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## The constitution of the mantle—I Thermodynamics of the olivine-spinel transition

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**Abstract**—A method of calculating the pressure required to cause  $Mg_2SiO_4$  to invert from the olivine to the spinel structure is described. It is based upon the fact that  $Mg_2SiO_4$  displays limited solid solubility in nickel orthogermanate ( $Ni_2GeO_4$ ) at high temperature.  $Ni_2GeO_4$  has a spinel structure. By means of a thermodynamic treatment of  $Ni_2GeO_4$ — $Mg_2SiO_4$  spinel solid solutions and their phase equilibria with olivine solid solutions, it is possible to calculate the free energy of the olivine-spinel transition for  $Mg_2SiO_4$ . This is found to be  $70,000 \pm 10,000$  J/mole at  $1500^\circ C$ .

The lattice constant of  $Mg_2SiO_4$  spinel is found by extrapolating the lattice constants of the spinel solid solutions. This, together with the lattice constants of  $Ni_2SiO_4$  and  $Mg_2GeO_4$  spinels obtained in an analogous manner, indicate that the increase in density when olivine transforms to spinel is  $11 \pm 3$  per cent.

The free-energy difference between the two forms when they are subjected to high pressures is  $P\Delta V$ , where  $\Delta V$  is the difference in molar volume at a pressure  $P_1$ . When this function becomes equal to the free energy of transition at zero pressure (obtained above), olivine will invert to spinel. Calculations on this basis indicate that a pressure equivalent to that at a depth of approximately  $500 \pm 140$  km within the earth will cause inversion. This result is in good agreement with the depth of the  $20^\circ$  discontinuity found by seismology.

### INTRODUCTION

SEISMOLOGICAL data, combined with investigations of density and electrical conductivity strongly suggest the presence of inhomogeneity in the upper levels of the mantle. Indications are that the inhomogeneity is most marked at a depth of about 400 km. JEFFREYS (1952) has inferred the presence of a discontinuity at this depth—the “ $20^\circ$  discontinuity”. BIRCH (1952) has produced evidence suggesting that the inhomogeneity occurs over a substantial depth range—perhaps from 300 to 800 km. Above and below these limits the mantle appears to be homogeneous.

JEFFREYS and BERNAL (see JEFFREYS, 1952) have suggested that the inhomogeneity and discontinuity are caused by a polymorphic inversion in olivine. BERNAL (1936) pointed out that  $Mg_2GeO_4$ , which is closely related to  $Mg_2SiO_4$ , is dimorphous, displaying both olivine and spinel structures. BERNAL therefore suggested that at high pressures, olivine-type  $Mg_2SiO_4$  might undergo inversion to a spinel form, possessing higher density. Subsequent laboratory compression experiments upon olivine have failed to produce the spinel polymorph, however.

Before the JEFFREYS-BERNAL hypothesis can be adequately assessed, some means of estimating the pressure required to produce this inversion must be found. In the following pages, such a method is described. It is based upon an investigation of sub-solidus phase equilibria in the system  $Ni_2GeO_4$ — $Mg_2SiO_4$ . Nickel orthogermanate ( $Ni_2GeO_4$ ) possesses a spinel structure. The ions  $Ni^{2+}$  and  $Mg^{2+}$  are similar in crystal chemical properties, and able to replace each other in many crystals and minerals. A similar resemblance occurs between  $Si^{4+}$  and  $Ge^{4+}$ . Therefore it seemed possible that some  $Mg^{2+}$  and  $Si^{4+}$  might be able to replace  $Ni^{2+}$  and  $Ge^{4+}$

in  $\text{Ni}_2\text{GeO}_4$ . This proved to be the case, and  $\text{Ni}_2\text{GeO}_4$  spinel was found to take up to 9 per cent of  $\text{Mg}_2\text{SiO}_4$  into solid solution at  $1500^\circ\text{C}$ . By a study of the properties of these solid solutions, and a thermodynamic investigation of their phase equilibrium relationships to co-existing olivine solid solutions, sufficient data may be secured to predict the stability range of  $\text{Mg}_2\text{SiO}_4$  spinel.

## 2. DETERMINATION OF FREE ENERGY OF TRANSITION

### (a) *Experimental*—*The system* $\text{Ni}_2\text{GeO}_4$ — $\text{Mg}_2\text{SiO}_4$

Sub-solidus phase equilibria in this system were investigated in the  $1200$ – $1500^\circ\text{C}$  range. The raw materials— $\text{GeO}_2$ ,  $\text{MgO}$ —were of reagent grade.  $\text{NiO}$  was formed by igniting nickel nitrate and calcining the product at  $1200^\circ\text{C}$ .  $\text{SiO}_2$  was prepared from pure quartz crystal which was crushed and leached with  $\text{HCl}$ .

After preliminary drying treatment,  $\text{GeO}_2$ ,  $\text{SiO}_2$ ,  $\text{MgO}$  and  $\text{NiO}$  were weighed out in amounts corresponding to various desired proportions of  $\text{Ni}_2\text{GeO}_4$  to  $\text{Mg}_2\text{SiO}_4$ . The mixture (amounting to 1 g for any preparation) was thoroughly ground together under benzene in order to secure intimate mixing, dried, and then formed into tablets in a small press. Tablets were held in air in a platinum-wound electric furnace which could be controlled at any desired temperature. Temperature was measured using a calibrated Pt–Pt 10 per cent Rh thermocouple. The length of the run varied according to the time necessary to achieve equilibrium, and the amount of  $\text{GeO}_2$  which was being lost by volatilization. (This becomes appreciable above  $1400^\circ\text{C}$  and must be corrected for.) The times necessary were determined by experience, and varied from 40 hr at  $1200^\circ\text{C}$  to 30 min at  $1500^\circ\text{C}$ . The tablet was then removed from the furnace, cooled in air, recrushed and reformed, and the procedure was repeated. In most cases this was sufficient to ensure equilibrium; sometimes, however, a third crushing was required.

The above procedure served to establish the approximate positions of phase boundaries; however, for more precise determination of the boundary on the spinel side, additional precautions were necessary. The main difficulty in sub-solidus studies is the attainment of a high degree of homogeneity in the sample so that complete equilibrium is ensured. To attain this,  $\text{NiO}$ — $\text{MgO}$  and  $\text{GeO}_2$ — $\text{SiO}_2$  were weighed out, mixed and formed into tablets separately. The  $\text{NiO}$ — $\text{MgO}$  tablets were held at  $1400^\circ\text{C}$  for several hours, crushed, and the procedure repeated twice. Similarly the  $\text{GeO}_2$ — $\text{SiO}_2$  tablets were melted at  $1300^\circ\text{C}$  for 2 hr, recrushed, and so on. These components which were by then individually homogeneous were weighed in the correct proportions to form a tablet of desired composition, which was then treated as above.

Samples so prepared were examined by optical and X-ray methods. The spinel solid solutions appear as green isotropic crystals under the petrographic microscope, whereas the olivine solid solutions are anisotropic and possess a high birefringence. Accordingly, it is possible to locate the two-phase boundary by observing the composition at which birefringent crystals make their appearance among the isotropic spinels. The location of the two-phase boundary on the olivine side of the system may be found in an analogous manner. Refractive indices of the spinels were determined using sulphur–selenium melts, whilst ordinary high RI liquids

sufficed for the olivines. By determining the refractive indices of the olivine solid solutions, the two-phase boundary may be located more accurately.

X-ray powder patterns of samples also locate the two-phase boundaries, and the results were found to agree with the optical examination. Trials with mixtures of  $\text{NG}_{100}$  and  $\text{NG}_{40}\text{MS}_{60}$  ( $\text{NG} = \text{Ni}_2\text{GeO}_4$ ,  $\text{MS} = \text{Mg}_2\text{SiO}_4$ ) demonstrated that the

Table 1. Phase equilibrium data and refractive indices for spinel solid solutions

Composition (mole %)	Temperature ( $\pm 10^\circ\text{C}$ )	Phases present	Refractive index $\pm 0.005$
$\text{NG}_{100}$	1360	Homogeneous spinel	2.082
$\text{NG}_{97}\text{MS}_3$	1360	Homogeneous	2.068
$\text{NG}_{94}\text{MS}_6^{a,b}$	1272	Two-phase	
$\text{NG}_{94}\text{MS}_6$	1360	Homogeneous	2.061
$\text{NG}_{94}\text{MS}_6^a$	1411	Homogeneous	
$\text{NG}_{94}\text{MS}_6$	1439	Homogeneous	
$\text{NG}_{94}\text{MS}_6^a$	1509	Homogeneous	
$\text{NG}_{93}\text{MS}_7$	1439	Homogeneous	
$\text{NG}_{92}\text{MS}_8^a$	1272	Two-phase	
$\text{NG}_{92}\text{MS}_8^a$	1411	Homogeneous	
$\text{NG}_{92}\text{MS}_8^a$	1509	Homogeneous	
$\text{NG}_{91}\text{MS}_9$	1470	Two-phase	2.046
$\text{NG}_{91}\text{MS}_9$	1439	Two-phase	
$\text{NG}_{90}\text{MS}_{10}^a$	1272	Two-phase	
$\text{NG}_{90}\text{MS}_{10}^a$	1411	Two-phase	
$\text{NG}_{90}\text{MS}_{10}$	1439	Two-phase	
$\text{NG}_{90}\text{MS}_{10}^a$	1509	Two-phase	
$\text{NG}_{88}\text{MS}_{12}$	1470	Two-phase	2.042
$\text{NG}_{88}\text{MS}_{12}$	1528	Two-phase	
$\text{NG}_{85}\text{MS}_{15}$	1470	Two-phase	2.037

<sup>a</sup> These samples were prepared using the special precautions to ensure homogeneity outlined previously.

<sup>b</sup> The inhomogeneity found in this sample was originally assumed to represent equilibrium, and consequently in the phase diagram first published (RINGWOOD, 1956) the spinel solvus was given a steep positive slope. However, subsequent work showed that it was impossible to obtain equilibrium at  $1200^\circ\text{C}$ , and hence it seemed possible that the inhomogeneity found in this run ( $1272^\circ\text{C}$ ) might be due to non-attainment of equilibrium. To check this, a sample of  $\text{NG}_{90}\text{MS}_{10}$  was held at  $800^\circ\text{C}$  in a "squeezer" type apparatus under a pressure of 12,000 bars. The product was fairly well crystallized, but gave a rather diffuse X-ray powder pattern. Optical and X-ray examination did not reveal the presence of olivine. Most of the  $\text{Mg}_2\text{SiO}_4$  must therefore be in solid solution. Accordingly the result referred to is probably not representative of equilibrium and the slope of the spinel solvus (Fig. 1) has been modified.

222 line of  $\text{NG}_{40}\text{MS}_{60}$  (olivine) could usually be identified when  $3\frac{1}{2}$  per cent of the olivine was present among the spinel. This corresponded to a tolerance of 2 per cent of pure  $\text{Mg}_2\text{SiO}_4$ . X-ray investigation also provided information on the lattice parameters of the spinel solid solutions and their structure.

### (b) Results

Results of these investigations are set out in Tables 1 and 2. The principal conclusions may be summarized:

- (i) Between  $1300$  and  $1500^\circ\text{C}$ ,  $\text{Ni}_2\text{GeO}_4$  spinels dissolve about 9 per cent of  $\text{Mg}_2\text{SiO}_4$  (Fig. 1).

(ii) Between 1200°C and 1500°C,  $\text{Mg}_2\text{SiO}_4$  olivines dissolve from 27 to 49 per cent of  $\text{Ni}_2\text{GeO}_4$  (Fig. 1).

(iii) The system is binary in the single-phase fields but ternary in the two-phase field.

Alpha and gamma refractive indices of homogeneous olivine solid solutions have been plotted in Fig. 2 on a mole per cent basis. The variation is linear in the

Table 2. Phase equilibrium data and refractive indices for olivine solid solutions

Composition (mole %)	Temperature $\pm 10^\circ\text{C}$	Phases present	Refractive index of olivine $\pm 0.01$	
			Alpha	Gamma
$\text{MS}_{100}$	1600	Homogeneous olivine	1.635	1.670
$\text{NG}_{20}\text{MS}_{80}$	1387	Homogeneous	1.687	1.745
$\text{NG}_{30}\text{MS}_{70}$	1396	Homogeneous	1.711	1.780
$\text{NG}_{30}\text{MS}_{70}$	1187	Two-phase (just)	1.700	1.750
$\text{NG}_{40}\text{MS}_{60}$	1187	Two-phase	1.710	1.770
$\text{NG}_{40}\text{MS}_{60}$	1387	Homogeneous	1.741	1.810
$\text{NG}_{45}\text{MS}_{55}$	1285	Two-phase	1.725	1.785
$\text{NG}_{50}\text{MS}_{50}$	1396	Two-phase	1.751	1.810
$\text{NG}_{50}\text{MS}_{50}$	1500	Two-phase	1.755	1.825
$\text{NG}_{50}\text{MS}_{50}$	1527	Homogeneous	1.763	1.840
$\text{NG}_{50}\text{MS}_{50}$	1411	Two-phase	1.740	1.815
$\text{NG}_{60}\text{MS}_{40}$	1396	Two-phase	1.760	1.820
$\text{NG}_{60}\text{MS}_{40}$	1411	Two-phase	1.750	1.820
$\text{NG}_{60}\text{MS}_{40}$	1500	Two-phase	1.765	1.840
$\text{NG}_{60}\text{MS}_{40}$	1527	Two-phase	1.770	1.855
$\text{NG}_{70}\text{MS}_{30}$	1411	Two-phase	1.760	1.830
$\text{NG}_{70}\text{MS}_{30}$	1500	Two-phase	1.770	1.845
$\text{NG}_{80}\text{MS}_{20}$	1411	Two-phase	1.775	—
$\text{NG}_{80}\text{MS}_{20}$	1500	Two-phase	1.780	1.855
$\text{NG}_{85}\text{MS}_{15}$	1470	Two-phase	1.790	1.860

single-phase field. Refractive indices are probably uncertain by  $\pm 0.01$  because of slight inhomogeneity in the samples and differential volatilization of  $\text{GeO}_2$  during formation. This error would tend to make  $(\gamma - \alpha)$  values somewhat too high.

Refractive indices of spinel solid solutions are plotted in Fig. 3. The values are the mean of many determinations and are probably internally consistent to  $\pm 0.005$ . Here too, the variation is linear in the single-phase field, within the limits of error of refractive index determination.

Although the system is binary in the single-phase field, it becomes ternary when the two-phase field is entered. This behaviour is due to the ability of  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$  to replace one another in crystals independently of  $\text{Ge}^{4+}$  and  $\text{Si}^{4+}$ . In the single-phase region,  $\text{Mg}^{2+}$  and  $\text{Si}^{4+}$  can only enter  $\text{Ni}_2\text{GeO}_4$  in the fixed ratio ( $2\text{Mg}^{2+} + \text{Si}^{4+}$ ). Similarly, in the olivine single-phase field,  $\text{Ni}^{2+}$  and  $\text{Ge}^{4+}$  can only enter  $\text{Mg}_2\text{SiO}_4$  in the fixed ratio ( $2\text{Ni}^{2+} + \text{Ge}^{4+}$ ). However, these fixed ratios are not necessary in the two-phase field. Consequently, Fig. 1 can only be used to show the phases

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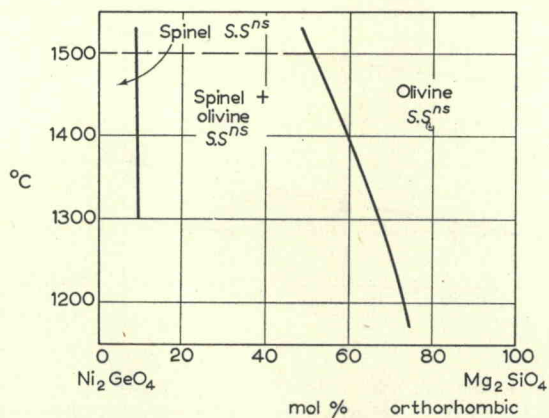


Fig. 1. Sub-solidus phase equilibria in pseudobinary system  $\text{Ni}_2\text{GeO}_4$ - $\text{Mg}_2\text{SiO}_4$ .

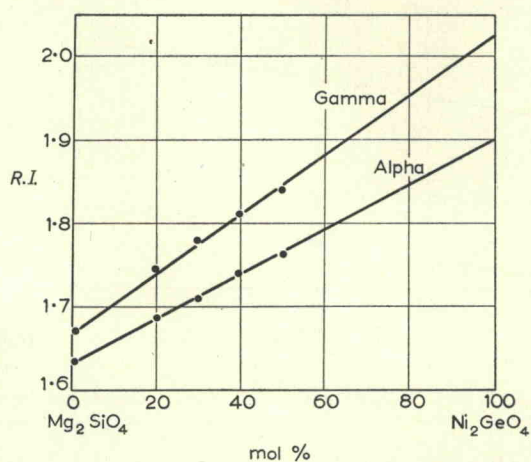


Fig. 2. Alpha and gamma indices of  $\text{Mg}_2\text{SiO}_4$ - $\text{Ni}_2\text{GeO}_4$  olivine-type solid solutions.

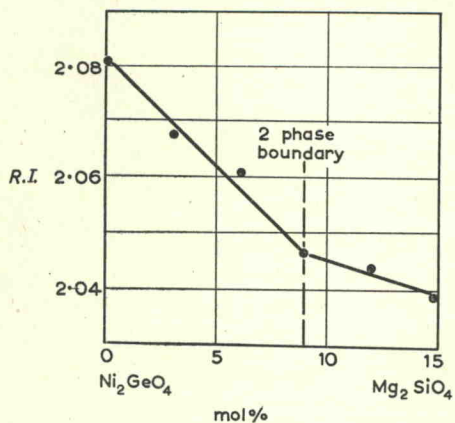


Fig. 3. Indices of refraction of  $\text{Ni}_2\text{GeO}_4$ - $\text{Mg}_2\text{SiO}_4$  spinel-type solid solutions.

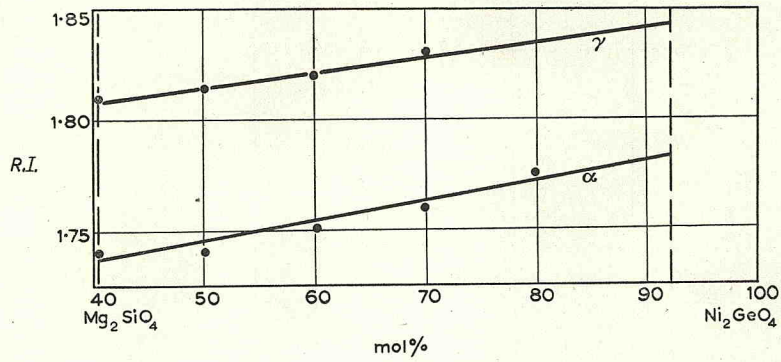


Fig. 4. Alpha and gamma indices of refraction of  $\text{Ni}_2\text{GeO}_4$ - $\text{Mg}_2\text{SiO}_4$  solid solutions across two-phase field at 1400°C. Broken lines indicate two-phase boundary.

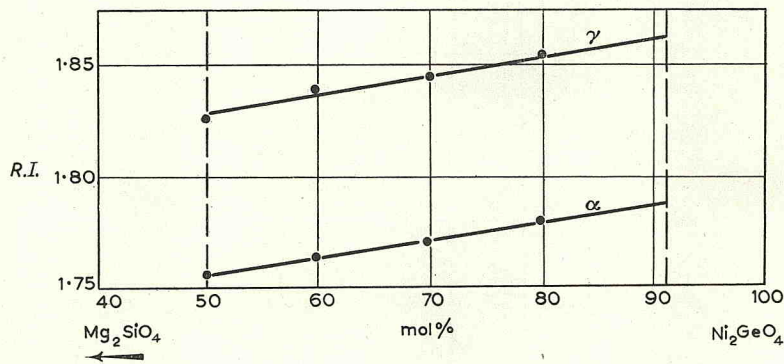


Fig. 5. Alpha and gamma indices of refraction of  $\text{Ni}_2\text{GeO}_4$ - $\text{Mg}_2\text{SiO}_4$  solid solutions across two-phase field at 1500°C. Broken lines indicate two-phase boundary.

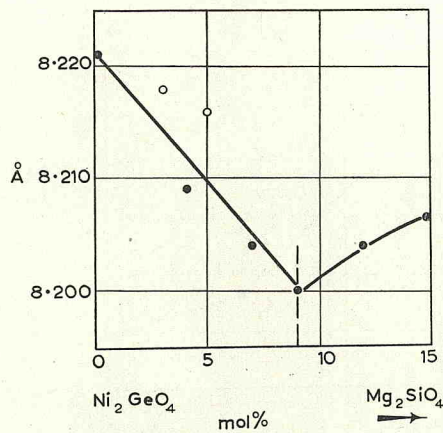


Fig. 6. Lattice constants of  $\text{Ni}_2\text{GeO}_4$ - $\text{Mg}_2\text{SiO}_4$  spinel-type solid solutions. Broken line indicates two-phase boundary. O—Anomalous values—see text.

present and their composition in the single-phase region. It does not give compositions of phases in equilibrium in the ternary region.

The effects of this deviation from binary equilibrium are shown in Figs. 3, 4, 5 and 6. In Figs. 4 and 5 refractive indices of olivines are plotted on a mole per cent basis across the two-phase field. Across this field they rise on the average by 0.035. Similarly, the refractive indices of spinels (Fig. 3) continue to decrease when they cross the two-phase boundary, but at a very much reduced rate. The same effect is seen in the lattice parameters of spinel solid solutions, which decrease with increasing content of  $\text{Mg}_2\text{SiO}_4$  until the two-phase boundary is reached, and then begin to increase very slightly (Fig. 6, Table 3).

Table 3. Lattice parameters of spinel solid solutions

Composition	$\text{\AA}$
$\text{NG}_{100}$	8.221
$\text{NG}_{97}\text{MS}_3$	8.218*
$\text{NG}_{96}\text{MS}_4$	8.209
$\text{NG}_{95}\text{MS}_5$	8.216*
$\text{NG}_{93}\text{MS}_7$	8.204
$\text{NG}_{91}\text{MS}_9$	8.200
-----Two-phase boundary.	
$\text{NG}_{88}\text{MS}_{12}$	8.204
$\text{NG}_{85}\text{MS}_{15}$	8.206

-----Two-phase boundary.

\* These values appear to be anomalous—Fig. 6. The particular samples were prepared by annealing the tablets for 100 hours at 1250°C, followed by crushing and heating for 3 hours at 1450°C. It is possible that equilibrium was not attained during the final heat treatment.

For the purpose of thermodynamic treatment it is necessary to find the composition of the olivine which is in equilibrium with spinel at the two-phase boundary on the spinel side of the diagram. This non-binary behaviour must therefore be analysed in greater detail.

The system  $\text{NiO—MgO—GeO}_2\text{—SiO}_2$  is a quaternary system which may be expressed in terms of the usual tetrahedral model. A plane through the orthosilicate-orthogermanate composition in the tetrahedron is depicted in Fig. 7. In order to construct the olivine solvus, the compositions of olivines in the two-phase fields of the binary systems  $\text{NG—MG}$ , and  $\text{NG—NS}$  at 1500°C are required. These have been obtained (unpublished data) and were found to be  $\text{NG}_{26}\text{MG}_{74}$  in the former system and  $\text{NG}_{42}\text{MG}_{58}$  in the latter. The olivine solvus for the system  $\text{NG—MS}$  at 1500°C is  $\text{NG}_{48}\text{MS}_{52}$  (Fig. 1). These data enable the olivine solvus for the orthosilicate-orthogermanate plane in the quaternary system to be constructed (Fig. 7). The corresponding spinel solvus has been approximately indicated, the only point known with precision being E, on the join  $\text{NG—MS}$ .

If the system  $\text{NG—MS}$  was behaving as a binary, then the spinel at E would be in equilibrium with olivine F on the binary join  $\text{NG—MS}$ . It was found (Fig. 4), however, that the refractive indices of the olivine in equilibrium with spinel E

( $\alpha = 1.79$ ,  $\gamma = 1.86$ ) were higher than those of olivine F ( $\alpha = 1.76$ ,  $\gamma = 1.835$ ). The composition of the unknown olivine must lie along the olivine solvus. The refractive indices of  $\text{Mg}_2\text{GeO}_4$  (RINGWOOD, 1956b),  $\text{Ni}_2\text{SiO}_4$  (RINGWOOD, 1956a),  $\text{Mg}_2\text{SiO}_4$ , are known, whilst the indices of the fictive olivine type  $\text{Ni}_2\text{GeO}_4$  can be found by extrapolation (Fig. 2). Accordingly, the refractive index variation of olivines along the olivine solvus can be found and the position of the unknown olivine G thus located.

By this method it is found that spinel of composition  $\text{NG}_{91}\text{MS}_9$  is in equilibrium at  $1500^\circ\text{C}$  with olivine of composition  $(\text{N}_{60}\text{M}_{40})_2(\text{G}_{45}\text{S}_{55})\text{O}_4$  along the tie line EG.

The accuracy of this result is determined principally by the probable accuracy

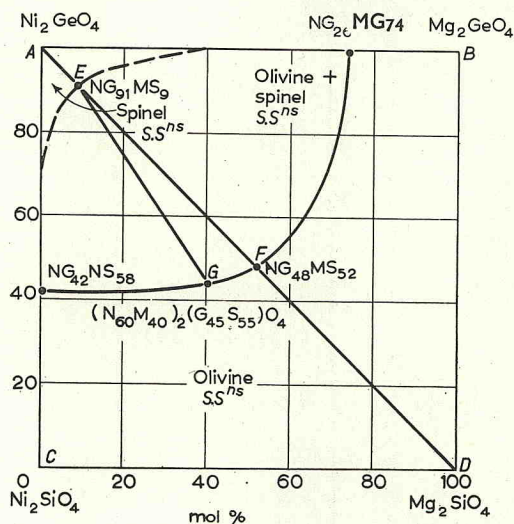


Fig. 7. Sub-solidus phase equilibria at  $1500^\circ\text{C}$  in system NG—MG—NS—MS

in measurement of refractive index ( $\pm 0.01$ ). This gives rise to a  $\pm 4$  per cent uncertainty in the Mg and Si fractions.

The assumption underlying the above derivation is that refractive indices of the solid solutions vary linearly with molar composition. Accumulated data on the optical behaviour of analogous solid solutions, e.g. WINCHELL (1933), BOWEN and SCHAIRER (1935), RINGWOOD (1956a), RINGWOOD (1956b), provide ample justification for this assumption. (See also appendix on "ideality".)

In fact, the correction for non-binary behaviour discussed in detail in the previous pages has only a minor effect upon the precision of later calculations compared to other sources of error, since the concentration factor involved is logarithmic. However, it was necessary to determine its order of magnitude.

The composition of the spinel solid solution at the two-phase boundary is  $\text{NG}_{91}\text{MS}_9$  at  $1500^\circ\text{C}$ . The uncertainty is estimated at  $\pm 1$  per cent  $\text{Mg}_2\text{SiO}_4$ . This value is used as a basis for the calculations in the next section. Compositions at lower temperatures have not been utilized, since it seems doubtful whether true equilibrium was always reached at temperatures below  $1350^\circ\text{C}$ .

In most cases, powder patterns of spinel phases gave evidence of slight lattice



distortion. The introduction of  $\text{Mg}_2\text{SiO}_4$  into the lattice causes a splitting of the high-angle reflection lines. The distortion is very slight—the width of splitting corresponds to a distance smaller than  $0.02 \text{ \AA}$  and the crystals remain isotropic under the microscope. The distortion must involve a reduction in symmetry. This distortion was not found in all samples, and it may be a displacive transition brought on during cooling. The transition is apparently capricious. Quenching specimens from  $1350^\circ\text{C}$  failed to stabilize the undistorted form, but sometimes when specimens were annealed for long periods at  $1200^\circ\text{C}$  and then heated at  $1450^\circ\text{C}$  until equilibrium was reached, undistorted patterns were obtained, which were suitable for lattice constant determination (Table 3).

(c) *Theory*

When  $\text{Mg}_2\text{SiO}_4$  becomes dissolved in  $\text{Ni}_2\text{GeO}_4$  the process may be pictured in two stages. First, energy must be supplied to the stable form (olivine) of  $\text{Mg}_2\text{SiO}_4$  in order to invert it to a hypothetical spinel form. Secondly, both spinels,  $\text{Ni}_2\text{GeO}_4$  and  $\text{Mg}_2\text{SiO}_4$ , undergo mixing and solid solution. There is a balance between the amount of (free) energy required to perform the inversion and the (free) energy involved in the mixing of  $\text{Ni}_2\text{GeO}_4$  and  $\text{Mg}_2\text{SiO}_4$ . If the energy of inversion is high, then only a small amount of  $\text{Mg}_2\text{SiO}_4$  will be able to enter into solid solution. If the inversion energy is low, then a considerable range of solid solutions may be formed. It is clear from this qualitative argument that there is a relationship between the free energy of transition between olivine and spinel  $\text{Mg}_2\text{SiO}_4$  and the amount of solid solution possible between  $\text{Mg}_2\text{SiO}_4$  and  $\text{Ni}_2\text{GeO}_4$ . This relationship will now be analysed more rigidly.

In the preceding section the compositions of coexisting olivine and spinel solid solutions in equilibrium at  $1500^\circ\text{C}$  were determined.  $\text{Mg}_2\text{SiO}_4$  was a component of both solid solutions.

Let  $\mu_1$  represent the chemical potential of  $\text{Mg}_2\text{SiO}_4$  in the olivine phase, and  $\mu_2$  represent the chemical potential of  $\text{Mg}_2\text{SiO}_4$  in the spinel.

$$\begin{aligned} \therefore \quad \mu_1 &= \mu_1^0 + RT \ln a_1 \\ \mu_2 &= \mu_2^0 + RT \ln a_2 \end{aligned}$$

where  $\mu_1^0$  = chemical potential of the pure olivine form of  $\text{Mg}_2\text{SiO}_4$  at  $1500^\circ\text{C}$ , and  $\mu_2^0$  = chemical potential of the pure spinel form of  $\text{Mg}_2\text{SiO}_4$ , whilst  $a_1$  = activity of  $\text{Mg}_2\text{SiO}_4$  in the olivine phase and  $a_2$  = activity of  $\text{Mg}_2\text{SiO}_4$  in the spinel phase.

At equilibrium,  $\mu_1 = \mu_2$

$$\therefore \quad \mu_2^0 - \mu_1^0 = RT \ln \frac{a_1}{a_2} = \Delta F^0$$

where  $\Delta F^0$  is the difference in chemical potential of the two pure modifications of  $\text{Mg}_2\text{SiO}_4$ , i.e.  $\Delta F^0$  is the molar free energy of transition of  $\text{Mg}_2\text{SiO}_4$  from olivine to spinel at  $1500^\circ\text{C}$ .

In order to find the difference in molar free energy between olivine and spinel-type  $\text{Mg}_2\text{SiO}_4$  it is therefore necessary to determine the activities of  $\text{Mg}_2\text{SiO}_4$  in

both solid solutions in equilibrium. To obtain these, the assumption is made that the solid solutions are *ideal*. The validity of this assumption is examined in detail in the appendix. In effect, ideality requires that  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$  ions mix randomly at their lattice positions with zero heat of mixing, and likewise for  $\text{Ge}^{4+}$  and  $\text{Si}^{4+}$ .

If the solid solutions behave ideally, then the activity  $a$  of an ion becomes equal to its ionic fraction  $n$ . The ionic fraction is the ratio of the number of specified ions to the total number of lattice sites available to them.

$$\text{i.e. } a_{\text{Mg}} = \frac{n_{\text{Mg}}}{n_{\text{Mg}} + n_{\text{Ni}}} = [\text{Mg}]$$

Similar relations hold for  $a_{\text{Ni}}$

$$\text{whilst } a_{\text{Si}} = \frac{n_{\text{Si}}}{n_{\text{Si}} + n_{\text{Ge}}} = [\text{Si}] \quad (\text{similarly for } a_{\text{Ge}})$$

The activity of a complex component such as  $\text{Mg}_2\text{SiO}_4$  is given not by  $[\text{Mg}_2\text{SiO}_4]$ , but by  $[\text{Mg}]^2[\text{Si}]$ —TEMPKIN (1945)\*.

$$\text{Accordingly, } \Delta F^0 = RT \ln \left\{ \frac{[\text{Mg}_1]^2[\text{Si}_1]}{[\text{Mg}_2]^2[\text{Si}_2]} \right\} \quad (1)$$

At  $1500^\circ\text{C}$  the composition of olivine and spinel in equilibrium have been determined (see previous section).

$$\text{Mg}_2 = 0.09, \quad \text{Si}_2 = 0.09, \quad \text{Mg}_1 = 0.40, \quad \text{Si}_1 = 0.55$$

$$R = 8.314 \text{ J/mole deg.}$$

Substituting these values in (1), the molar free energy of transition between olivine and spinel type  $\text{Mg}_2\text{SiO}_4$  may be found.

$$\Delta F^0 = 70,000 \text{ J/mole at } 1500^\circ\text{C}.$$

When the probable experimental error in composition determination is considered (Section 2b), a value of

$$\Delta F^0 = 70,000 \pm 10,000 \text{ J/mole at } 1500^\circ\text{C} \text{ is found.}$$

The value for  $\Delta F^0$  when the composition correction for deviation of olivine from binary composition is not applied is 71,000 J/mole. It appears therefore that the correction calculated in Section 2b was not really significant. It was, however, necessary to determine its magnitude.

### 3. EFFECT OF PRESSURE UPON TRANSITION

According to Le Chatelier's theorem, increasing pressure should tend to favour the stability of the polymorph with the higher density, in this case the spinel modification.

At the transition point where the two polymorphs are in equilibrium, their free energies ( $F$ ) are equal.

\* This follows, since  $\text{Mg}_2\text{SiO}_4$  cannot be considered as an individual molecule mixing ideally with  $\text{Ni}_2\text{GeO}_4$  molecules, in which case Raoult's law would apply, and the activity of  $\text{Mg}_2\text{SiO}_4$  would be equal to its mole fraction. In this case  $\text{Mg}^{2+}$  and  $\text{Ni}^{2+}$  ions mix ideally at octahedral lattice sites, whilst  $\text{Si}^{4+}$  and  $\text{Ge}^{4+}$  are entirely separate, mixing ideally at tetrahedral sites. The entropy of mixing is therefore calculated on an entirely different basis and gives rise to the expression above.

The Gibbs free energy is given by

$$F = E + PV - TS$$

where  $S$  = entropy,  $V$  = molar volume and  $E$  = internal energy.

$$\text{At equilibrium, } F_1 = F_2, \quad P_1 = P_2, \quad T_1 = T_2$$

$$E_1 + PV_1 - TS_1 = E_2 + PV_2 - TS_2$$

$$(E_1 - TS_1) - (E_2 - TS_2) = P(V_2 - V_1) = P \Delta V$$

The quantity on the left is the difference in free energy between the two phases at zero pressure, which has already been determined as 70,000 J/mole at 1500°C.

$$\therefore \text{ at equilibrium, } P\Delta V = 70,000$$

where  $\Delta V$  is the difference in molar volume between the two polymorphs.

The next step is to find  $\Delta V$ . The density (and hence the molar volume) of olivine are known. It becomes necessary to find the density of  $\text{Mg}_2\text{SiO}_4$  spinel. This can be calculated from the lattice constant of the spinel. This quantity may be obtained by several methods.

(a) The lattice constant of  $\text{MgSiO}_4$  spinel may be derived from data on  $\text{Ni}_2\text{GeO}_4$ — $\text{Mg}_2\text{SiO}_4$  solid solutions (Fig. 6, Table 3). The value of the lattice constant of  $\text{Mg}_2\text{SiO}_4$  spinel found by extrapolation is 7.99 Å. This leads to a spinel density 14 per cent higher than that of the olivine.

This result has been obtained assuming the applicability of Vegard's law—i.e. that the lattice constants of the solid solutions vary linearly with molar composition. This assumption depends upon whether the solid solutions are essentially ideal—a subject which is discussed in the appendix. Anticipating the discussion, it may be said that there is sufficient justification for the application of Vegard's law.

(b) ROY and ROY (1954) have prepared the spinel and olivine modifications of  $\text{Mg}_2\text{GeO}_4$ , a compound closely analogous to  $\text{Mg}_2\text{SiO}_4$ . They found a density difference between the two forms of 8 per cent. Although this does not necessarily imply that the corresponding density difference in  $\text{Mg}_2\text{SiO}_4$  is also 8 per cent, it furnishes a useful approximation.

BERNAL (1936) calculated a density difference of 9 per cent for the olivine-spinel transition based upon X-ray data of GOLDSCHMIDT (1931). This data is now known to be inaccurate, and hence the agreement between BERNAL's result and that of ROY and ROY is somewhat fortuitous.

(c) Spinel solid solutions of  $\text{Ni}_2\text{SiO}_4$  in  $\text{Ni}_2\text{GeO}_4$  have been prepared and their lattice parameters determined (Table 4, Fig. 8). A lattice constant of 8.026 Å for  $\text{Ni}_2\text{SiO}_4$  spinel is found by extrapolation. Calculations on this basis give rise to a 9 per cent density difference between the olivine and spinel forms of  $\text{Ni}_2\text{SiO}_4$ . The lattice parameters of  $\text{Ni}_2\text{SiO}_4$  olivine were determined by TAYLOR (1930).

(d) The olivine-spinel transition in  $\text{Mg}_2\text{SiO}_4$  involves a rearrangement of oxygen ions into a close-packed cubic structure with the  $\text{Mg}^{2+}$  and  $\text{Si}^{4+}$  occupying octahedral and tetrahedral holes respectively. In silicates, the nearest approach to the close-packed spinel structure is given by pyrope  $\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$ . The

unit cell of pyrope contains 96 oxygen ions and has a lattice parameter of 11.51 Å. If the oxygen ions in  $\text{Mg}_2\text{SiO}_4$  spinel are as close-packed as in pyrope, the corresponding lattice constant for the spinel (32 oxygen ions per unit cell) would be 7.98 Å, in good agreement with the 7.99 Å deduced by direct extrapolation (Method (a)). This value involves a density difference between olivine and spinel of 14.5 per cent.

Table 4. Lattice parameters of  $\text{Ni}_2\text{GeO}_4(\text{NG})\text{—Ni}_2\text{SiO}_4(\text{NS})$  solid solutions

Composition	Lattice constant Å
$\text{NG}_{100}$	8.221
$\text{NG}_{96}\text{NS}_4$	8.216
$\text{NG}_{92}\text{NS}_8$	8.205
$\text{NG}_{90}\text{NS}_{10}$	8.201
$\text{NG}_{88}\text{NS}_{12}$	8.199
$\text{NS}_{100}$ (extrap.)	8.026

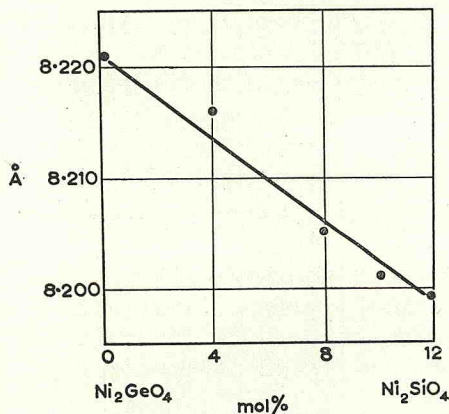


Fig. 8. Lattice constants of  $\text{Ni}_2\text{GeO}_4\text{—Ni}_2\text{SiO}_4$  solid solutions.

(e) An approximate lattice constant for  $\text{Mg}_2\text{SiO}_4$  spinel can be calculated directly, based upon the geometry of the spinel lattice which is constructed from  $\text{MgO}_6$  octahedra and  $\text{SiO}_4$  tetrahedra. The  $\text{Mg—O}$  distance in magnesium oxide is 2.10 Å and the  $\text{O—O}$  distance is 2.60 Å. Using these values, a figure of 8.14 Å is obtained for the lattice constant of  $\text{Mg}_2\text{SiO}_4$  spinel. This involves a density difference of 8.5 per cent with the olivine. In fact, this derivation assumes an arrangement of perfect tetrahedra and octahedra in the spinel lattice. It is likely that there is some distortion and reduction of bond lengths because of sharing effects leading to a higher density than that calculated. Accordingly, the 8.5 per cent density difference calculated on this basis is likely to prove a minimum estimate.

From the preceding independent methods, the increase in density associated with the olivine-spinel transition may be placed at  $11 \pm 3$  per cent. This gives rise to a difference in molar volume ( $\Delta V$ ) between the two polymorphs of  $4.4 \pm 1 \text{ cm}^3$  at 1 atmosphere pressure. In general, since  $\Delta V$  is to some extent a function of pressure and temperature, it becomes necessary to investigate the behaviour of  $\Delta V$  under high  $P, T$  conditions. It is a fortunate occurrence that olivines and spinels have characteristically small compressibilities and coefficients of thermal expansion. Because of this,  $\Delta V$  is relatively unaffected over the wide range of high temperature and pressure conditions which might be expected in the mantle.

Preliminary calculations indicate that  $\text{Mg}_2\text{SiO}_4$  olivine might be expected to invert to spinel at pressures corresponding to depths of 300–600 km in the mantle. BIRCH (1952) has calculated the strain of the constituents of the mantle as a function of depth, and finds that the strain at 400 km is about 3 per cent equivalent to a 9 per cent volume decrement.

Accordingly, the difference in molar volume of the two polymorphs in the transition region may be placed at  $4.0 \pm 1 \text{ cm}^3$ . (This approximation ignores the effect of differing compressibilities for olivine and spinel polymorphs, but trial calculations show that this correction is not significant.)

Accordingly, the difference in free-energy  $\Delta F$ , due to differential compression of the two polymorphs as a function of pressure, is  $P\Delta V = 4.0 P \text{ cm}^3 \text{ bar} = 0.4 PJ$  ( $P$  in bars). When  $\Delta F$  equals the free energy of transition of the two forms at zero pressure, found previously to be 70,000 J at 1500°C, the two polymorphs will be in equilibrium.

∴

$$0.40P = 70,000$$

$$P = 1.75 \times 10^5 \text{ bars}$$

The probable range of error is found calculating the accumulated errors in the various steps which have led to this result. Accordingly, the maximum pressure which is required to produce equilibrium between the two forms is  $2.33 \times 10^5$  bars, whilst the minimum is  $1.20 \times 10^5$  bars. Thus the equilibrium pressure for the olivine-spinel transition at 1500°C may be placed at  $(1.75 \pm 0.55) \times 10^5$  bars.

#### 4. INVERSION OF OLIVINE IN THE MANTLE

Before these results are applied to the mantle, the effect of other variables must be examined.

The temperature at which the transition pressure was deduced was 1500°C. Most estimates of temperature in the mantle in the region where the transition was predicted range from 1500 to 2500°C (GUTENBERG, 1951). Therefore the effect of increasing temperature upon the equilibrium pressure must be examined.

It will be shown in Part II that the effect of increasing temperature above 1500°C will be to increase the free energy of transition. This is due to the fact that olivine has a higher entropy than spinel. Accordingly, the pressure required to cause inversion will be greater than that calculated for temperatures above 1500°C. This aspect will be treated in detail in Part II.

A second factor of some relevance is that the olivine of the mantle probably contains about 5–10 per cent of  $\text{Fe}_2\text{SiO}_4$  in solid solution. A second component

in a solid solution may raise or lower the transition free energy for the polymorphic inversion of the pure form. The direction in which this particular transition would be affected is not known, but from analogy with solid-liquid phase equilibria, and other polymorphic inversions in ideal solid solutions, the effect is not likely to modify the results previously obtained to any large extent.

There is some evidence that  $\text{Fe}_2\text{SiO}_4$  may have a greater tendency to take on the spinel structure than  $\text{Mg}_2\text{SiO}_4$ , in which case it would lower the transition free energy. This is suggested by the work of ROMELJN (1953), who observed that  $\text{Ni}_2\text{GeO}_4$  and  $\text{Co}_2\text{GeO}_4$  both possessed the spinel structure, whilst the stable form of  $\text{Mg}_2\text{GeO}_4$  possessed the olivine structure. ROMELJN suggested that the spinel structure of transition metal ortho germanates may be favoured by a magnetic interaction of the transition ions.

If this is the case with  $\text{Fe}_2\text{SiO}_4$ , the spinel solid solution with  $\text{Mg}_2\text{SiO}_4$  would have a somewhat greater content of  $\text{Fe}_2\text{SiO}_4$  than the olivine with which it was in equilibrium. An investigation of this point is at present in progress.

In Part II, it is pointed out that spinels can take into solid solution compounds with  $\text{ABO}_3$ -type formulae at high temperatures, and that if a spinel-olivine transition occurred in the mantle, the spinel would probably dissolve  $\text{MgSiO}_3$ , and excess Al, Ca, Cr, and Ti which form separate phases in the upper mantle. If this occurs, the preferential solubility of these components in the spinel would have the effect of stabilizing the spinel at the expense of olivine at *smaller* pressures than those previously calculated.

The previous calculations have been made using the assumption of ideality for NG—MS solid solutions. In the appendix, evidence supporting this assumption is cited. However, if some deviation from ideality does occur, it is probable that the deviation would be positive in nature. This would also make the equilibrium transition pressure *smaller* than that calculated.

#### CONCLUSIONS

The preceding calculations indicate that a spinel modification of  $\text{Mg}_2\text{SiO}_4$  should become thermodynamically stable at  $1500^\circ\text{C}$  in the pressure range  $(1.75 \pm 0.55) \times 10^5$  bars. In the mantle these pressures are reached at depths of  $500 \pm 140$  km. The following extraneous factors present could modify the actual depth of transition.

- (i) Increase of temperature above  $1500^\circ\text{C}$  in the mantle would increase the transition pressure.
- (ii) The effect of  $\text{Fe}_2\text{SiO}_4$  in solid solution is not known. Some evidence suggests it would decrease the transition pressure.\*
- (iii) The presence of  $\text{MgSiO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ , which are likely to be preferentially soluble in the spinel phase, will decrease the transition pressure.
- (iv) Departures from ideality in NG—MS solid solutions will probably decrease the transition pressure.

It therefore seems that these factors if present may have the net effect of decreasing the transition pressure. Accordingly, it is concluded the olivine in the

\* Since confirmed (Author's note).

mantle probably begins to invert to spinel at depths less than 500 km. The bearing of this result of the constitution of the mantle is discussed in Part II.

## APPENDIX

*Ideal behaviour of solid solutions*

An ideal solution is defined as one which obeys Raoult's law—i.e. the activity of a component is equal to its mole fraction. The most important properties of an ideal solid solution are that the mutually replacing ions (or atoms) are distributed at random in their appropriate lattice positions and that the heat of mixing is zero ( $\Delta H = 0$ ). These conditions are likely to be approached most closely when the replacing ions are similar in size and charge.

The following indirect methods enable the ideality of a solid solution to be investigated.

(i) The heat of mixing of the components of an ideal solid solution is zero. Therefore the heats of solution of members of an ideal solid-solution series in a suitable solvent will vary linearly with composition. This may be investigated directly by means of solution calorimetry.

(ii) The volume change of mixing for an ideal solution is zero. Accordingly, the densities of members of an ideal solid-solution series will vary linearly with composition. This may be studied directly, or by X-ray methods. Vegard's law, which states that the lattice parameters of members of an ideal solid-solution series vary linearly with composition, is a consequence of this property.

The volume change of mixing for any solid solution ( $\Delta V$ ) is also a reflection of  $\Delta H$ . A negative value of  $\Delta V$  reflects a negative value of  $\Delta H$ , since it implies that the ions are closer together in the solution due to an increase in bonding energy. The opposite applies for positive values of  $\Delta V$ .

(iii) If a close resemblance exists between crystal chemical properties and thermochemical properties of components, then a close approach to ideality at high temperature may be expected.

In the case of the olivine and spinel solid solutions under consideration, the discussion may be conveniently broken into three parts, although it should be realized that this division is somewhat artificial.

- (a) Data relating to the ideality of the  $\text{Ni}^{2+}$ — $\text{Mg}^{2+}$  replacement.
- (b) Data relating to the ideality of the  $\text{Ge}^{4+}$ — $\text{Si}^{4+}$  replacement.
- (c) Structural effects arising from double replacement in the solid solution—particularly lattice distortion.

(a) *The  $\text{Ni}^{2+}$ — $\text{Mg}^{2+}$  diadochy.*  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$  ions possess the same charges and similar ionic radii ( $\text{Ni}^{2+} = 0.69 \text{ \AA}$ ,  $\text{Mg}^{2+} = 0.66 \text{ \AA}$ ).  $\text{Ni}^{2+}$  has a substantially higher ionization potential resulting in a more pronounced tendency to form bonds with some covalent and directed character. However, in oxide compounds the bonds are octahedrally directed, and since the ionic co-ordination of  $\text{Ni}^{2+}$  with oxygen is also octahedral, no complexities are to be expected from this factor. The principal effect is a slight shortening of the effective radius of  $\text{Ni}^{2+}$ , giving  $\text{NiO}$  and  $\text{MgO}$  similar lattice constants.

Calorimetric data are not available for solid solutions of  $\text{Ni}$ — $\text{Mg}$  compounds.

However, heats of solution in hydrofluoric acid have been determined for solid solutions of  $\text{Fe}_2\text{SiO}_4$ — $\text{Mg}_2\text{SiO}_4$  and  $\text{MgSiO}_3$ — $\text{FeSiO}_3$ . Since there is generally a closer resemblance between corresponding  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$  compounds than between  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  compounds, data upon these  $\text{Fe}^{2+}$ — $\text{Mg}^{2+}$  solid solutions are illuminating.

SAHAMA and TORGESON (1949) found that the heats of solution of members of these solid solutions varied linearly between end members. This means that the  $\text{Mg}^{2+}$ — $\text{Fe}^{2+}$  diadochy must be ideal in these cases. BOWEN and SCHAIERER (1935) calculated latent heats of melting from phase equilibria in the system  $\text{Fe}_2\text{SiO}_4$ — $\text{Mg}_2\text{SiO}_4$ , and from their results concluded that the system behaves ideally. In view of these results, the conclusion seems justified that analogous  $\text{Ni}^{2+}$ — $\text{Mg}^{2+}$  mix-crystals are probably ideal.

Table 5. Lattice constants of NG—MG and CG—MG solid solutions

NG =  $\text{Ni}_2\text{GeO}_4$

MG =  $\text{Mg}_2\text{GeO}_4$

CG =  $\text{Co}_2\text{GeO}_4$

Composition	Lattice constant (Å)
$\text{NG}_{100}$	8.221
$\text{NG}_{90}\text{MG}_{10}$	8.224
$\text{NG}_{85}\text{MG}_{15}$	8.225
$\text{MG}_{100}$ (extrap.)	8.25
$\text{CG}_{100}$	8.321
$\text{CG}_{90}\text{MG}_{10}$	8.314
$\text{MG}_{100}$ (extrap.)	8.25

This conclusion is supported by an examination of lattice constants of solid solutions of  $\text{Mg}_2\text{GeO}_4$  in  $\text{Ni}_2\text{GeO}_4$  and  $\text{Co}_2\text{GeO}_4$  (Table 5). The lattice constant of  $\text{Mg}_2\text{GeO}_4$  spinel has been obtained by extrapolating the values given in Table 5. In both solid-solution series the extrapolated lattice constant is  $8.25 \pm 0.02$  Å. This agrees with the value of 8.255 Å found directly by ROY and ROY (1954).

In view of the large extrapolation involved, the lattice parameters of the solid solutions must to a high degree vary linearly with composition. A slight deviation from linearity (i.e. from Vegard's law) would have thrown these values far out. Accordingly, the  $\text{Mg}^{2+}$ — $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$ — $\text{Co}^{2+}$  diadochies in germanate spinels probably display a close approach to ideality.

(b) *The  $\text{Ge}^{4+}$ — $\text{Si}^{4+}$  diadochy.*  $\text{Ge}^{4+}$  and  $\text{Si}^{4+}$  have similar charges, and both tend to form tetrahedrally directed bonds with appreciable covalent character. There are pronounced differences in ionic radii— $\text{Si}^{4+}$  0.42 Å,  $\text{Ge}^{4+}$  0.53 Å, but this is not significant, since their bonds with oxygen are only about 50 per cent ionic. When  $\text{Ge}^{4+}$  substitutes for  $\text{Si}^{4+}$  in a crystal, it has only a small effect on the lattice constants, indicating that  $\text{Ge}^{4+}$  and  $\text{Si}^{4+}$  have about the same size in crystals (GOLDSCHMIDT, 1931).



In Table 6, the melting temperatures of isostructural silicates and germanates are compared. In each case, the m.p. of the germanate is very similar to that of the silicate, and slightly below. The melting temperature of a crystal is a property which is very sensitive to changes in the internal energy balance and distribution within a crystal. The fact that substitution of  $\text{Ge}^4$  for  $\text{Si}^4$  has such a slight effect on melting point is strong evidence pointing towards the equivalence of  $\text{Ge}^4$  and  $\text{Si}^4$  in crystals—i.e. of ideality.

Table 6. Melting temperatures of isostructural silicates and germanates ( $^{\circ}\text{C}$ )

$\text{Mg}_2\text{SiO}_4$	(1)	1890
$\text{Mg}_2\text{GeO}_4$		1830
$\text{Zn}_2\text{SiO}_4$	(2)	1512
$\text{Zn}_2\text{GeO}_4$		1490
$\text{NaAlSi}_3\text{O}_8$	(3)	1118
$\text{NaAlGe}_3\text{O}_8$		1067
$\text{KAlSi}_3\text{O}_8$	(3)	1170
$\text{KAlGe}_3\text{O}_8$		1122

(1) RINGWOOD (1956)

(2) INGERSON, MOREY and TUTTLE (1948)

(3) GOLDSMITH (1950)

In the former two examples in Table 6, complete solid solutions with very small melting intervals and a continuous melting curve of the Roozeboom I type are found. With regard to these, GORANSEN (1942) has stated: "However, it is found from a study of silicate equilibria relations that systems which are miscible in the solid as well as the liquid state approach this condition of ideality, and when miscible in all proportions both in the liquid and solid state may be treated as ideal".

Further evidence of ideality may be derived from  $\text{Ni}_2\text{GeO}_4$ — $\text{Ni}_2\text{SiO}_4$  spinel solid solutions (Table 4, Fig. 8). In Section 3 it was shown that the calculated density difference between  $\text{Ni}_2\text{SiO}_4$  spinel and olivine based upon the above results was 8.5 per cent. This figure is consistent with the corresponding values obtained by several independent methods and suggests that the Ge—Si diadochy in the spinel must be obeying Vegard's law.

(c) *Structural effects arising from double replacement in the solid solution.* In the previous sections, evidence has been put forward indicating that when  $\text{Ni}^{2+}$ — $\text{Mg}^{2+}$  or  $\text{Ge}^4$ — $\text{Si}^4$  replacement occurs separately in crystals, the replacement is essentially ideal. On general grounds, therefore, it would be expected that when double replacement occurs—i.e. when  $\text{Ni}^{2+}\text{Ge}^4$  replace  $\text{Mg}^{2+}\text{Si}^4$ , the replacement would also approach ideality. This is indicated by the lattice constant data for the NG—MS spinel solid solutions. The lattice constant for  $\text{Mg}_2\text{SiO}_4$  spinel found by extrapolation leads to results for the density difference between spinel and olivine  $\text{Mg}_2\text{SiO}_4$  which are in reasonable agreement with the corresponding density

differences found by other methods (Section 3). This implies that Vegard's law is being accurately obeyed and that the double replacement is essentially ideal at high temperatures.

However, at low temperatures the NG—MS spinels are found to be slightly distorted (Section 2b). This is indicated by splitting of high-angle diffraction lines, corresponding to differences in interplanar spacing of 0.02 Å. This distortion therefore involves a reduction of symmetry. The amount of distortion is, however, very small and unlikely to affect free-energy relationships to any significant degree. At high temperatures the distortion evidently disappears, giving rise to a normal series of spinels (Table 3).

This distortion may cause a positive deviation from ideal behaviour. Although separate replacement of Ni<sup>2+</sup> by Mg<sup>2+</sup> and Ge<sup>4+</sup> by Si<sup>4+</sup> might be ideal, it can happen that when two foreign ions such as Mg<sup>2+</sup> and Si<sup>4+</sup> are introduced simultaneously into a lattice, some strain is set up. This is because lattice stabilities are dependent upon ionic radius ratios, and although Mg<sup>2+</sup> and Si<sup>4+</sup> might be able to fit satisfactorily into a spinel lattice structure separately, the radius ratio Mg<sup>2+</sup>/Si<sup>4+</sup> is such that some strain is introduced when both enter together. This has apparently happened here. Solution of Mg<sup>2+</sup> and Si<sup>4+</sup> separately is found not to cause splitting.

Although the conclusion is drawn that high-temperature solid solutions of Ni<sub>2</sub>GeO<sub>4</sub> and Mg<sub>2</sub>SiO<sub>4</sub> are probably essentially ideal, the above point is important, since it indicates that *if deviation from ideality did occur, the deviation is most likely to be positive in nature*, i.e. tending towards segregation of phases.

The calculations in Section 2c show that the effect of this non-ideal behaviour will be to produce inversion from olivine to spinel at a shallower depth in the mantle than is found assuming ideal behaviour.

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