} = 20$ kcal/mol; x is the molar fraction of Mg_2SiO_4 in the solution.

dimensionless parameter $L = \Delta H^{Sp}_{Fe}/\Delta H^{Sp}_{Mg}$ is varied. Figure 1 shows level lines for $\lambda(P, T, x)$, $\xi(P, T, x)$ and $\psi(P, T, x)$ for a fixed pressure in T-x coordinates. Table 1 gives the component activities as functions of composition for several temperatures. The deviations from ideal behavior are on average several per cent, so we have not used a graphical form for the activity-composition relationships.

There are various scales for the energies of cation preference for the tetrahedral and octahedral positions: Ulusov's [11], Reznitskiy's [14], and O'Neil and Navrotsky's [12, 13]. The differences between them should be dependent on the cation mixing model. As we are using an ideal-mixing model, we take the thermodynamic parameters derived in the analogous approximation for the pure phases [10]: $\Delta E^{Sp}_{Mg} = 24.1$, and $\Delta E^{Sp}_{Fe} = 29.7$ kcal/mol and $\Delta V^{Sp}_{Mg} = \Delta V^{Sp}_{Fe}$ -0.5 cm^3/mol. Figure 2 shows equilibrium curves for $\lambda(T)$ at 100 kbar for all these solid solutions. Pressure does not have a great effect (because ΔV is small), as is evident from the inset. Figure 3 shows the excess configurational mixing entropy as a function of temperature for the various compositions. The arrows indicate the deviations in the entropy from the level corresponding to completely ordered spinel $S^{id} = -2R[x \ln x + (1 - x)\ln(1 - x)]$. The entropies calculated in this way correspond to the stable equilibrium forms, and they should be the ones
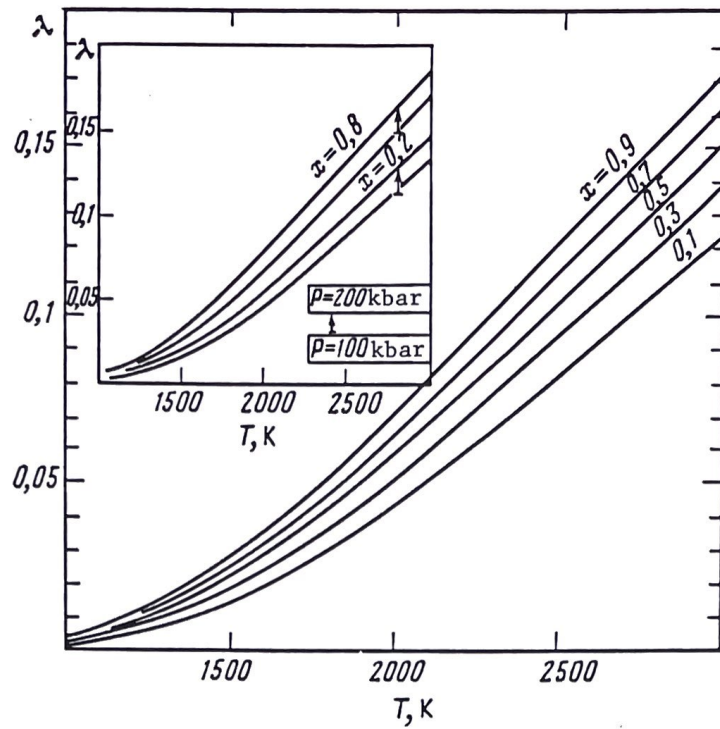
Fig. 2. Temperature dependence of the degree of inversion for $(Mg, Fe)_2SiO_4$ spinel, where x is the molar fraction of Mg_2SiO_4 in the solution. The inset shows the changes in the positions of the $\lambda(T)$ curves as the pressure increases; ΔE_{Mg}^{Sp} 24.1 kcal/mol, $\Delta E_{Fe}^{Sp} = 29.7$ kcal/mol, $\Delta V_{Fe,Mg}^{Sp} = -0.5$ cm^3/ mol.
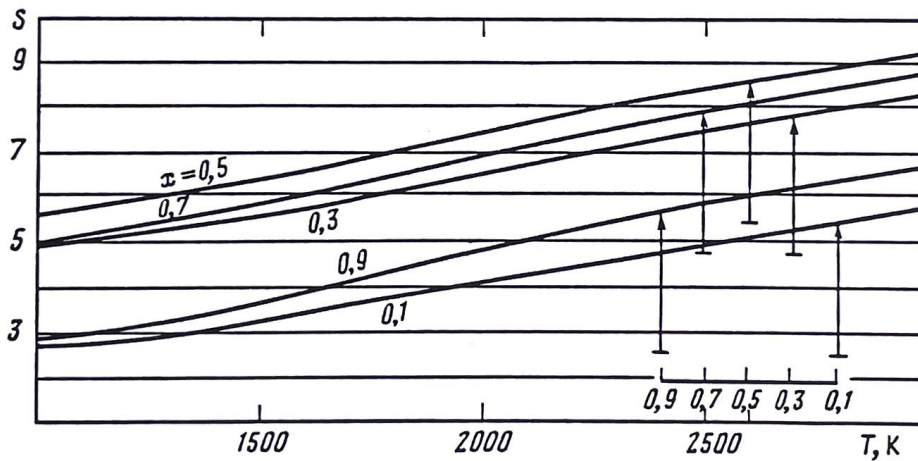

Fig. 3. Dependence of the entropy in cal/mol·K on temperature and composition for partially disordered $(Mg, Fe)_2SiO_4$. The arrows indicate the deviations from the level corresponding to complete ordering. Here x is the molar fraction of Mg_2SiO_4 in the solution; $\Delta E_{Mg}^{Sp} = 24.1$ kcal/mol, $\Delta E_{Fe}^{Sp} = 29.7$ kcal/mol, $\Delta V_{Fe,Mg}^{Sp} = -0.5$ cm^3/mol.

tabulated in handbooks. One can get substantial errors from using the high-temperature entropy values corresponding to nonequilibrium completely ordered forms in calculating phase-equilibrium curves (see an analysis of these effects in [9, 10, 15]).

Disordering-kinetic studies can indicate whether equilibrium is attained in calorimetric experiments.

There have been many studies [4, 9, 10, 15] on the effects of cation disordering on the positions of univariant solid-state equilibrium curves, in which it has been shown that the effects may be substantial; the slope of a phase-equilibrium curve may reverse in P-T coordinates if the heat of reaction is comparable with that of disordering and the values are opposite in sign [9, 10].

Here we will consider the effects of disordering on the line positions in the olivine-spinel phase diagram for the solid-solution series forsterite-fayalite (in P - X coordinates). For clarity, we neglect the presence of the modified β spinel and exclude the corresponding equilibria.

Let us write the phase-equilibrium conditions. The olivines $[Mg_y Fe_{(1-y)}]_2$ SiO_4 have the same formula as the spinel, but (Mg^{2+}, Fe^{2+})-(Si^{4+}) disordering is not observed in the latter minerals. The (Mg^{2+}, Fe^{2+}) ordering over the two types of octahedral positions [16] can be neglected because of the low degrees of order. Let y be the molar fraction of Mg_2SiO_4. Then the molar Gibbs energy of olivine is

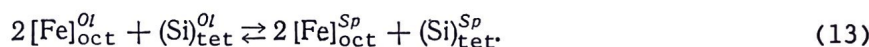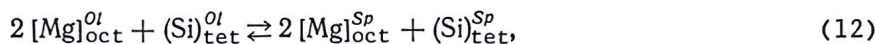$$G^{Ol} = yG^{Ol}_{Mg}(P, T) + (1-y)\, G^{Ol}_{Fe}(P, T) + \Delta G^{Ol}(y, P, T),$$

where $\Delta G^{ol} = \Delta E^{ol} - T\Delta S^{ol} + P\Delta V^{ol}$; with $G^{Ol}_{Mg,Fe}$ the Gibbs energies of the pure phases. In the ideal-solution approximation

$$\Delta E^{ol} = \Delta V^{ol} = 0,$$
$$\Delta S^{ol} = -2R[y \ln y + (1-y)\ln(1-y)].$$

The transition from the low-pressure phase (olivine) to the high-pressure one (spinel) can be represented as

$$2\,[Mg]^{Ol}_{oct} + (Si)^{Ol}_{tet} \rightleftarrows 2\,[Mg]^{Sp}_{oct} + (Si)^{Sp}_{tet}, \tag{12}$$

$$2\,[Fe]^{Ol}_{oct} + (Si)^{Ol}_{tet} \rightleftarrows 2\,[Fe]^{Sp}_{oct} + (Si)^{Sp}_{tet}. \tag{13}$$

The corresponding equilibrium constants are

$$\widetilde{K}_{Mg} = \exp(\Delta G_{Mg}/RT), \quad \widetilde{K}_{Fe} = \exp(\Delta G_{Fe}/RT),$$

where $\Delta G_{Mg,Fe} = G^{Sp}_{Mg,Fe} - G^{Ol}_{Mg,Fe}$. We use (12) and (13) to write the equations for the law of mass action:

$$\frac{y^2}{(1-\xi-\psi)\left(\dfrac{\xi}{2}\right)^2} = \widetilde{K}_{Mg}(P, T) \tag{14}$$

$$\frac{(1-y)^2}{(1-\xi-\psi)\left(1-x-\dfrac{\psi}{2}\right)^2} = \widetilde{K}_{Fe}(P, T). \tag{15}$$

We now combine (7), (8), (14) and (15) to get a system of four equations for the four unknown functions of temperature and pressure x, y, ξ and ψ in the parameter range corresponding to divariant two-phase equilibrium. Let the coordinates of the reactions in (12) and (13) be ξ_1 and ξ_2, in which case those equations can be written in a unified form as equilibrium conditions in respect of the internal degrees of freedom (we introduce the reaction basis):

$$\frac{\partial G}{\partial \xi} = 0, \ \frac{\partial G}{\partial \psi} = 0, \ \frac{\partial G}{\partial \zeta_1} = 0, \ \frac{\partial G}{\partial \zeta_2} = 0.$$

Here G is the Gibbs energy of the olivine-disordered spinel assemblage.

To demonstrate the main effect (equilibrium-line displacement), we first consider the special case $K_{Mg}^{Sp} = K_{Fe}^{Sp} = K^*$, which has independent significance because of the similarities between the preference energies ΔE for numerous cations [10-14]. We denote by $\overset{\circ}{x}(P, T)$ and $\overset{\circ}{y}(P, T)$ the values of the concentrations corresponding to equilibrium between olivine and completely ordered spinel ($\xi = \psi = 0$), which are evidently defined by the conditions $(1-\overset{\circ}{y})^2/(1-\overset{\circ}{x})^2 = \widetilde{K}_{Fe}$ and $\overset{\circ}{y}^2/\overset{\circ}{x}^2 = \widetilde{K}_{Mg}$. We substitute into (14) and (15) to get after simple steps that

$$x = \overset{\circ}{x} + \frac{\overset{\circ}{x}(1-\overset{\circ}{x})}{\overset{\circ}{y}-\overset{\circ}{x}}(\nu - 1),$$

$$y = \overset{\circ}{y} + \frac{\overset{\circ}{y}(1-\overset{\circ}{y})}{\overset{\circ}{y}-\overset{\circ}{x}}\left(\frac{\nu-1}{\nu}\right),$$

where $\nu = 2/(2-\lambda)\sqrt{1-\lambda}$, and $\lambda = 4/(3+\sqrt{1+8K^*})$. It is readily seen that $\nu > 1$, so the sign of the displacement in the equilibrium phase diagram ($x-\overset{\circ}{x}$, $y-\overset{\circ}{y}$) is dependent on the sign of $\overset{\circ}{y}-\overset{\circ}{x}$. According to [17, 18], $\overset{\circ}{y} > \overset{\circ}{x}$, throughout the composition range, so the entire diagram is displaced towards low pressures, and the spinel stability region enlarges.

Let us now consider the general case $K_{Mg}^{Sp} \neq K_{Fe}^{Sp}$. The solution to (7), (8), (14) and (15) can be represented in parametric form:

$$x = \frac{[(2-\lambda)(1-\lambda) - K_{Fe}^{Sp}\lambda^2](1-\lambda + \lambda K_{Mg}^{Sp})}{2\lambda(K_{Mg}^{Sp} - K_{Fe}^{Sp})(1-\lambda)}, \tag{16}$$

$$y = \sqrt{\widetilde{K}_{Mg}}\frac{K_{Mg}^{Sp}}{K_{Mg}^{Sp} - K_{Fe}^{Sp}}\frac{(2-\lambda)(1-\lambda) - K_{Fe}^{Sp}\lambda}{2\sqrt{1-\lambda}}, \tag{17}$$

$$\xi = [(2-\lambda)(1-\lambda) - \lambda^2 K_{Fe}^{Sp}]/[\lambda(K_{Mg}^{Sp} - K_{Fe}^{Sp})], \tag{18}$$

$$\psi = [K_{Mg}^{Sp}\lambda^2 - (2-\lambda)(1-\lambda)]/[\lambda(K_{Mg}^{Sp} - K_{Fe}^{Sp})]. \tag{19}$$

Parameter λ is defined by an algebraic equation of fourth degree $\sum\limits_{i=0}^{4} D_i\lambda^i = 0$, whose coefficients are

$$D_0 = 4B^2 - 1, \quad D_1 = 1 - 12B^2, \quad D_2 = 9B^2 + 4BC,$$

$$D_3 = -\frac{C}{2}BK_{Fe}^{Sp}\sqrt{\widetilde{K}_{Fe}}, \quad D_4 = C,$$

where

$$B = (\sqrt{\widetilde{K}_{Mg}}K_{Mg}^{Sp} - \sqrt{\widetilde{K}_{Fe}}K_{Fe}^{Sp})/2(K_{Mg}^{Sp} - K_{Fe}^{Sp}),$$

$$C = B(1 - K_{Fe}^{Sp}) + \frac{1}{2}K_{Fe}^{Sp}\sqrt{\widetilde{K}_{Fe}}.$$

The phase diagram for olivine-spinel equilibrium has been repeatedly examined for $(Mg_xFe_{(1-x)})_2SiO_4$ solutions [17, 18]. In [8], this diagram, without the β phase, was constructed by calculation in the ideal-mixing approximation from data on the standard energies of formation of the pure phases and the equation of state in the form $\int\limits_0^P VdP$. In the terms of our study, [8] gave the functions $\overset{\circ}{x}(P, T)$ and $\overset{\circ}{y}(P, T)$. As was shown above, the disordered spinel solution cannot be considered

as ideal. If we solve (16-19) numerically and use $\overset{\circ}{x}$ and $\overset{\circ}{y}$ from [8] as parameters, we get the lines in the modified diagram of Fig. 4 (see also Table 2). At 1000 K, there is virtually no displacement, while at 2000 K it is ~ 5 kbar in the ferroan region or ~ 10 kbar in the magnesian one. Certain difficulties are encountered in comparing the observed and calculated diagrams because of uncertainties in the experimental pressure (see discussion in [5]). The corresponding systematic error in the experiments shifts the diagram along the pressure scale, i.e., produces an effect analogous to that considered here involving expansion of the stability region of a disordered phase. The theoretical cigar-shaped region is somewhat narrower than the observed one on appropriate transfer [17, 18] (the discrepancy does not exceed 10 kbar).

ADIABATIC GRADIENT IN THE SPINEL STABILITY ZONE

The view that there is vigorous convection in the Earth's mantle has stimulated interest in the adiabatic gradient $(dP/dT)_A$ in multiphase mineral assemblages [1, 5, 7, 8]. The view that the temperature distribution in the mantle is adiabatic (isentropic) enables one to construct the temperature profile by chemical-thermodynamics methods. Various features of the adiabatic temperature distributions have been established in regions with divariant, monovariant, and nonvariant equilibria [7, 8, 19, 20]. Here we consider this for disordering solutions.

The entropy increases on disordering, so heat is absorbed; a pressure change with adiabatic insulation will affect the equilibrium disorder (degree of inversion). The maximum excess mixing entropy occurs for spinel with $\xi = 2x/3$, $\psi = 2(1 - x)/3$, and is $\Delta S = \{3\ln 3 - 2\ln 2\} \simeq 3.8$ cal/mol.K. The corresponding temperature change (reduction) is $\Delta T \simeq T\Delta S/C_p$. According to [7], $C_p^{\text{Mg}_2\text{SiO}_4}$ (2000 K) $\simeq 40.0$ cal/mol.K, so $\Delta T \simeq 200$ K. Adiabatic compression alters (increases) the temperature in the spinel-stability range (50-250 kbar) also by $\simeq 200$ K. These values would indicate that adiabatic disordering in spinel can produce a substantial retardation in the temperature rise in the mantle, but this is not so, because the degree of disorder attained is small ($\sim 2\%$).

The adiabatic (isentropic) condition can be put in differential form: $dS(P, T, x, \xi, \psi) = 0$. We take the composition as fixed to get

$$\frac{\partial S}{\partial P}dP + \frac{\partial S}{\partial T}dT + \frac{\partial S}{\partial \xi}\frac{\partial \xi}{\partial P}dP + \frac{\partial S}{\partial \psi}\frac{\partial \psi}{\partial P}dP + \frac{\partial S}{\partial \xi}\frac{\partial \xi}{\partial T}dT + \frac{\partial S}{\partial \psi}\frac{\partial \psi}{\partial T}dT = 0. \tag{20}$$

We now use the conditions for equilibrium as regards ξ and ψ to get

$$\frac{\partial \psi}{\partial P} = \frac{1}{\Delta}\left[\frac{\partial V}{\partial \xi}\frac{\partial^2 G}{\partial \xi \partial \psi} - \frac{\partial V}{\partial \psi}\frac{\partial^2 G}{\partial \xi^2}\right],$$

$$\frac{\partial \psi}{\partial T} = \frac{1}{\Delta T}\left[\frac{\partial H}{\partial \psi}\frac{\partial^2 G}{\partial \xi^2} - \frac{\partial H}{\partial \xi}\frac{\partial^2 G}{\partial \psi \partial \xi}\right],$$

$$\frac{\partial \xi}{\partial P} = \frac{1}{\Delta}\left[\frac{\partial V}{\partial \psi}\frac{\partial^2 G}{\partial \xi \partial \psi} - \frac{\partial V}{\partial \xi}\frac{\partial^2 G}{\partial \psi^2}\right], \tag{21}$$

$$\frac{\partial \xi}{\partial T} = \frac{1}{\Delta T}\left[\frac{\partial H}{\partial \xi}\frac{\partial^2 G}{\partial \psi^2} - \frac{\partial H}{\partial \psi}\frac{\partial^2 G}{\partial \xi \partial \psi}\right],$$

where $\Delta = \dfrac{\partial^2 G}{\partial \psi^2}\dfrac{\partial^2 G}{\partial \xi^2} - \left(\dfrac{\partial^2 G}{\partial \xi \partial \psi}\right)^2$. In deriving (21) we have used the fact that $\partial H/\partial \xi = T\partial S/\partial \xi$, $\partial H/\partial \psi = T\partial S/\partial \psi$ by virtue of the equilibrium conditions. We combine (20) and (21) and introduce the standard symbols $\partial S/\partial T = C_p/T$, $\partial S/\partial P = -\alpha V$, where α is the thermal-expansion coefficient and C_p is the specific heat at constant pressure, which gives us an expression for $(dT/dP)_A$ along the adiabat:
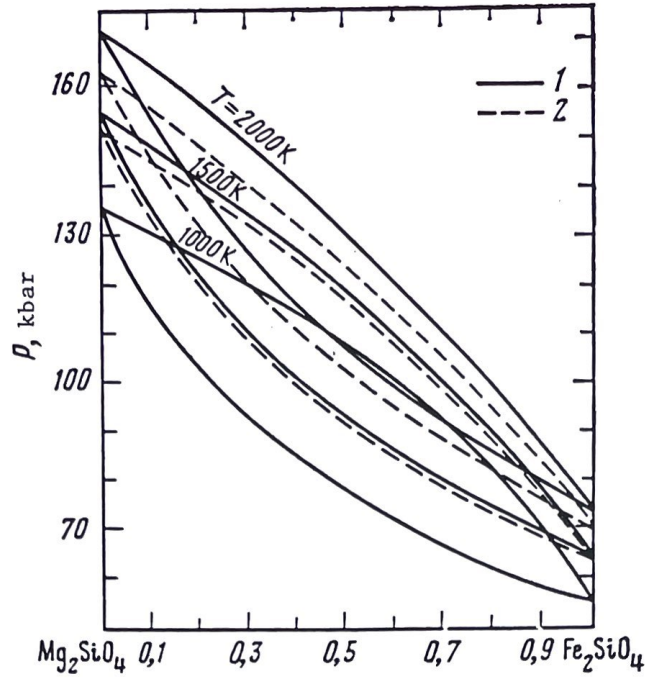
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Fig. 4. Displacement of the diagram for equilibrium between olivine and γ spinel on incorporating disordering in the spinel: 1) diagrams from ideal-solution approximation in [8]; 2) diagrams constructed from (16) and (17) in this paper; $\Delta E_{Mg}^{Sp} = 24.1$ kcal/mol, $\Delta E_{Fc}^{Sp} = 29.7$ kcal/mol, $\Delta V_{Fe,Mg}^{Sp} = -0.5$ cm^3/mol.

Table 2

Equilibrium Concentrations of FeO_4 in Coexisting Solutions of Olivine and γ Spinel $(Mg, Fe)_2SiO_4$

P, kbar	Disordering not taken into account						Disordering taken into account					
	Olivine			γ-spinel			Olivine			γ-spinel		
	1000*	1500	2000	1000	1500	2000	1000	1500	2000	1000	1500	2000
60	0,89	—	—	0,98	—	—	0,89	—	—	0,98	—	—
80	0,48	0,71	0,91	0,82	0,89	0,96	0,48	0,69	0,85	0,82	0,88	0,93
100	0,23	0,42	0,60	0,61	0,70	0,80	0,23	0,40	0,54	0,61	0,68	0,75
120	0,07	0,22	0,36	0,30	0,49	0,61	0,07	0,20	0,31	0,29	0,46	0,54
140	—	0,07	0,19	—	0,22	0,40	—	0,06	0,14	—	0,18	0,30
160	—	—	0,06	—	—	0,16	—	—	0,01	—	—	0,03

*T, K.

$$\left(\frac{dT}{dP}\right)^A = \frac{\alpha VT + \left[\left(\frac{\partial H}{\partial \xi}\frac{\partial V}{\partial \xi}\right)\frac{\partial^2 G}{\partial \psi^2} + \left(\frac{\partial H}{\partial \psi}\frac{\partial V}{\partial \psi}\right)\frac{\partial^2 G}{\partial \xi^2} - \left(\frac{\partial H}{\partial \xi}\frac{\partial V}{\partial \psi} + \frac{\partial H}{\partial \psi}\frac{\partial V}{\partial \xi}\right)\frac{\partial^2 G}{\partial \xi \partial \psi}\right]\frac{1}{\Delta}}{C_p + \left[\left(\frac{\partial H}{\partial \xi}\right)^2\frac{\partial^2 G}{\partial \psi^2} + \left(\frac{\partial H}{\partial \psi}\right)^2\frac{\partial^2 G}{\partial \xi^2} - 2\frac{\partial H}{\partial \xi}\frac{\partial H}{\partial \psi}\frac{\partial^2 G}{\partial \xi \partial \psi}\right]\frac{1}{T\Delta}} . \quad (22)$$

The ideal-mixing model gives explicit expressions (see (1)-(4)) for the derivatives appearing in (22)

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Table 3

Adiabatic Gradient in Disordering Spinel $(Mg_x Fe_{(1-x)})_2 SiO_4$ at 200 kbar, $x = 0.8$

T, K	$(dT/dP)_A^1$, K/kbar	$(dT/dP)_A^2$, K/kbar	λ	ξ	ψ
1500	0,860	0,826	0,033	0,032	0,001
2000	1,147	1,087	0,080	0,075	0,005
2500	1,434	1,357	0,133	0,122	0,010
3000	1,721	1,634	0,184	0,167	0,017

Note: $(dT/dP)_A^1$ without allowance for disordering, $(dT/dP)_A^2$ with disordering.

$$\frac{\partial H}{\partial \xi} = \Delta H_{Mg}, \quad \frac{\partial H}{\partial \psi} = \Delta H_{Fe}, \quad \frac{\partial V}{\partial \xi} = \Delta V_{Mg}, \quad \frac{\partial V}{\partial \psi} = \Delta V_{Fe}.$$

$$\frac{\partial^2 G}{\partial \xi^2} = RT \left[\frac{1}{\lambda(1-\lambda)} + \frac{2x}{\xi(2x-\xi)} \right], \quad \frac{\partial^2 G}{\partial \psi^2} = RT \left[\frac{1}{\lambda(1-\lambda)} + \frac{2(1-x)}{\psi(2-2x-\psi)} \right],$$

$$\frac{\partial^2 G}{\partial \xi \partial \psi} = \frac{RT}{\lambda(1-\lambda)}.$$

We substitute in (22) for the equilibrium functions $\xi(P, T, x)$, and $\psi(P, T, x)$ to get a first-order ordinary differential equation, whose solution is the desired curve $T = T_A(P)$ (the adiabat).

Let us now consider the adiabatic gradient in the ferromagnesian spinel stability region. We need to specify the specific heat and thermal-expansion coefficient. We will use the values for the pure phases recommended in [8]: C_p (cal/mol.K) = 43.3 (α-Fe_2SiO_4), 43.0 (γ-Fe_2SiO_4), 43.0 (α-Mg_2SiO_4), 42.6 (γ-Mg_2SiO_4), α (K^{-1}) = 3.2 × 10^{-5} (α-Fe_2SiO_4), 2.6 × 10^{-5} (γ-Fe_2SiO_4), 2.9 × 10^{-5} (α-Mg_2SiO_4), 2.4 × 10^{-5} (γ-Mg_2SiO_4), while the parameters for the solution are calculated from

$$C_p = x C_p^{Mg_2SiO_4} + (1-x) C_p^{Fe_2SiO_4},$$

$$\alpha = [\alpha^{Mg_2SiO_4} V^{Mg_2SiO_4} x + \alpha^{Fe_2SiO_4} V^{Fe_2SiO_4}(1-x)] / [x V^{Mg_2SiO_4} + (1-x) V^{Fe_2SiO_4}].$$

The results in Table 3 enable one to compare the $(dT/dP)_A$ along with the adiabat calculated with and without allowance for the disordering from (22); the discrepancy is several percent and increases with temperature.

The above general formulas also allow us to consider the particular case of stoichiometric Mg_2SiO_4. Here it is sufficient to pass to the limit $x \to 1$, $\psi \to 0$ in (22). Then for $(dT/dP)_A$ we have

$$\left(\frac{dT}{dP}\right)_A = \left[\alpha V + \frac{\frac{\partial H^{Sp}}{\partial \xi} \cdot \frac{\partial V^{Sp}}{\partial \xi}}{T \frac{\partial^2 G^{Sp}}{\partial \xi^2}} \right] \Bigg/ \left[\frac{C_p}{T} + \frac{\left(\frac{\partial H^{Sp}}{\partial \xi}\right)^2}{T^2 \frac{\partial^2 G^{Sp}}{\partial \xi^2}} \right]. \tag{23}$$

We can simplify (23) in the ideal-mixing approximation:

$$\left(\frac{dT}{dP}\right)_A^{\text{ld}} = \left(\alpha V + \frac{\Delta H_{\text{Mg}}^{Sp}\Delta V_{\text{Mg}}^{Sp}}{RT^2 f(\xi)}\right) \Big/ \left(\frac{C_p}{T} + \frac{(\Delta H_{\text{Mg}}^{Sp})^2}{RT^3 f(\xi)}\right), \qquad (24)$$

where

$$\Delta H_{\text{Mg}}^{Sp} = \partial H^{sp}/\partial\xi, \quad \Delta V_{\text{Mg}}^{Sp} = \partial V^{sp}/\partial\xi, \quad f(\xi) = (4-3\xi)/\xi(1-\xi)(2-\xi).$$

The equilibrium degree of order is given by

$$\xi = 4/[3 + \sqrt{1 + 8\exp(\Delta H_{\text{Mg}}^{Sp}/RT)}].$$

If we can neglect the volume change on disordering,

$$\left(\frac{dT}{dP}\right)_A = \left(\frac{dT}{dP}\right)_A^0 \left[1 + \frac{(\Delta H_{\text{Mg}}^{Sp})^2}{C_p RT^2}\frac{1}{f(\xi)}\right]^{-1},$$

where $(dT/dP)_A^0 = \alpha VT/C_p$ is the classical value for the adiabatic gradient.

The maximum correction to the gradient occurs when $\partial^2 G/\partial\xi^2$ is close to zero, but for $\partial^2 G/\partial\xi^2 \to 0$ we have $\partial\xi/\partial T \to \infty$, i.e., there is a discontinuity corresponding to a phase transition. Phase transitions of the first kind in mineral disordering do occur [21]. In that case, there is a jog on the phase-transition curve in P-T coordinates, as the curve coincides in part with the equilibrium curve. This situation is common to all univariant phase reactions [5, 7, 8, 19, 20]. A characteristic feature is the negative slope of the equilibrium curve, which leads to stepwise temperature reduction.

DISCUSSION

One result is the demonstration that $(\text{Mg, Fe})_2\text{SiO}_4$ is nonideal, which is due to Mg^{2+}, Fe^{2+}, and Si^{4+} disordering. This non-ideality is related to disordering being superimposed on the standard picture of virtually ideal isomorphous replacement of magnesium by iron in the spinel, while the dependence of excess mixing functions on composition is a consequence of excluding the internal parameters characterizing the disorder by means of the equilibrium conditions. A specific feature of these nonideal solutions is that the activity coefficients are dependent not only on the composition but also on temperature. As a result, the nonconfigurational mixing entropy varies on heating even for constant composition, which causes changes in characteristics such as the specific heat, slope of the adiabat in P-T coordinates, etc. The analysis enables us to calculate the displacement of the olivine-spinel phase boundary associated with disordering, as this boundary lies at the edge of the spinel stability region for the upper mantle. Proper correction for nonideal behavior in $(\text{Mg, Fe})_2\text{SiO}_4$ may also lead to reconsideration of our views on the positions of the univariant equilibrium curves bounding the spinel stability region for the lower mantle; one expects that the corresponding nonideal behavior associated with disordering will occur with other phases such as $(\text{Mg, Fe})\text{SiO}_3$ having the ilmenite structure [4].

A natural extension of this model is to abandon ideal mixing at all stages. The most interesting point concerns the deviations from ideal behavior on cation disordering. The ideal-mixing model corresponds to the interaction between adjacent atoms being negligibly weak, while the distribution over the positions is random, i.e., short-range order is completely ignored. The next approximation is the regular-mixing model [11-13], which is based on the additional interaction energy and amounts in our terms to redefining the preference energy $\Delta E_{\text{Mg}}^{Sp} = \Delta E_{\text{Mg}}^{Sp^0} + \xi\Delta E_{\text{Mg}}^{Sp^1} + \psi\Delta E_{\text{Mg}}^{Sp^2}$, and $\Delta E_{\text{Fe}}^{Sp} = \Delta E_{\text{Fe}}^{Sp^0} + \xi\Delta E_{\text{Fe}}^{Sp^1} + \psi\Delta E_{\text{Fe}}^{Sp^2}$ with an unchanged expression for the configurational entropy [11-13]. It is then clearly possible to incorporate the changes in interaction parameters on disordering. It can be shown that this extension for spinel does not lead to a first-order phase transition in the calculations. To obtain a model with a phase transition on disordering such as is observed for MgAl_2O_4 (spinel) [11, 12], it is necessary either to use nonlinear

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functions $\Delta H = \Delta H^0 + \xi \Delta H' + \xi^2 \Delta H'' + \ldots$, or to abandon the assumption that the configurational entropy is ideal and to calculate it from some statistical model with allowance for the short-range order [21].

In conclusion we note that we have assumed thermodynamic equilibrium in relation to the internal degrees of freedom ξ and ψ, i.e., the disordering is considered to occur instantaneously. When one considers processes such as convection, one has to bear in mind that the characteristic relaxation time to equilibrium is accompanied by at least one further time parameter characterizing the rate of change in the P-T conditions, so the concept of instantaneous kinetics can be given an exact sense. We lack reliable evidence on spinel disordering kinetics, so no such estimate can be made here.

MAIN RESULTS

1. A simple model has been proposed for disordering in $(Mg, Fe)_2SiO_4$ solid solutions, which enables one to calculate the degree of inversion and the excess mixing energy as explicit functions of temperature and composition.

2. The values used for the preference energies mean that the degree of spinel inversion is slight ($\sim 2\%$) at the P and T of the upper mantle, so the deviations from ideal behavior are slight. On the other hand, the change in mixing entropy due to disordering (Fig. 3) is not small ($\sim 100\%$).

3. The theoretical olivine-spinel equilibrium diagram has been derived for the entire series of Fo-Fa solid solutions. Allowance for spinel disordering shifts the diagram with respect to pressure by 5-10 kbar.

4. Formulas have been obtained for calculating the adiabatic gradient in the stability region for disordered spinel. It is shown that the gradient in the transitional mantle zone may be reduced by several percent on account of disordering in the spinel.

REFERENCES

1. Zharkov, V. N. and V. P. Trubitsyn, 1980. Fizika planetnykh nedr [The Physics of Planetary Interiors], Nauka, Moscow.
2. Vinnik, L. A., 1984. Dokl. AN SSSR, v. 274, No. 2, p. 296.
3. Lees, A. C., M. S. T. Bukowinski and R. Jeauloz, 1983. J. Geophys. Res., v. 88, No. B10, p. 8145.
4. Barsukov, V. L. and V. S. Urusov, 1982. Geokhimiya, No. 12, p. 1729.
5. Jeanloz, R. and A. B. Thompson, 1983. Rev. Geophys. Space Phys., v. 21, p. 51.
6. Kuskov, O. L., R. F. Galimzyanov, and N. I. Khitarov, 1983. Dokl. AN SSSR, v. 270, No. 3, p. 577.
7. Truskinovskiy, L. M., O. L. Kuskov and N. I. Khitarov, 1983. Geokhimiya, No. 9, p. 1222.
8. Truskinovskiy, L. M., O. L. Kuskov and N. I. Khitarov, 1985. Geokhimiya, No. 5, p. 579.
9. Jackson, I. N. S., R. C. Liebermann and A. E. Ringwood, 1974. Earth and Planet. Sci. Lett., v. 24, p. 203.
10. Navrotsky, A., 1977. Earth and Planet. Sci. Lett., v. 33, p. 437.
11. Urusov, V. S., 1983. Phys. Chem. Min., v. 9, p. 1.
12. O'Neil, H. St. C. and A. Navrotsky, 1983. Amer. Miner., v. 68, p. 184.
13. O'Neil, H. St. C. and A. Navrotsky, 1984. Amer. Miner., v. 69, p. 733.
14. Reznitskiy, L. A., 1984. V kn.: Itogi nauki i tekhniki. Ser. khimicheskaya termodinamika i ravnovesiya, T. 6 [In: Surveys of Science and Engineering: Series Chemical Thermodynamics and Equilibria, V. 1], Izd. VINITI, Moscow, p. 3.
15. Kuskov, O. L. and R. F. Galimzyanov, 1984. Geokhimiya, No. 1, p. 101.
16. Urusov, V. S. and N. R. Khisina, 1985. Mineral. Zh., v. 7, p. 3.
17. Ringwood, A. E., 1981. The Composition and Petrology of the Earth's Mantle [Russian translation], Nedra, Moscow.
18. Akimoto, S., 1975. In: The Upper Mantle [Russian translation], Mir, Moscow, p. 60.
19. Truskinovskiy, L. M., O. L. Kuskov and N. I. Khitarov, 1983. Dokl. AN SSSR, v. 274, No. 5, p. 1064.

20. Truskinovskiy, L. M., O. L. Kuskov and N. I. Khitarov, 1985. Dokl. AN SSSR, v. 285, No. 1, p. 83.
21. Senderov, E. E., 1980. Phys. Chem. Miner., v. 6, p. 251.

THE COMPOSITION OF APATITE FROM METAMORPHIC ROCKS*

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Studies have been made on apatite from metamorphic rocks of various facies in the Kola peninsula and Karelia, the Ukraine, Siberia and Central Asia. The metamorphogenic apatite contains very low levels of minor components. Specimens from greenschists have minimal levels of Sr, Ba, Mn and Na but elevated amounts of SO_3 and Cl; ones from the amphibolite facies have lower SO_3 and Cl contents, but the amounts of Sr, Mn and Na are higher, the maximum values being found in the granulite facies, but these are still lower by factors of 5-20 than those in apatite from gabbros, carbonatites, diorites and alkalic rocks.

Apatite is always present in metamorphic rocks, at least in small amounts, as an accessory mineral [1, 2]; the exact level varies considerably with the composition and facies and is dependent mainly on the original sediment composition.

Apatite from granulite-facies metamorphic rocks have so far been largely neglected, since usually the levels in granulites are minute and the mineral is difficult to isolate. I have examined accessory apatite from metamorphic rocks of various facies in various parts of the USSR: hypersthene granites in the Bug and Aldan areas, cordierite gneisses containing hypersthene at Slyudyanka and in the southwestern Baykal region, and Anabar sapphirine-pyroxene granulites. In all these rocks, the apatite consists of small transparent colorless prismatic crystals (< 0.05 mm) containing no visible inclusions. It is usually evenly distributed in leucocratic hypersthene granites, whereas in melanocratic rocks it forms small clumps and nodules in close association with almandine, zircon, and rutile. The levels in leucocratic granites usually do not exceed 0.5%, though some specimens contain up to 2%. In the Aldan, Anabar, and Slyudyanka melanocratic granulites the apatite is not so evenly distributed, the levels being 0.5-3%, usually ~2%. The diopside and spinel-forsterite calciphyres from the granulite suite in the Bug area have apatite levels of 1-5%; it forms rounded colorless grains of size 0.1-1 mm.

Apatite is always present in all rocks in the amphibolite facies: Precambrian gneisses, migmatites, amphibolites, and schists, where it is fairly evenly

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