

STRUCTURAL BASIS OF THE OLIVINE-SPINEL STABILITY RELATION

BARCLAY KAMB, *California Institute of Technology,¹
Pasadena, California 91109.*

ABSTRACT

Since both the spinel and olivine structures for $(\text{Mg, Fe})_2\text{SiO}_4$ are based on closest packing of oxygen atoms, and since both involve $(\text{Mg}^{2+}, \text{Fe}^{2+})$ in six-coordination and Si^{4+} in four-coordination, an explanation is needed for the much greater stability of the olivine structure at atmospheric pressure, and for the greater density of the spinel structure, which allows it to be stabilized under high pressure. The explanation lies in Pauling's rules for edge sharing by coordination polyhedra in ionic crystals. The olivine structure is unfavorable relative to spinel as far as the types of shared edges are concerned, but this is counterbalanced by shortening of the shared edges. The spinel structures that are stable at 1 atm are those for which edges shared between coordination octahedra shorten relative to unshared edges. For the required interatomic distances $\text{Si}-\text{O}$ and $\text{Mg}-\text{O}$, the shared edges in the spinel structure for Mg_2SiO_4 must be much longer than the unshared edges, whereas the olivine structure allows the shared edges to shorten in a natural way. The reduced density of the olivine structure is another consequence of the shared-edge shortening, which allows the Mg^{2+} ions to separate farther from one another than in spinel, expanding the structure. These concepts rationalize the occurrences of the spinel and olivine structure types among AB_2O_4 compounds generally, at 1 atm. The transition between the two structure types depends on the cation valences and electronegativities in an understandable way, and the latter dependence explains why the olivine-spinel transition pressure is lower for Fe_2SiO_4 than for Mg_2SiO_4 .

INTRODUCTION

Magnesium-iron orthosilicate plays an important role in mineralogical models of the earth's interior. A polymorphic transition from the olivine to the spinel form of $(\text{Mg, Fe})_2\text{SiO}_4$ is considered in most models to be an important contributor to the comparatively large density increase that occurs in the mantle at depths of about 400 km. While for practical purposes it may be adequate simply to know the empirical thermodynamic parameters defining this transition, without regard to any underlying structural basis for it, nevertheless a structural understanding seems desirable, and may be of help in reasoning about other possible phase changes in the earth.

For many phase changes that occur under pressure, the structural basis is immediately apparent as an increase in the coordination number of the cations. Such phase changes can be understood structurally in terms of the concepts of ionic size and of radius ratio in relation to coordination number (Pauling, 1960, p. 540). For the olivine-spinel transition in Mg_2SiO_4 , however, these concepts alone are insufficient,

¹ Division of the Geological Sciences, Contribution No. 1500.

because the cation coordination numbers are the same in both structures, and both structures are based on closest packing of oxygen ions. It is not therefore immediately apparent why the olivine structure should be much more stable than the spinel structure at ordinary pressures, or why the spinel structure should be denser than the olivine structure, and hence stabilizable under pressure.

This paper offers an explanation for these facts, which are, it develops, understandable within the framework of Pauling's rules for the stabilizing structural features of ionic crystals.¹

THE STRUCTURES

The olivine structure is based on a hexagonal-closest packed arrangement of oxygen ions, in which silicon atoms are placed in tetrahedral coordination, and magnesium (or iron) in octahedral coordination. Since the cation distribution within the h.c.p. arrangement of oxygen ions has lower symmetry than that of ideal hexagonal closest packing itself (space group $P6_3/mmc$ for ideal h.c.p., space symmetry $P2_1/bmn$ for olivine referred to the same orientation), a distortion from the ideally close-packed oxygen arrangement can occur in the olivine structure. Structure analysis (Gibbs, Moore, and Smith, 1963; Hanke, 1963; Smith, Majumdar, and Ordway, 1965) shows that such a distortion is indeed present; it allows the average Si—O distance to decrease to 1.625 Å from the 1.83 Å that would be required in ideal closest packing with the observed average Mg—O distance of 2.12 Å.

The spinel structure is based on a cubic-closest-packed arrangement of oxygen ions, with the cations again in tetrahedral and octahedral coordination. It seems likely that in Mg_2SiO_4 and Fe_2SiO_4 spinels, the Mg^{2+} or Fe^{2+} ions will be in six-coordination and the Si in four-coordination, as in olivine, so that these will be normal-type spinel structures (Ringwood and Seabrook, 1962; Dacheille and Roy, 1960).² Experimental con-

¹ The paper is offered as a tribute to Dr. Linus Pauling, on the occasion of his receipt of the Roebing Medal of the Mineralogical Society of America (November 1967).

² From IR spectra, Ni_2SiO_4 was interpreted as a normal spinel by Tarte and Ringwood (1962). Because of the ambivalent 4- or 6-coordination of Ge, it seems reasonable to assume that if Mg_2GeO_4 forms a normal spinel, so also does Mg_2SiO_4 . From X-ray powder data, Mg_2GeO_4 and Fe_2GeO_4 spinels were determined as normal by Durif-Varambon, Bertaut, and Pauthenet (1956), but as inverse (in the case of Mg_2GeO_4) by Dacheille and Roy (1960). The latter authors argued for the inverse structure on the basis of IR spectra, but their method of interpretation also led them to the unlikely conclusion that the olivine forms of Mg_2SiO_4 and Mg_2GeO_4 should be inverse (Si and Ge in 6-coordination). The spectral features used by Dacheille and Roy to conclude that Mg_2GeO_4 is inverse are very similar to features in the spectrum of Ni_2SiO_4 spinel interpreted by Tarte and Ringwood (1962) as indicating a normal structure. The bond-orbital hybridization and ligand field theory considerations used by Hafner (1960, Fig. 6) to deduce a preference for the tetra-

firmation that the spinel type is normal for spinels ranging in composition from Fe_2SiO_4 to $(\text{Mg}_{0.5}\text{Fe}_{0.5})\text{SiO}_4$, based on X-ray powder line intensities and infrared absorption spectra, has been reported by Sclar and Carrison (1966b). The symmetry is again lower than that of the ideal closest-packed oxygen arrangement (space group $Fm\bar{3}m$ for c.c.p. degrades to $Fd\bar{3}m$, with doubling of the cell dimensions, for spinel). The actual distortion from the ideal arrangement thus made possible has not yet been determined experimentally for the spinel forms of Mg_2SiO_4 and Fe_2SiO_4 . However, from the lattice constants $a = 8.075 \text{ \AA}$ for Mg_2SiO_4 spinel¹ and 8.234 \AA for Fe_2SiO_4 spinel (Ringwood, 1959), we can deduce the values $x = 0.366$ and 0.365 , respectively, for the one variable structure parameter, the x coordinate for oxygen, on the basis of the assumption that the Si—O distance is the same as in the olivine forms, 1.625 and 1.634 \AA , which are normal values for orthosilicates (Smith and Bailey, 1963). The corresponding Mg—O and Fe—O distances are then 2.09 and 2.14 \AA . They are within the ranges 2.07 – 2.22 \AA and 2.09 – 2.29 \AA of individual Mg—O and Fe—O distances in the olivines (Smith, Majumdar, and Ordway, 1965), and they are close to the distances 2.10 \AA in periclase and 2.15 \AA in wüstite.

From this comparison it is evident that the olivine and spinel forms of $(\text{Mg}, \text{Fe})_2\text{SiO}_4$ have the same basic type of ionic coordination and packing. In both structures, also, the electrostatic valence rule (Pauling, 1960, p. 547) is satisfied exactly, each oxygen ion being coordinated by one silicon and three magnesium or iron ions. We must therefore look more

hedral site in the case of Ti^{4+} , which has a completed electron octet and no d electrons, imply the same conclusion for Si^{4+} (and also for Ge^{4+} , with ten d electrons). However, this conclusion for Ti^{4+} contradicts the observed inverse structure for the ulvöspinel TiMg_2O_4 and TiFe_2O_4 . Evans (1966, p. 173) states that quadrivalent cations show the strongest preference for octahedral sites in the spinel structure, but energy calculations (Hafner, 1960) indicate that for $\text{A}^{4+}\text{B}_2^{2+}\text{O}_4$ spinels, the tetrahedral site is electrostatically preferred by the A^{4+} cation in case the oxygen parameter x is less than 0.385 , a condition satisfied in the normal spinel structure for Mg_2SiO_4 and Fe_2SiO_4 .

¹ Spinel in the composition range $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$ to Fe_2SiO_4 have been synthesized, but for more magnesium-rich compositions, the high-pressure phase so far synthesized (called β - Mg_2SiO_4) is non-cubic, possibly a distortion of the spinel structure (Ringwood, 1968). The lattice constant $a = 8.075 \text{ \AA}$ quoted for pure Mg_2SiO_4 spinel is that of the hypothetical, (cubic) spinel phase (γ - Mg_2SiO_4), and is obtained by extrapolating linearly from $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$ to Mg_2SiO_4 the spinel lattice constants determined by Ringwood (1968). Akimoto and Ida (1966) originally reported a provisional lattice constant of $a = 8.07 \pm 0.02 \text{ \AA}$ for pure γ - Mg_2SiO_4 , which they thought to have synthesized, and Sclar and Carrison (1966b) proposed an extrapolated value of 8.09 \AA . This small possible uncertainty in cell size for γ - Mg_2SiO_4 does not significantly affect the discussion given here, and this discussion applies specifically to the true spinels rather than to the non-cubic β - Mg_2SiO_4 , whose structure is not yet known.

closely at structural details in order to understand the differences in stability and density between the two polymorphs.

THE STABILIZING FEATURE OF SPINELS

The oxygen coordinate $x=3/8$ corresponds to an ideal closest-packed arrangement of oxygen ions in the spinel structure. Of the 58 spinels and thiospinels for which x has been determined (see listing by Wyckoff, 1965, p. 75 ff.), all but one have $x \geq 3/8$ within experimental error, and for most, x lies in the range 0.380 to 0.390. This suggests that the condition $x > 3/8$ is important in stabilizing the spinel structure. $x > 3/8$ represents an enlargement of the tetrahedra and a contraction of the octahedra, relative to the undistorted close-packed oxygen arrangement. $x=0.387$ corresponds to equal sizes for the occupied tetrahedral and octahedral interstices, and $x=0.381$ corresponds to a structure that incorporates in the tetrahedral and octahedral positions ions that are of equal size when referred to the same coordination number, the contraction in interatomic distance on going from six- to four-coordination being assumed 7 percent as appropriate to Mg^{2+} and Al^{3+} (Pauling, 1960, p. 537). Thus in the majority of spinels, the tetrahedrally-coordinated cations are inherently larger than the octahedrally-coordinated ones, contrary to what would be expected from radius-ratio considerations alone. This is exemplified by the seemingly odd situation in spinel itself, $MgAl_2O_4$ (Fischer, 1967), where Mg^{2+} (ionic radius 0.65 Å) has ligancy 4 and Al^{3+} (radius 0.50 Å) ligancy 6, contrary to the normal occurrence of Mg^{2+} in octahedral coordination and the common occurrence of Al^{3+} in tetrahedral coordination in silicates.

The significance of the x coordinate for spinel stability is its relation to distortions in the coordination polyhedron of oxygen about the six-coordinated cation. When $x=3/8$, the polyhedron is a regular octahedron; when $x \neq 3/8$, it is a distorted octahedron with D_{3d} symmetry, the distortion being "prolate" when $x > 3/8$ and "oblate" when $x < 3/8$ (see Hafner, 1960). In the normal spinel structure AB_2O_4 , the octahedron about each B cation shares six edges with adjacent BO_6 octahedra. When $x > 3/8$, the six shared edges becomes shortened relative to the six unshared edges. Thus in $MgAl_2O_4$ (with $x=0.387$), the shared edges are 2.58 Å in length, while the unshared edges are 2.87 Å. The shortening of shared polyhedral edges is very widely observed in mineral structures, and its stabilizing feature for ionic crystals has been explained by Pauling (1960, p. 561). The importance of this stabilization can be appreciated from the fact that, while Pauling's rules for ionic crystals are intended to apply primarily to the more stable ionic structures such as those that occur as minerals, rather than to less stable ones that can sometimes be

produced artificially, nevertheless the known spinels, both natural and artificial, show almost without exception¹ a significant amount of shared-edge shortening.

STABILIZATION OF OLIVINE

In olivine, the particular distribution of cations in the tetrahedral and octahedral interstices of the hexagonal-close-packed oxygen arrangement leads to a notably different set of polyhedral corner- and edge-sharing relationships than is present in the c.c.p.-based spinel structure. The relationships are compared in Table 1. While in spinel there is just one type of 6-coordinated site, in olivine there are two, having different poly-

TABLE 1. RELATIONS OF COORDINATION POLYHEDRA

		Number		Average cation-cation distances (Å)	
		Olivine	Spinel	Olivine	Spinel
Shared corners	Mg-Mg	6	0	3.64	—
	Mg-Si	6	12	3.31	3.35
	Si-Si	0	0	—	—
Shared edges	Mg-Mg	3	6	3.13	2.85
	Mg-Si	3	0	2.74	—
	Si-Si	0	0	—	—
Shared faces		0	0	—	—

hedral relationships: each Mg₁ octahedron shares four edges with adjacent Mg octahedra and two edges with Si tetrahedra, while each Mg₂ octahedron shares two edges with adjacent Mg octahedra and one edge with a Si tetrahedron. The numbers in Table 1 represent an average over these two sites.

From the point of view of Pauling's third rule, which expresses the destabilizing effect of shared polyhedral edges (Pauling, 1960, p. 559), the relationships in olivine appear unfavorable in comparison with those in the spinel structure (Table 1). The presence in olivine of three edges shared between Si tetrahedra and Mg octahedra, when in spinel the shared edges are between Mg octahedra only, is decidedly unfavorable in terms of the third rule's explicit recognition of shared edges as a more destabilizing feature for cations of larger charge and lower ligancy. To some extent this may be counterbalanced by the fewer shared Mg—Si corners in olivine, but Pauling's rules do not explicitly attach any im-

¹ The one exception, Ag₂MoO₄, is discussed later.

portance to this feature. Another possibly counterbalancing factor is the presence in the spinel structure of relatively short Si—Si distances of 3.49 Å, four for each Si atom, whereas in olivine the shortest Si—Si distances are 3.63 Å (twice) and 4.76 Å (twice); but these distances do not correspond to shared elements between SiO₄ tetrahedra, and again fall outside the considerations of Pauling's rules.

The decisive counterbalancing factor is the shortening of shared polyhedral edges. In the olivine structure, unshared MgO₆ octahedral edges average 3.13 Å, while edges shared between octahedra average 2.84 Å, a shortening comparable to that in MgAl₂O₄. Unshared SiO₄ tetrahedral edges average 2.76 Å, while edges shared between a SiO₄ tetrahedron and a MgO₆ octahedron average 2.54 Å. The shortening of shared edges in this structure arises in a natural way that is closely linked to the overall contraction of the SiO₄ tetrahedron from its size in an undistorted close-packed oxygen array. As shown in Figure 1, the three shared Mg—Mg edges are the O—O centerlines between the apex of one SiO₄ tetrahedron and the base of the tetrahedron next along in the direction of the *a* axis; the three shared Mg—Si edges are the edges outlining the base of the tetrahedron. In the undistorted, ideal close-packed geometry, the "empty" tetrahedron outlined by these six shared edges is equal in size to the "filled" SiO₄ tetrahedron. Shrinking the base of the tetrahedron, the apex remaining fixed, has simultaneously the effects of decreasing the average Si—O distance and shortening all of the shared edges. This feature—a very anisotropic shrinkage of the SiO₄ tetrahedron (shown in exaggerated form in Fig. 1)—is the main component of the distortion of the oxygen arrangement in olivine away from the ideal close-packed geometry. In addition there is some contraction of the apex of the tetrahedron toward the base (to shorten further the Si—O distance), adjacent tetrahedra moving closer together by the amount of the contraction.

While in the olivine structure, therefore, the contraction of the SiO₄ tetrahedron leads naturally and perhaps inevitably to the shortening of shared polyhedral edges, just the opposite is true in the spinel structure. In the spinel structure for Mg₂SiO₄ (with $x=0.366$), the unshared edges are 2.86 Å long, whereas the shared edges are 3.06 Å—almost a complete reversal of the relationship in olivine. In having x markedly less than 3/8 (with the consequent lengthening of shared octahedral edges), Mg₂SiO₄ spinel is conspicuously at variance with other spinels, as discussed earlier. The geometry of the spinel structure makes this an unavoidable feature for Mg₂SiO₄, it being the direct consequence of the contraction of the SiO₄ tetrahedron. This basic difference between these otherwise rather similar structures is, I suggest, the primary cause of the large difference in stability between the olivine and spinel forms of Mg₂SiO₄.

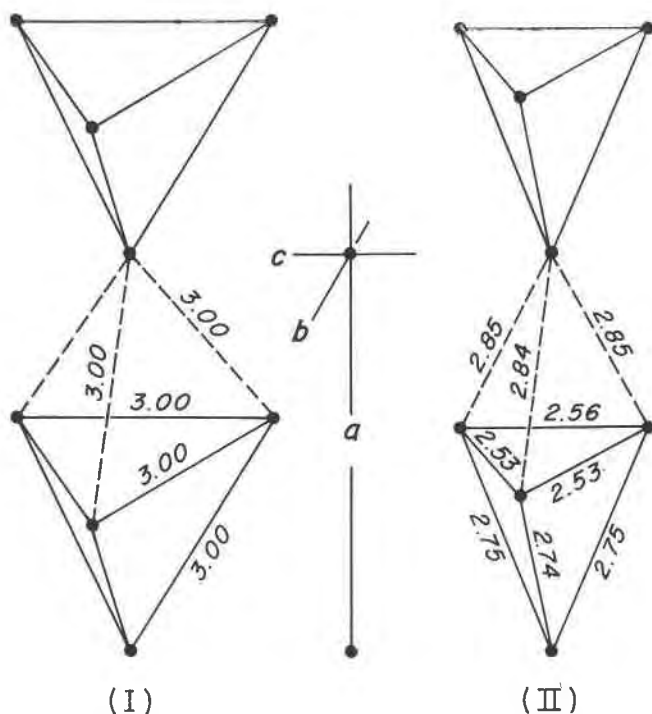


FIG. 1. Geometry of distortion of the SiO_4 tetrahedra in olivine. On the left (I) are shown undistorted tetrahedra as they occur in the ideal hexagonal close-packed oxygen arrangement with $\text{Mg}-\text{O}$ distance 2.12 \AA , and on the right (II), the contracted tetrahedra as they occur in the actual forsterite structure. The a axis translation is from the tip of one tetrahedron to the next, as shown, and the orientations of the b and c axes are as indicated by the axial cross. (The tetrahedra are mirror symmetric across (011) .) The three edges of the base of each tetrahedron (perpendicular to the a axis) are shared with adjacent MgO_6 octahedra. The three dashed lines, which, together with the tetrahedron base, outline can "empty" tetrahedron of oxygen atoms, are the $\text{O}-\text{O}$ edges shared between MgO_6 octahedra.

This explanation makes it possible to understand why the olivine \rightarrow spinel transition for Fe_2SiO_4 takes place at a pressure ($\sim 38 \text{ kb}$: Ringwood, 1959; Akimoto and Fujisawa, 1966; Ringwood and Major, 1966; Sclar and Carrison, 1966a) so much lower than for Mg_2SiO_4 ($\sim 155 \text{ kb}$: Akimoto and Ida, 1966).¹ The electronegativity of Fe^{2+} (1.8) is significantly higher than that of Mg^{2+} (1.2) (Pauling, 1960, p. 93), so that the bonding in Fe_2SiO_4 is appreciably less ionic ($\sim 50\%$) than in Mg_2SiO_4 .

¹ Ringwood (1968) reports the olivine $\rightarrow \beta\text{-Mg}_2\text{SiO}_4$ transition at about 180 kb. An olivine $\rightarrow \gamma\text{-Mg}_2\text{SiO}_4$ transition would presumably lie at somewhat higher pressure, perhaps near 200 kb, as suggested by Sclar and Carrison (1966b).

($\sim 75\%$). Since shared-edge shortening is a requirement for ionic bonding only, and therefore becomes a less important stabilizing factor as the degree of ionic character of the bonding decreases, the destabilizing effect of $x < 3/8$ for Fe_2SiO_4 spinel will be less than for Mg_2SiO_4 . The energy decrease for Fe_2SiO_4 spinel on this account is offset to some extent by the fact that x is slightly smaller for Fe_2SiO_4 than for Mg_2SiO_4 . For Ni_2SiO_4 spinel, on the other hand, x probably increases slightly (to 0.367), so that the full effect of the increased electronegativity (1.8 for Ni^{2+} also) is realized, and the transition pressure drops to 18 kb (Ringwood, 1962).

AB₂O₄ COMPOUNDS IN GENERAL

The proposed explanation of relative spinel-olivine stability for Mg_2SiO_4 can also be used to predict more generally the structures of AB_2O_4 minerals and synthetic compounds at atmospheric pressure. If the only determinative factor is the shortening of shared polyhedral edges, the spinel structure will be preferred when the tetrahedral group must enlarge relative to an ideal close-packed geometry, and the olivine structure when the tetrahedron must contract. This is a condition on the ratio d_B/d_A of the average octahedral (B—O) and tetrahedral (A—O) bond lengths: $d_B/d_A > 2/\sqrt{3} = 1.155$, olivine; $d_B/d_A < 1.155$, spinel. In Table 2, d_B/d_A is listed for a number of minerals and inorganic compounds of AB_2O_4 or $\text{ABB}'\text{O}_4$ type. The bond lengths d used to calculate the d_B/d_A values in Table 2 are where possible the bond lengths in the actual structures listed, or, where parameter determinations have not been made, they are bond lengths in similar structures. For the $\text{ABB}'\text{O}_4$ -type compounds, d_B is taken as the average of B—O and B'—O distances. For the inverse spinels (marked † in Table 2), the bond lengths used are those that would correspond to a hypothetical normal structure,¹ and for the compounds with $d_B/d_A < 0.85$, the bond lengths correspond to a hypothetical normal spinel structure in which the Sr—O and Ba—O distances are shortened by 7 percent relative to their values in the (6-coordinated) oxides; these hypothetical d_B/d_A values are enclosed in parenthesis in Table 2. Many more minerals and synthetic compounds of spinel and olivine type could be listed, but the main effort here was to list examples defining the limits of the spinel and olivine structure types.

The entries in Table 2 are grouped in accordance with the structure

¹ This is done to define the maximum extent of possible variation of d_B/d_A in spinels, d_B/d_A for the inverse structure always lying closer to 1 than for the normal structure if we assume, as did Hafner (1960), that d_B is the average of the expected bond lengths for the two cations statistically distributed over the B site. For TiFe_2O_4 , the Ti—O distance of 4-coordinated Ti^{4+} is estimated as the Ti—O distance in rutile, shortened by 7% because of change in ligancy; the unexpectedly short Ti—O distance for tetrahedrally coordinated Ti^{4+} in Ba_2TiO_4 (Bland, 1961) is rather uncertain experimentally.

TABLE 2. (B-O)/(A-O) RATIOS FOR AB₂O₄ STRUCTURES

Other	1.83	K ₂ SO ₄	arcanite
	1.64	LiKSO ₄	—
Olivine	1.46	γ-Ca ₂ SiO ₄	T _β →
	1.40	LiFePO ₄	triphylite
	1.34	Ca ₂ GeO ₄	—
	1.33	Fe ₂ SiO ₄	fayalite
	1.30	Mg ₂ SiO ₄	forsterite
	1.23	Cr ₂ BeO ₄	—
	1.23	LiMgVO ₄	P _{sp} →
	1.22	Mn ₂ GeO ₄	—
	1.21	AlGaBeO ₄	—
	1.18	Al ₂ BeO ₄	chrysoberyl
	Spinel	1.38	Ag ₂ MoO ₄
1.28		Na ₂ WO ₄	—
1.28		Na ₂ MoO ₄	—
1.22		LiNiVO ₄	—
1.15		Fe ₂ GeO ₄	—
1.15		Mg ₂ GeO ₄	T _{ol} →
(1.12)		MgIn ₂ O ₄ †	—
(1.10)		TiFe ₃ O ₄ †	ulvöspinel
1.02		MgCr ₂ O ₄	magnesiochromite
0.98		ZnAl ₂ O ₄	gahnite
0.98		MgAl ₂ O ₄	spinel
0.96	LiCrGeO ₄	—	
0.94	MnAl ₂ O ₄	galaxite	
(0.87)	Fe ₃ O ₄ †	magnetite	
Other	0.81	SrAl ₂ O ₄	—
	0.77	BaGa ₂ O ₄	—

† See text.

type stable at atmospheric pressure and room temperature. For natural minerals, $d_B/d_A = 1.155$ divides the spinels from the olivine-type structures, as predicted. The synthetic germanates of magnesium, iron, nickel, and cobalt fall at ~ 1.15 , but the exact position is uncertain, there being as yet no accurate determinations of the size of the GeO₄ tetrahedron. It is noteworthy that Mg₂GeO₄ is dimorphous at atmospheric pressure: at low temperatures the spinel structure is stable, but above 810°C it goes over to the olivine structure (Dachille and Roy, 1960). No corresponding transformations have been observed for Fe₂GeO₄ or Ni₂GeO₄, but it is possible that they exist at temperatures higher than yet investigated.

For Mg₂GeO₄, the energy change ΔE of the spinel→olivine transforma-

tion is $+3.7$ kcal mole⁻¹, showing that at $d_B/d_A = 1.15$ there remains a considerable stabilization in favor of the spinel structure. It is likely that this results from the more favorable polyhedral edge-sharing relations in spinel, as discussed earlier—the fact that the olivine structure involves octahedron-tetrahedron shared edges, whereas spinel involves only octahedron-octahedron shared edges. Because of this feature, one can expect that stabilization of the olivine structure by shared-edge shortening will first become possible at a value of d_B/d_A greater than the limiting value $2/\sqrt{3}$ based on geometrical considerations alone. For the germanates, the transition appears to be at $d_B/d_A = 1.19$, and for the vanadates, at $d_B/d_A = 1.22$, as shown by the data in Table 2.

The transition value of d_B/d_A increases with increasing oxidation number n of the A^{n+} atom. For $n = 2$, the transition lies below $d_B/d_A = 1.18$, for $n = 4$ at about 1.19, and for $n = 5$ at about 1.22. For $n = 6$ (tungstates and molybdates)¹ the transition lies above $d_B/d_A \sim 1.3$. No tungstates or molybdates are known to have the olivine structure, but both Na_2WO_4 and Na_2MoO_4 transform above $\sim 500^\circ\text{C}$ to birefringent polymorphs (Hoermann, 1928) whose structures are not known; they may well be of olivine type, analogously to the high-temperature form of Mg_2GeO_4 .

Dependence of the transition value of d_B/d_A on n can be understood in terms of the electrostatic interactions associated with shared polyhedral edges. Increase in n involves an increased charge on the A atoms (the electronegativities remaining roughly constant) and a decreased charge on the B atoms, so that the destabilization due to A—B shared edges becomes progressively more important than that due to B—B shared edges, favoring the spinel structure in which A—B shared edges do not occur.

In the extreme case of Ag_2MoO_4 , the rare tolerance of a spinel structure for x markedly less than $3/8$ ($0.364 \pm .002$) is further promoted by a considerable covalent character of the Ag—O bonds, as expected from the relatively large electronegativity of silver (1.9) and the commonly strong indications of covalent bonding in silver compounds (as in Ag_2O).

This effect, the influence of partial covalent character in the bonding, is the same as discussed earlier in explaining the olivine \rightarrow spinel transition pressures of Mg_2SiO_4 and Fe_2SiO_4 . It explains the existence, at accessible temperatures, of a high-temperature olivine polymorph of Mg_2GeO_4 but not of Fe_2GeO_4 or Ni_2GeO_4 . It also accounts for the fact

¹ Oxygen parameters have not been determined for Na_2MoO_4 and Na_2WO_4 , so that the d_A/d_B values are rather uncertain; the values given in Table 2 are estimated on the basis of the Mo—O distance in Ag_2MoO_4 (Donohue and Shand, 1947) and the comparison of isomorphous tungstates and molybdates of scheelite type by Sillén and Nylander (1943).

that LiNiVO_4 forms as a spinel whereas LiMgVO_4 has an olivine-type structure, which, incidentally, transforms to the spinel type under pressure (Blasse, 1963b).

The dependence of structure type on d_B/d_A provides an explanation for the "expandability" of the octahedral site in the olivine structure and the contrasting "inexpandability" in spinel. The expandability is seen in the readiness of the olivine structure (particularly the Mg_2 site) to accept Ca^{2+} ions. In contrast, Ca-bearing spinels are unknown (with possible exception of CaIn_2O_4 , reported to be a distorted spinel of hausmannite type: Ensslin and Valentiner, 1947).

For completeness there are included in Table 2 some examples to define in terms of d_B/d_A the outer limits of stability of the spinel and olivine structure types. At low d_B/d_A the tolerance of the spinel structure for a relatively large four-coordinated cation finally breaks down; in the examples listed, the B cations then go over entirely to tetrahedral coordination, forming a silica-like tetrahedral framework, in the interstices of which the A cations find a suitably large coordination. At large d_B/d_A the relatively expandable octahedral sites of the olivine structure finally are not large enough; there then enters a diversity of possible structures related to the various polymorphs of K_2SO_4 , Na_2SO_4 , and intermediate compounds. Ca_2SiO_4 lies almost at the transition to this diverse realm, as shown by the fact that the γ polymorph, with olivine structure, transforms successively on heating to three high-temperature polymorphs related to sulfate structure types.

Of course, it must be remembered that the effort to define the stability limits of the olivine and spinel structures in terms of the single parameter d_B/d_A is an oversimplification, since in reality various factors must be involved. The dependences of the d_B/d_A transition value on the B electronegativity and on the A valence state are examples, already discussed. Other significant factors are the individual cation/anion radius ratios, and special features of the covalent bonding contributions, such as those that influence the normal or inverse cation distributions in spinels. The effect of these factors is illustrated by Li_2WO_4 and LiZnVO_4 which, though falling within the d_B/d_A range for tungstate spinels and vanadate olivines ($d_B/d_A \cong 1.21$ and 1.25 , respectively) have instead the phenakite-type structure, with all cations in tetrahedral coordination. Under pressure, LiZnVO_4 transforms directly to a spinel, without passing through any olivine form of intermediate density (Blasse, 1963a).

In spite of these complicating factors, however, the concept of spinel \leftrightarrow olivine stability as being governed primarily by the polyhedral edge-sharing relationships is a simple and useful one, and is borne out by the data in Table 2. The concept serves to make understandable the general

dependence of the structure type on the sizes of the A and B cations, deduced empirically by Goldschmidt (see Wells, 1963, p. 503).

PAULING'S THIRD RULE

In view of the fact that polyhedral edge-sharing relationships in olivine and spinel make the olivine structure comparatively unfavorable in terms of Pauling's third rule, it seems desirable to suggest slight amplification of this rule so as to give explicit recognition to the counter-balancing effects of shared-edge shortening as follows: "The presence of shared edges and especially of shared faces in a coordinated structure decreases its stability; the effect is large for cations of large valence and small ligancy, but it can be counterbalanced by a shortening of the shared polyhedral edges." Such amplification of the rule would help also in removing its seeming contradiction with the presence of shared octahedral faces in corundum, which, in spite of the shared faces, is preferred over other structures with edge-sharing only.¹

STABILIZATION OF THE SPINEL STRUCTURE UNDER PRESSURE

Because the bond-stretching force constant for Si—O is much larger than for Mg—O, compression of the Mg₂SiO₄ spinel structure under pressure will have the effect of increasing the oxygen parameter x (increase in size of tetrahedron relative to octahedron). In accordance with the model of spinel-olivine stability proposed, one might imagine that the spinel structure would become stabilized relative to olivine at the pressure at which x reaches 0.372, corresponding to the ratio $d_B/d_A = 1.19$ for olivine-spinel transition in the germanates, estimated above. The value of x at the observed olivine→spinel transition pressure of ~ 155 kb for Mg₂SiO₄ (Akimoto and Ida, 1966) can be calculated from the appropriate finite-strain dependence of a on P , $a(P) = a(0)(P/P_0 + 1)^{-0.0815}$ where $P_0 = 486$ kb (see Anderson, 1967), with the assumption that the Si—O bond length remains unchanged so that all of the compression is taken up in shortening the Mg—O distance. The result is $x = 0.369$; while increased over the value $x = 0.366$ at atmospheric pressure, it falls short of reaching 0.372. This indicates that the stabilization of the spinel phase is not entirely due to a changing energy relation between the spinel

¹ Mertens and Zemann (1966) have shown that shared-edge shortening is not enough to account entirely for the stability of corundum in relation to a bixbyite-type structure, and that recoil of the cations away from the polyhedron centers is probably also an important factor. Recoil of the Mg²⁺ ions (and Si⁴⁺ also, though to a lesser extent, except in γ -Ca₂SiO₄) away from shared edges occurs in the olivine structure (see Smith, Majumdar, and Ordway, 1965), and probably is an additional feature tending to stabilize this structure. No recoil can occur in the spinel structure, because of symmetry constraints.

and olivine structures under pressure, but also significantly to the $P\Delta V$ contribution to the relative free energy, favoring the denser spinel structure.

This conclusion raises the basic question why the spinel structure for Mg_2SiO_4 is in fact denser than the olivine structure. The fact that both structures are based on closest packing of oxygen ions and involve the same cation coordinations would on first sight seem to require the same or very similar densities for the two phases, in contradistinction to the 10 percent difference in density that actually exists (forsterite 3.22 g cm^{-3} , Mg_2SiO_4 spinel 3.55 g cm^{-3}).

Some difference in density can be attributed to the fact that the average Mg—O distance is longer in forsterite than in the spinel phase— 2.12 \AA as compared to 2.09 \AA . The difference in bond length is mainly attributable to the Mg_2 site, for which the average bond length is 2.14 \AA . This is the site that readily accepts calcium ions in the series forsterite-monticellite, an indication that structural strains set up in the distortion from ideal close-packed geometry are such as to "distend" the Mg_2 octahedral site and favor inclusion of somewhat larger cations in it. However, as far as Mg_2SiO_4 is concerned, the increase in average Mg—O bond length could at the most decrease the olivine density by 4%, if it affected all dimensions of the structure in the same proportion—which is unlikely, since the SiO_4 tetrahedra are not involved. Some other factors must play a role in the increased density of the spinel phase.

The most important factor is, I propose, basically the same one that results in the difference in stability between the olivine and spinel phases at atmospheric pressure—the effect of shortening of shared polyhedral edges. More precisely, it can be identified as the *cause* of the shortening of shared edges. Pauling (1960, p. 561) has explained the phenomenon of shared-edge shortening as the result of the tendency for cations in closely adjacent polyhedra (which share edges or faces) to get as far away from one another as possible, so as to decrease the electrostatic repulsive energy between them, while retaining the appropriate cation-anion contact distance. In general terms, the tendency for the cations to withdraw from one another, subject to the other constraints operating, should result in a decreased density for structures where this withdrawal occurs. Such an effect is clearly seen in the polymorphs of TiO_2 . The densities decrease with the number of shared edges per TiO_6 octahedron, and hence with the extent of shared-edge contraction and cation-cation withdrawal: rutile, two shared edges per octahedron, $\rho = 4.25 \text{ g cm}^{-3}$; brookite, three shared edges, $\rho = 4.13$; anatase, four shared edges, $\rho = 3.90$.

The average Mg—Mg distance across shared octahedral edges increases from 2.85 \AA in the Mg_2SiO_4 spinel structure to 3.13 \AA in olivine.

If this increase were to affect the cell dimensions proportionally, the density decrease for olivine would be three times as large as actually observed. So the problem here is to account for why the effect is no larger than it is. Again, as in the effect of the Mg—O bond length, it cannot be expected that in general the Mg—Mg distance across shared edges will be directly coupled to the cell dimensions and hence to the density, although this is in fact the case in the spinel structure.

If it were possible to construct an olivine-type structure for Mg_2SiO_4 in which all the bond-length constraints were satisfied but in which the shared polyhedral edges did not shorten, then by comparison one could see directly the effect of shared-edge shortening and cation-cation distances on the density. This is in fact the case for the TiO_2 structures cited above. But, as mentioned earlier, it does not appear to be possible in the olivine-type structure, the contraction of the SiO_4 tetrahedron apparently leading inevitably, under the Mg—O distance constraint, to a shortening of the shared edges.

To understand in detail the factors that govern the decreased density of olivine it is necessary to examine the structure on an axis-by-axis basis. The c axis is easily interpreted: it is just twice the Mg_1 — Mg_1 distance of 2.99 Å across a shared octahedral edge, and hence contributes directly a factor $2.99/2.85 = 1.05$ to the increased density of the spinel phase—half of the total effect. The a axis on the other hand is unaffected by the Mg—Mg distance across shared edges, since all such distances lie in the (100) plane. Instead, its length is determined mainly by the way in which the SiO_4 tetrahedron contracts. The height of the tetrahedron (from one face to the opposite vertex) is 2.17 in the spinel structure, where the tetrahedron is regular, but in the olivine structure, the height in the direction that contributes to the length of the a axis is 0.15 Å longer, owing to the very anisotropic way in which the tetrahedron contracts, as discussed earlier (Fig. 1). A lengthening of the ~ 4.7 Å olivine a -axis by this amount would contribute a factor $\sim 4.7/4.55 = 1.03$ to the increased density of the spinel phase. In the b direction, the Mg—Mg distance across shared edges is very large (3.20 Å), but this does not directly determine the b axial length, since linkage across shared corners intervenes. Moreover, the effect tends to be cancelled by a recoil of the Mg_2 atom by 0.11 Å away from its octahedron center, in a direction taking it away from the Mg_1 atoms with which it shares octahedral edges. The net effect is better described by the change in average Mg—O bond length discussed earlier, contributing a factor $2.12/2.09 = 1.015$. In combination, these factors lead to a density increase for spinel by the amount $1.05 \times 1.03 \times 1.015 = 1.10$, the observed value.

In reality the a and b axial lengths are influenced by additional small

distortion effects, so that the actual factors appropriate to these axes are 1.02 and 1.03 respectively, but the additional effects do not appear to be of general enough significance to warrant a detailed discussion of them. The fact remains that by means the three main effects cited—the change in shared-edge Mg—Mg distance as it affects the c axis, the anisotropic distortion of the SiO_4 tetrahedron so as to elongate in the direction of the a axis, and the increase in average Mg—O distance as reflected in the b axis—we are able to account reasonably for the decreased density of olivine relative to the spinel structure for Mg_2SiO_4 .

CONCLUSION

In proposing structural explanations for physical properties, one must guard against facile *a posteriori* rationalizations that are arbitrarily contrived to fit particular facts, and that have no general validity or significance. The explanation of spinel-olivine stability proposed here is based on general concepts of ionic crystal stability that were codified in the form of specific rules by Pauling (1960), and that were very successfully used by him in the determination of complex mineral structures and in the recognition of erroneous proposed structures. The emphasis here on the importance of shared-edge shortening as the principal stabilizing factor in a polymorphic transition would seem to be of general significance and interest. It provides an example of the type sought by Smith and Bailey (1963, p. 809), in which the influence of shared polyhedral edges on free energies outweighs that of bond lengths.

It would be desirable to translate these qualitative explanations into quantitative ones, which would, for example, be able to predict the actual energy differences of about 15, 4.7, and 1.5 kcal mole⁻¹ between the spinel and olivine forms of Mg_2SiO_4 , Fe_2SiO_4 , and Ni_2SiO_4 , respectively. It would also be desirable to account for the spinel-olivine relations by means of complete calculations of crystal energy, for example by the methods of Born (Pauling, 1960, p. 505). However, such calculations can at present rarely be made with sufficient accuracy to be of much help, as illustrated by the difficulties in accounting in this way for polymorphism of the sodium chloride *vs.* cesium chloride type in the alkali halides (Pauling, 1960, p. 523; Fumi and Tosi, 1962) and for the corundum-bixbyite relation for Al_2O_3 (Mertens and Zemann, 1966).

In contrast, the simple qualitative approach presented here gives, I think, a helpful type of direct insight that is difficult if not impossible to obtain with complex calculations. As such, it will probably continue to be of general value in reasoning about structure type in relation to phase stability.

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Manuscript received, December 18, 1968; accepted for publication, June 10, 1968.