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COMPUTER-SIMULATED CRYSTAL STRUCTURES OF OBSERVED AND HYPOTHETICAL Mg_2SiO_4 POLYMORPHS OF LOW AND HIGH DENSITY

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ABSTRACT

The crystal structures of nine different polymorphs of Mg_2SiO_4 have been simulated using the distance least squares (DLS) method. The DLS method, when used with small weights for the O–O distances, corresponds to crystal structure model building using elastically flexible coordination polyhedra, where the dimensions and the shape of the polyhedra are defined by the interatomic distances and the flexibility of the polyhedra is given by the weights assigned to the distances. The comparison of the geometrically refined structure (*D*-structure) of an olivine with the experimentally determined structure shows that the interatomic distances are reproduced by the *D*-structure with a mean deviation of 0.04 Å. A detailed comparison of the *D*-structures calculated for six hypothetical Mg_2SiO_4 polymorphs and for the observed polymorphs (olivine, β-Mg_2SiO_4, γ-Mg_2SiO_4) suggests that the observed distortions of the coordination polyhedra are the consequence of the geometric adjustments of these polyhedra to each other. The interatomic distances and angles are strained in response to the adjustment stresses. In forsterite the shared edges between different polyhedra appear to be partly shortened because of the adjustment requirements and partly because of the electrostatic cation-cation interactions across the shared edges. Therefore an extension and amendment of Pauling's third rule regarding shared edges is proposed: *Ionic structures with shared polyhedral edges and faces can only be stable if their geometry allows the shortening of the shared polyhedral edges. When adjustment stresses force a shared edge to be long, this is a particularly destabilizing feature of the crystal structure.* The *D*-structure calculations on high density polymorphs of Mg_2SiO_4 suggest that one of the high pressure phases of Mg_2SiO_4 may have the Sr_2PbO_4 structure. It was found that this structure contains the same type of chains of edge shared octahedra of composition SiO_4 found in stishovite. Because of the relatively small size of the magnesium atom and the relatively large size of the silicon atom the calculated volume of Mg_2SiO_4 in the K_2MgF_4 structure type is high, thus making it unlikely to be a high pressure modification of Mg_2SiO_4. General packing considerations make it improbable that any phase, or combination of phases, could achieve for Mg_2SiO_4 a volume substantially lower than 77 percent of its volume in the olivine phase. Further density increases at higher pressures should only be possible by decreased interatomic distances and not by changes in coordination number.

INTRODUCTION

In the past ten years a large amount of highly precise experimental data on the crystal structures of inorganic compounds has been gathered. Various attempts have been made to systematize this knowledge according to different viewpoints. But, short of doing an experi-

mental investigation, we still are not able to give a definite concrete answer to the question: what is the crystal structure of a certain chemical compound at given P, T conditions? Using the available empirical knowledge we can supply partial answers and predict with reasonable success interatomic distances and coordination numbers of anions around cations. To take as a specific example the compound Mg_2SiO_4, we can say that at atmospheric pressure and room temperature the Mg atoms should be surrounded octahedrally by oxygen atoms (although Mg is known to occur in 4-, 5-, and 8- coordination against oxygen) while the Si-atoms should be tetrahedrally coordinated (however six coordinated silicon is also known). Assuming octahedrally coordinated Mg and tetrahedrally coordinated Si we can predict that the interatomic distances Mg–O and Si–O should be about 2.1 and 1.6 Å, but we have no way of predicting in which way the Mg and Si-coordination polyhedra should be connected to each other. Out of the multitude of possible polyhedral linkages, three, the olivine type, the β-Mg_2SiO_4-type and the spinel phase are known to be stable at various pressures. Their crystal structures have been determined. But we could not predict from the structure types what the details of the structures would be. Our knowledge of bonding mechanisms is so incomplete that we cannot predict *a priori* which distortions of interatomic distances and of bond angles should occur in a given crystal structure and more importantly which effect these distortions would have on the stability of a structure. The particular problems of the polymorphism of Mg_2SiO_4 and/or of the polyhedral distortions in olivine have been discussed by Hanke (1965), Kamb (1968), Birle *et al.* (1968), and Moore and Smith (1970). These authors used Pauling's rules for ionic compounds and mostly qualitative geometrical arguments in their interpretations of the observations. In this paper I am trying to put the geometrical arguments on a more *quantitative* basis than has been done before.

Observed Polymorphs of Mg_2SiO_4

Three polymorphs of Mg_2SiO_4 are known presently (Table 1). Only one of these, forsterite or α-Mg_2SiO_4, occurs as a mineral. The crystal structure of forsterite can conveniently be described as consisting of an approximately hexagonal close packed (h.c.p.) arrangement of oxygen atoms in which one half of the octahedral coordination sites is occupied by Mg-atoms and one eighth of the tetrahedral sites by Si-atoms. This hexagonal close packing of the oxygen atoms was recognized by Bragg and Brown (1926) and helped them to solve the crystal structure of olivine. Although a spinel phase of the composition

Table 1. Observed and hypothetical Mg_2SiO_4 structure types.
X: experimental unit cell data; L: unit cell from DLS;
S: synthetic; N: naturally occuring; H: hypothetical;
Z: formula units per unit cell; V: volume per Mg_2SiO_4;
D: density for chemical composition $(Mg_{0.9}Fe_{0.1})_2SiO_4$.

Compound		Z	Space Group		a	b	c	V	D
Forsterite (4:4)	SN	4	Pbnm	X[1]	4.762Å	10.225Å	5.994Å	73.0Å^3	3.34g.cm^{-3}
				L	4.79	10.19	5.85	71.4	3.42
β-Mg_2SiO_4	S	8	Ibmm	X[2]	8.248	11.444	5.696	67.2	3.63
				L	8.16	11.68	5.71	68.0	3.59
γ-Mg_2SiO_4(normal)	(SN)	8	Fd3m	X[3]	8.091	8.091	8.091	66.2	3.69
				L	8.12	8.12	8.12	66.9	3.65
γ-Mg_2SiO_4(inverse)	H	8	Fd3m	L	8.17	8.17	8.17	68.2	3.58
Model I (7:1)	H	4	P2/m	L	10.11	5.77	4.70	68.6	3.56
Model II (6:2)	H	4	C2/m	L	10.05	5.75	4.87	70.4	3.47
Model III (8:0)	H	4	C2/m	L	10.03	5.77	4.52	65.4	3.73
Sr_2PbO_4-type	H	2	Pbam	L	4.98	8.85	2.75	60.6	4.03
K_2MgF_4-type	H	2	I4/mmm	L	3.51	3.51	10.45	64.5	3.53

1) Birle et al., 1968; 2) Moore and Smith, 1970; 3) Ringwood and Major, 1970

$(Mg_{0.74}Fe_{0.26})_2SiO_4$ has been described as a mineral (ringwoodite, Binns, 1970) pure γ-Mg_2SiO_4 has not been found in nature nor has it been synthesized yet. The Mg-richest spinel in the system Mg_2SiO_4–Fe_2SiO_4 synthesized so far is $(Mg_{0.8}Fe_{0.2})_2SiO_4$, and it is conceivable, but not at all certain, that pure γ-Mg_2SiO_4 might form at still higher pressures (see the discussion by Ringwood and Major, 1970). The γ-$(Mg, Fe)_2SiO_4$ structure appears to be the normal spinel type (Kamb, 1968). It is based on a cubic close packed (c.c.p.) arrangement of oxygen atoms, as is the structure of β-Mg_2SiO_4, the other high-pressure polymorph of Mg_2SiO_4. Moore and Smith (1970) determined the crystal structure of the β-phase from a powder pattern of a sample of composition $(Mg_{0.9}Ni_{0.1})_2SiO_4$, while Morimoto *et al.* (1970) studied, by single crystal methods, the isostructural compounds Mn_2GeO_4 and Co_2SiO_4. The β-Mg_2SiO_4 phase should be formulated as $Mg_4OSi_2O_7$, since it contains discrete $Si_2O_7^{6-}$ groups and one of the oxygen atoms is bonded only to the octahedrally coordinated Mg-atoms. According to Ringwood and Major (1970) the β-Mg_2SiO_4 structure is the stable phase at pressures between 120 kb and 200 kb for compositions between Mg_2SiO_4 and $(Mg_{0.8}Fe_{0.2})_2SiO_4$.

Hypothetical Polymorphs of Mg_2SiO_4

In order to shed further light on the reasons for the relative stabilities of α-, β-, and γ-Mg_2SiO_4 phases it is useful to investigate other hypothetical phases which are geometrically possible but which have not yet been observed. Starting with an h.c.p. array (*ABA*) of oxygen atoms and without limiting the size of the unit cell, there is an infinite

number of ways in which we can stuff the octahedral and tetrahedral holes with Mg and Si atoms in order to achieve the Mg_2SiO_4 stoichiometry and at the same time satisfy Pauling's electrostatic valence rule. If we limit ourselves to the unit cell dimensions of forsterite, at least three different centrosymmetric arrangements yielding M_2XO_4 structure types are possible. These three types which to my knowledge have never been observed, will be called models I, II, and III. If we visualize the olivine structure in its pseudohexagonal setting, four of the Mg-atoms per unit cell are approximately at a height of zero (between the *A* and *B* layers) and the remaining four Mg-atoms are at a height of 1/2 (between the *B* and the *A* layers). The Si-atoms are distributed over such remaining tetrahedral voids which do not share faces with the Mg coordination octahedra. Model I is constructed by placing seven Mg atoms at height zero and one at 1/2 (7:1), while models II and III have respectively a distribution of 6:2 and 8:0. The positions of the silicon atoms are then determined by the Mg distribution. Model II could actually be described in a trigonal space group, but in order to facilitate comparison between the three structures the monoclinic setting was preferred (Table 1). Model II is identical with the "hypothetical structure with olivine stoichiometry" mentioned by Birle *et al.* (1968).

A fourth hypothetical model is the inverse spinel with silicon in octahedral coordination, and half the magnesium in tetrahedral coordination $(SiMg)^{[6]}Mg^{[4]}O_4$, a possibility which was discussed and rejected by Kamb (1968) for γ-Mg_2SiO_4 (the superscripts in the brackets indicate the coordination number of the atoms). A fifth hypothetical model is the high-pressure Mn_2GeO_4 structure type (isostructural with Sr_2PbO_4, Trömel, 1965). This material was prepared by Wadsley, Reid, and Ringwood (1968), who determined its crystal structure and also proposed that Mg_2SiO_4 might possibly adopt this structure type at very high pressures (200 to 300 kb according to Ringwood, 1970). In this type the silicon atoms are octahedrally coordinated, while the magnesium atoms have six near oxygen atoms in a trigonally prismatic six coordination and a seventh atom at a slightly larger distance. A sixth hypothetical model is the K_2MgF_4 structure type (Brehler and Winkler, 1954) which is adopted by Ca_2GeO_4 at 110 kb and 900°C (Reid and Ringwood, 1970). These authors consider the possibility that this structure might be another high pressure type for Mg_2SiO_4: magnesium would then have nine-coordination and silicon six-coordination, $Mg_2{}^{[9]}Si^{[6]}O_4$. According to Reid and Ringwood (1970) the structure should be denser than either the constituent oxides or the Sr_2PbO_4 type.

The six hypothetical structures selected and discussed here are of course not presented in an attempt to enumerate all conceivable Mg_2SiO_4 structure types. They are merely used as examples to illustrate the approach discussed in this paper.

Geometric Determination of the Crystal Structures

The nine crystal structures of Mg_2SiO_4 were refined geometrically by distance least squares (DLS) using the program written by Villiger (1969). A DLS refinement of a crystal structure is possible whenever the interatomic distances used as input to the refinement can be predicted with sufficient accuracy. The procedure followed these steps:

1) Average Mg–O and Si–O distances were derived from the empirical effective ionic radii tabulated by Shannon and Prewitt (1969), taking due account of both the coordination of oxygen atoms around the cations and the cation coordination around the oxygen atoms. For easier comparison with the forsterites refined by Hanke (1965) and by Birle *et al.* (1968), which both had the composition $Fo_{0.9}Fa_{0.1}$, a 10 percent Fe-component was assumed throughout, resulting in an imput value of d(Mg,Fe–O) of 2.105 Å for Mg in six and O in four coordination (instead of 2.10 Å for pure Mg–O bonds). Therefore in the following discussions "Mg" always means "$Mg_{0.9}Fe_{0.1}$". For four coordinated magnesium the value d(Mg–O) = 1.955 Å, determined in $K_2Mg_5Si_{12}O_{30}$ was used (Khan, Baur, and Forbes, 1972). The radius of magnesium in trigonally prismatic coordination was assumed to be the same as in octahedral coordination. The distance Mg–O for nine-coordinated Mg was taken to be 3 percent larger than for eight-coordinated Mg. Shannon and Prewitt (1969) have pointed out that in highly symmetrical structures, such as perovskites, the calculated interatomic distances are systematically longer than the observed distances. The same effect can be observed for compounds crystallizing in the K_2MgF_4 type, as a survey of the a cell parameters of 22 such compounds showed. Accordingly the Si–O distance of six coordinated silicon in the K_2MgF_4 type was taken to be 3 percent smaller than the calculated sum of the radii of silicon and oxygen.

2) The individual Mg–O and Si–O distances were calculated from the extended electrostatic valence rule (Baur, 1970; 1971a) for those oxygen atoms for which Pauling's (1960) second rule for ionic crystals was not satisfied. In the equation for the individual cation-oxygen distances

$$d(M\text{–O}) = (d(\text{M–O})_{\text{mean}} + b\Delta p_0)\ \text{Å} \qquad (1)$$

b was taken as 0.12 Å/v.u. for Mg and as 0.091 Å/v.u. for Si (Baur,

1970). This calculation was only necessary for β-Mg_2SiO_4 and for the K_2MgF_4 type. No attempt has been made (for the high pressure phases) to account for the possible shortening of bonds under hydrostatic pressure. While the compressibilities of many minerals are known, the effects of high pressure in complicated structures on the bonds themselves are not known. For pressures around 100 kb the shortening of cation-anion bonds may very well amount to less than 1 percent of the bond length at atmospheric pressure (as can be estimated from the compressibility values tabulated by Birch, 1966).

3) In order to account for the well known shortening of shared edges (Pauling, 1960, rule 3 for ionic compounds), any edge shared between two coordination polyhedra was assumed to be 0.15 Å shorter than an unshared edge. The shortening of shared edges has no effect on the sum of the lengths of all edges in a tetrahedron or octahedron as has been pointed out by Drits (1971). Consequently care was taken to lengthen the unshared edges by the same amount by which the shared edges were shortened. This calculation was straightforward for the tetrahedra because in the structures considered they either share no edges or half of their edges. For the octahedra the sum of the lengths of the edges (Σ) was obtained from $(\Sigma) = 12\sqrt{2d}\ (\text{M–O})_{\text{mean}}$ (Drits, 1971). The length of an unshared edge was then

$$d(\text{O–O})_{\text{unsh}} = \frac{(\Sigma) - qd(\text{O–O})_T + 0.15n}{m + n}\ (\text{Å}) \qquad (2)$$

where q and $d(\text{O–O})_T$ are the number and the length of the tetrahedral edges shared with the octahedron, and m and n are the numbers of the unshared edges and those shared with other octahedra, respectively.

4) Each of the M–O distances was assigned a weight which was proportional to the Pauling electrostatic bond strength of the corresponding bond. All the O–O distances were given the same weight, which was set arbitrarily at 0.07 of the weight assigned to the tetrahedral Si–O bond. This weighting scheme (Baur, 1971b) gives substantially different results from the weighting applied by Meier and Villiger (1969) who assign to the O–O distances weights from 0.3 to 0.5 relative to a weight of 1.0 for (Si, Al)–O. With such relatively high values for the weights of the O–O distances the coordination polyhedra tend to remain rather regular, while the smaller values used here allow distortions in O–O distances of the same magnitude as observed experimentally in olivine and comparable crystal structures.

5) The calculated M–O and O–O distances with their assigned weights were the input for a distance least-squares refinement (Shoe-

maker and Shoemaker, 1967; Meier and Villiger, 1969) using the computer program written by Villiger (1969). The DLS method depends on the fact that in a crystal structure the number of crystallographically independent interatomic distances exceeds the number of positional coordinates of the individual atoms plus the number of unit cell parameters, which together define the geometry of the crystal structure. By adjusting the parameters by least-squares to fit the predicted values of the interatomic distances a geometrically refined structure (*D*-structure) can be obtained. The interatomic distances in the refined *D*-structure will usually deviate from the input values because of geometrical constraints which do not allow all predicted distances to attain their ideal lengths. As has been shown previously (Baur, 1971b) the DLS-method becomes particularly powerful when the input distances can be predicted with high precision. This precision in predicting individual interatomic distances is possible by using the data and the approaches of Shannon and Prewitt (1969), Baur (1970, 1971a), and Drits (1971).

The resulting unit cell and positional parameters for all nine structures are presented in Tables 1 and 2. For forsterite and β-Mg_2SiO_4 the experimental values are listed as well. For models I, II, and III the monoclinic angle β was not varied, since attempts to vary it resulted in a divergence of the refinement. The Sr_2PbO_4-type was subjected to the additional constraint that the $a:b:c$ ratio had to be similar to the one observed for Mn_2GeO_4 (Wadsley *et al.*, 1968). The K_2MgF_4-type was constrained to give as small a resulting volume as could be reconciled with likely Mg–O and Mg–Mg distances. In order to do this the Mg–O distances had to deviate from the values required by the equation (1). The DLS input values for all the structures except forsterite are recorded in Table 4, the weights are omitted because they can be calculated easily.

Comparison of Observed and *D*-structure of an Olivine

A detailed comparison of the geometrically refined structure of forsterite with the experimental results of Birle *et al.* (1968) shows that the mean deviation between the calculated and the observed interatomic distances is 0.04 Å (Table 3). The Si–O distances of the *D*-structure (column 4), which were given the highest weight in the refinement are of course essentially unchanged compared to the DLS-input (the deviations are in the third place after the decimal point). This is simply a consequence of the weighted least-squares process. The Mg–O distances are reasonably close to the DLS-input values because 0.33 is still a relatively high weight. The mean value of the

Table 2. Calculated positional coordinates ($x10^4$) for three experimental and six hypothetical Mg_2SiO_4 structures. Experimental values for forsterite from Birle et al. (1968), for β-Mg_2SiO_4 from Moore and Smith (1970), standard deviations in parentheses.

	x	y	z
Forsterite			
Si(DLS)	0945	4078	2500
(Exp)	0731(3)	4057(1)	2500
Mg(1)	0000	0000	0000
(Exp)	0000	0000	0000
Mg(2)	0056	2632	7500
(Exp)	0103(3)	2774(2)	7500
O(1)	2499	0907	7500
(Exp)	2342(7)	0919(4)	7500
O(2)	2832	0578	2500
(Exp)	2799(7)	0522(4)	2500
O(3)	2312	3370	4707
(Exp)	2219(5)	3365(3)	4657(5)
β-Mg_2SiO_4			
Si(DLS)	1303	1255	2500
(Exp)	1316(12)	1268(8)	2500
Mg(1)	2297	0000	7500
(Exp)	2271(13)	0000	7500
Mg(2)	2500	2500	7500
(Exp)	2500	2500	7500
Mg(3)	0000	3701	0000
(Exp)	0000	3675(7)	0000
O(1)	0300	0000	2500
(Exp)	0496(38)	0000	2500
O(2)	4799	0000	7500
(Exp)	4702(37)	0000	7500
O(3)	0040	2348	2500
(Exp)	9779(25)	2353(18)	2500
O(4)	2557	3751	0168
(Exp)	2550(19)	3757(12)	0245(26)
γ-Mg_2SiO_4 (normal)			
Si	1250	1250	1250
Mg	5000	5000	5000
O	2416	2416	2416
γ-Mg_2SiO_4 (inverse)			
Mg	1250	1250	1250
Mg,Si	5000	5000	5000
O	2630	2630	2630

	x	y	z
Model I			
Si(1)	8420	5000	8752
Si(2)	3226	0000	8824
Mg(1)	5000	5000	0000
Mg(2)	0000	0000	5000
Mg(3)	0000	5000	5000
Mg(4)	5000	0000	5000
Mg(5)	2482	2527	4990
O(1)	3154	5000	2105
O(2)	1642	5000	7757
O(3)	8305	0000	2334
O(4)	3330	0000	2309
O(5)	0851	2601	2287
O(6)	5932	2281	2210
Model II			
Si	3330	0000	8987
Mg(1)	0000	0000	0000
Mg(2)	5000	0000	5000
Mg(3)	2500	2500	5000
O(1)	8194	0000	2220
O(2)	3341	0000	2353
O(3)	0908	2703	2253
Model III			
Si	3309	0000	8538
Mg(1)	0000	0000	5000
Mg(2)	5000	0000	5000
Mg(3)	2500	2500	5000
O(1)	8292	0000	2219
O(2)	3337	0000	2163
O(3)	0864	2606	2196
Sr_2PbO_4-type			
Si	0000	0000	0000
Mg	0819	3329	5000
O(1)	2164	0448	5000
O(2)	3925	3087	0000
K_2MgF_4-type			
Si	0000	0000	0000
Mg	0000	0000	3740
O(1)	0000	5000	0000
O(2)	0000	0000	1647

Table 3. Olivine, input to DLS and DLS-results compared with the experimental results for olivine (Birle et al., 1968). The multipliers refer to the number of distances per coordination polyhedron. The symbols in square brackets indicate shared polyhedral edges and define the polyhedron with which the edges are shared. The DLS-results refer to the refinement with unit cell dimensions held constant at the experimental values.

	Input to DLS	Weights in DLS	DLS Result	Exp. Result		Input to DLS	Weights in DLS	DLS Result	Exp. Result
Si-O(1)	1.639Å	1.00	1.64Å	1.61Å	2xO(1)-O(3)	3.112Å	0.07	3.09Å	3.13Å
Si-O(2)	1.639	1.00	1.64	1.65	2xO(2)-O(3)	3.112	0.07	3.30	3.36
2xSi-O(3)	1.639	1.00	1.64	1.64	Mg(2)-O(1)	2.105	0.33	2.11	2.18
O(1)-O(2)	2.752	0.07	2.69	2.74	Mg(2)-O(2)	2.105	0.33	2.11	2.06
2xO(1)-O(3)	2.752	0.07	2.75	2.76	2xMg(2)-O(3)	2.105	0.33	2.13	2.22
2xO(2)-O(3)[M1]	2.602	0.07	2.62	2.56	2xMg(2)-O(3)	2.105	0.33	2.12	2.07
O(3)-O(3)[M2]	2.602	0.07	2.65	2.59	2xO(1)-O(3)	3.038	0.07	3.03	3.03
2xMg(1)-O(1)	2.105	0.33	2.13	2.09	2xO(1)-O(3)[M1]	2.888	0.07	2.90	2.86
2xMg(1)-O(2)	2.105	0.33	2.10	2.08	2xO(2)-O(3)	3.038	0.07	3.16	3.19
2xMg(1)-O(3)	2.105	0.33	2.11	2.14	2xO(2)-O(3)	3.038	0.07	2.92	2.94
2xO(1)-O(2)	3.112	0.07	3.02	3.03	O(3)-O(3)	3.038	0.07	3.35	3.41
2xO(1)-O(2)[M1]	2.962	0.07	2.96	2.86	2xO(3)-O(3)	3.038	0.07	2.99	3.00

Table 4. DLS-input values for Mg_2SiO_4 polymorphs based on cubic and hexagonal close packing. Shared polyhedral edges are identified. The multipliers refer to the number of distances per coordination octahedron.

β-Mg_2SiO_4					
Si-O(1)	1.658Å	4xMg(1)-O(4)	2.105Å	2xO(4)-O(4)	3.052Å
Si-O(3)	1.628	4xO(1)-O(4)	3.052	2xMg(3)-O(2)	2.079
2xSi-O(4)	1.628	4xO(2)-O(4)[M3]	2.902	2xMg(3)-O(3)	2.118
O(1)-O(3)	2.671	2xO(4)-O(4)[M2]	2.902	2xMg(3)-O(4)	2.118
2xO(1)-O(4)	2.671	2xO(4)-O(4)	3.052	O(2)-O(2)[M3]	2.915
2xO(3)-O(4)	2.671	2xMg(2)-O(3)	2.105	2xO(2)-O(3)[M3]	2.915
O(4)-O(4)	2.671	4xMg(2)-O(4)	2.105	2xO(2)-O(4)	3.065
Mg(1)-O(1)	2.145	4xO(3)-O(4)[M3]	2.902	O(2)-O(3)	3.065
Mg(1)-O(2)	2.065	4xO(3)-O(4)	3.052	2xO(3)-O(4)	3.065
γ-Mg_2SiO_4 (normal)					
4xSi-O	1.639Å	6xMg-O	2.105Å	6xO-O	3.052Å
6xO-O	2.677	6xO-O[M]	2.902		
γ-Mg_2SiO_4 (inverse)					
4xMg-O	1.955Å	6x(Mg,Si)-O	1.940Å	6xO-O	2.819Å
6xO-O	3.193	6xO-O[M]	2.669		
Model I					
Si(1)-O(1)	1.639Å	4xO(1)-O(6)	2.977Å	4xO(4)-O(6)	3.112Å
Si(1)-O(2)	1.639	4xO(1)-O(6)	2.977	4xO(4)-O(6)[M5]	2.962
2xSi(1)-O(5)	1.639	2xO(6)-O(6)	2.977	2xO(6)-O(6)	3.112
O(1)-O(2)	2.752	2xO(6)-O(6)	2.977	Mg(5)-O(1)	2.105
2xO(2)-O(5)	2.752	2xMg(2)-O(3)	2.105	Mg(5)-O(2)	2.105
2xO(1)-O(5)[M5]	2.602	4xMg(2)-O(5)	2.105	Mg(5)-O(3)	2.105
O(5)-O(5)[M3]	2.602	4xO(3)-O(5)	3.052	Mg(5)-O(4)	2.105
Si(2)-O(3)	1.639	4xO(3)-O(5)[M5]	2.902	Mg(5)-O(5)	2.105
Si(2)-O(4)	1.639	2xO(5)-O(5)	3.052	Mg(5)-O(6)	2.105
2xSi(2)-O(6)	1.639	2xO(5)-O(5)[M3]	2.902	O(1)-O(6)	3.127
O(3)-O(4)	2.752	2xMg(3)-O(2)	2.105	O(2)-O(6)	3.127
2xO(4)-O(6)	2.752	4xMg(3)-O(5)	2.105	O(4)-O(5)	3.127
2xO(3)-O(6)[M5]	2.602	4xO(2)-O(5)	3.142	O(1)-O(2)[M5]	2.977
O(6)-O(6)[M4]	2.602	4xO(2)-O(5)[M5]	2.992	O(1)-O(4)	3.127
2xMg(1)-O(1)	2.105	2xMg(4)-O(4)	2.105	O(2)-O(3)	3.127
4xMg(1)-O(6)	2.105	4xMg(4)-O(6)	2.105	O(3)-O(4)[M5]	2.977
Model II					
Si-O(1)	1.639Å	4xO(1)-O(3)	2.977Å	2xO(3)-O(3)	3.112Å
Si-O(2)	1.639	4xO(1)-O(3)	2.977	2xMg(3)-O(1)	2.105
2xSi-O(3)	1.639	2xO(3)-O(3)	2.977	2xMg(3)-O(2)	2.105
O(1)-O(2)	2.752	2xO(3)-O(3)	2.977	2xMg(3)-O(3)	2.105
2xO(1)-O(3)[M3]	2.602	2xMg(2)-O(2)	2.105	2xO(2)-O(3)	3.112
2xO(2)-O(3)	2.752	4xMg(2)-O(3)	2.105	2xO(1)-O(3)	3.112
O(3)-O(3)[M2]	2.602	4xO(2)-O(3)[M3]	2.962	2xO(1)-O(2)[M3]	2.962
2xMg(1)-O(1)	2.105	4xO(2)-O(3)	3.112	2xO(1)-O(2)	3.112
4xMg(1)-O(3)	2.105				
Model III					
Si-O(1)	1.639Å	4xMg(1)-O(3)	2.105Å	2xO(2)-O(3)	3.142Å
Si-O(2)	1.639	4xO(1)-O(3)	3.052	2xMg(3)-O(1)	2.105
2xSi-O(3)	1.639	4xO(1)-O(3)[M3]	2.902	2xMg(3)-O(2)	2.105
O(1)-O(2)	2.752	2xO(3)-O(3)[M2]	2.902	2xMg(3)-O(3)	2.105
2xO(1)-O(3)[M3]	2.602	2xO(3)-O(3)	3.052	2xO(2)-O(3)	3.142
2xO(2)-O(3)	2.752	2xMg(2)-O(2)	2.105	2xO(1)-O(2)[M3]	2.992
O(3)-O(3)[M2]	2.602	4xMg(2)-O(3)	2.105	2xO(1)-O(2)	3.142
2xMg(1)-O(1)	2.105	4xO(2)-O(3)[M3]	2.992		

Mg(2)–O distance in the *D*-structure is slightly higher (2.121 Å) than the mean Mg(1)–O distance (2.109 Å). The same is true of the observed structure, where the values are 2.135 and 2.103 Å, respectively. This particular similarity between the *D*-structure and the actual structure lends further credence to Kamb's (1968) interpretation "that structural strains set up in the distortion from ideal close-packed geometry are such as to distend the Mg(2) octahedral site". The *D*-structure however does not reflect at all the distribution of individual Mg–O distances observed in forsterite, which vary from 2.06 to 2.22 Å in length. This variation is not connected with variations in the electrostatic bond strengths received by the oxygen atoms, because all anions in the forsterite structure are exactly saturated (in terms of Pauling's second rule). However it has been shown by Hanke (1965) and by Birle *et al.* (1968) that the longer Mg–O distances in the Mg(2)–O octahedron (and longer distances in the Si–O tetrahedron) involve oxygen atoms which participate in edges shared between different polyhedra. This is in accord with Pauling's third rule regarding shared polyhedral edges, which are generally energetically not favorable, because of cation-cation repulsion across this shared edge, but nevertheless occur in many crystal structures. Very often, in dominantly ionic compounds, the cation-anion distances involving anions in the shared edges are lengthened (Kamb, 1968, calls this 'recoil' of the cations), while the anion-anion distances within the shared edge are shortened in comparison with unshared edges. This allows a wider separation of the cations and increases therefore the stability of the compound. The stabilizing influence of cation recoil is demonstrated by the observed metal-fluorine distances in rutile-type fluorides (Baur and Khan, 1971) and by the lattice energy calculations on these fluorides (Baur, 1961). Because the geometric refinement procedure does not explicitly provide for electrostatic interactions between cations, it is not surprising that the Mg–O distances do not reflect variations which are due to these ionic forces.

The oxygen-oxygen distances in the edges of the tetrahedra and the octahedra of the *D*-structure deviate significantly from the input values and are very similar to the experimental values. This is true both for the very long edges in the Mg-octahedra, which are observed as 3.36 and 3.41 Å, and are calculated in the *D*-structure to be 3.30 and 3.35 Å, and for the short edges which without exception are also shared edges. This is unexpected because shared edges are generally thought to be short because of the electrostatic interactions between the cations. The DLS refinement shows however that part of the shortening must be attributed to the adjustment stresses due to the

fitting of the polyhedra to each other (Baur, 1971b). The observed difference between the average lengths of the shared and the unshared edges in the octahedra is 0.26 Å (Table 5), while in the *D*-structure it is 0.17 Å. This can be taken to mean that 2/3 of the difference is due to adjustment stresses, and only 1/3 due to electrostatic interactions. For the tetrahedron the differences (Table 5) are 0.18 Å and 0.09 Å respectively, that is 1/2 of the difference can be attributed to adjustment stresses. It cannot be argued that the DLS-results merely reflect the DLS-input values, because even when all O–O distances in the octahedra were entered with the same length, the computed shared edges still tended to be short. In order to obtain shared and unshared tetrahedral edges of the same length, the input values of the shared edges had to be 0.15 Å *longer* than those for the unshared edges. Furthermore the experiences with the DLS-refinements of β-Mg_2SiO_4 and the hypothetical structures show that the small input values for the shared edges can easily be overridden when the geometric adjustments so require.

D-structures of Other $Mg_2^{[6]}Si^{[4]}O_4$ Polymorphs

The geometric refinement of β-Mg_2SiO_4, reported by Baur (1971b) is considered to be more precise than the X-ray structure determination by Moore and Smith (1970), which is based on powder data. The DLS positional parameters reported in Table 2 are slightly different from those given in the earlier publication (Baur, 1971b), because the older geometric refinement was based on d(Mg–O)mean = 2.085 Å and the mean value of the lengths of the polyhedral edges was not kept constant, as actually is required (Drits, 1971). The mean deviation between the *D*-structure bond lengths and the experimental bond lengths for β-Mg_2SiO_4 is 0.073 Å. This deviation must be partly due to experimental error in the powder data refinement since an analogous calculation for β-Co_2SiO_4 gave a mean deviation between *D*-structure and observed structure of only 0.027 Å, which apparently is related to the fact that β-Co_2SiO_4 was determined with higher precision by single crystal diffraction. An inspection of the averaged dimensions of some key distances in β-Mg_2SiO_4 (Table 5) shows that the only major difference between the *D*-structure and the experimental structure concerns the length of the shared and the unshared edges in the Mg-coordination octahedra: the observed average lengths are equal, the calculated lengths are longer for the *shared* edges. The difference between observed and calculated structure is of the same type as for forsterite and seems to be connected with the fact that the

Table 5. Comparison of average distances involving shared and unshared edges and corners in the polymorphs of Mg_2SiO_4, which are based on close-packing of oxygen. The multipliers refer to the number of the distances or edges per one formula unit of Mg_2SiO_4. M: octahedral cation; T: tetrahedral cation; O: oxygen; X: experimental; LC: DLS based on experimental cell constants; LV: DLS based on refinement with varied cell constants; N: normal; I: inverse.

		Octahedra				Tetrahedra					Sum of Shared		
		Edges			Corners	Edges			Corners		Edges	Corners	Both
		Shared M-M	Shared O-O	Unshared O-O	Shared M-M	Shared T-M	Shared O-O	Unshared O-O	Shared T-M	Shared T-T			
Forsterite	X	3x3.14Å	2.86Å	15x3.12Å	6x3.70Å	3x2.73Å	2.57Å	3x2.75Å	6x3.27Å		6	12	18
	LC	3x3.05	2.92	15x3.09	6x3.76	3x2.62	2.63	3x2.72	6x3.35		6	12	18
	LV	3x3.00	2.97	15x3.05	6x3.74	3x2.61	2.62	3x2.73	6x3.29		6	12	18
β-Mg_2SiO_4	X	6.5x2.93	2.95	11x2.95				6x2.67	10x3.33	0.5x2.90Å	6.5	10.5	17
	LC	6.5x2.92	2.98	11x2.93				6x2.67	10x3.34	0.5x2.87	6.5	10.5	17
	LV	6.5x2.94	2.96	11x2.93				6x2.67	10x3.34	0.5x2.96	6.5	10.5	17
γ-Mg_2SiO_4	N LV	6x2.86	3.04	12x2.86				6x2.68	12x3.35		6	12	18
γ-Mg_2SiO_4	I LV	6x2.89	2.59	12x2.90				6x3.19	12x3.39		6	12	18
Model I	LV	4.5x2.90	3.03	12x2.97	3x3.74	3x2.45	2.73	3x2.64	6x3.50		7.5	9	16.5
Model II	LV	3x2.88	3.05	15x3.00	6x3.78	3x2.56	2.65	3x2.71	6x3.37		6	12	18
Model III	LV	6x2.89	3.04	9x2.92		3x2.31	2.79	3x2.55	6x3.53		9	6	15

geometric model neglects the electrostatic interactions. It was already observed by Moore and Smith (1970) that "there is no systematic pattern of shortening of shared edges in the β-structure". However they did not discuss this point further because of the low accuracy of their crystal structure determination. The present geometric refinement gives additional evidence on this point, as does the structure determination of β-Co_2SiO_4 by Morimoto *et al.* (1970) who observed that in this structure the mean lengths of the shared and the unshared edges are also approximately equal.

The shared edges are longer than the unshared edges in the *D*-structure of the normal spinel model of γ-Mg_2SiO_4, and in the three hypothetical models I to III (Table 5). For these cases we have no observed structure with which we could compare the results and, except for normal γ-Mg_2SiO_4, we have no experimental cell parameters which could be kept constant. The comparison of the results of the cell parameter data (Table 1) however is reassuring. The DLS-refined individual cell constants and the unit cell volumes do not deviate by more than 2 percent from the observed values, and the important mean distances show the same trends. We can therefore conclude that among the structures studied here only forsterite and the inverse spinel type can provide for the energetically advantageous shortening of the shared edges. At this point it should be stressed that the DLS-refinement of forsterite and β-Mg_2SiO_4 does provide a partial implicit recognition of ionic interactions as long as the geometric refinement is constrained to the observed unit cell constants (see LC in Table 5) because the overall dimensions of the observed structure are forced upon the *D*-structure. The refinement with variable cell constants (LV in Table 5) is free of this constraint and is therefore a model which actually does not "know" anything about electrostatics, except for the shortening by 0.15 Å of the input values of the shared polyhedral edges.

Crystal Chemical Significance

The use of the weighted distance least squares method, as proposed here, with high weights for the cation-anion distances and relatively small weights for the anion-anion distances, is similar to the application of a simple force model in which the lengths of the bonds correspond to the lengths of elastic springs and the weights are proportional to the strengths of the springs (to the restoring forces). Since the only distances used as input are within the coordination polyhedra (central cation-oxygen distances and oxygen-oxygen edges), one could also say that the model deals with elastically flexible coordination

polyhedra. The lengths of the edges define the angles subtended by the cation-cation distances at the central cation, the flexibility of the polyhedra is defined by the assigned weights. The mutual adjustment of the different polyhedra results in deformations of these polyhedra with consequent changes of the cation-anion and anion-anion distances and anion-cation-anion angles, that is the distances and angles are strained in response to the adjustment stresses. The advantage of the least squares method is that all the different distances can be considered simultaneously even in a complicated structure. The surprisingly good agreement found for the case of forsterite between the observed and the *D*-structure proves that this approach can be a useful tool for the prediction of the details of crystal structures.

The refinement of the forsterite and spinel phases of Mg_2SiO_4 fully supports Kamb's (1968) reasoning regarding the relative stabilities of these two structures: "While the contraction of the SiO_4 tetrahedron [in forsterite] leads naturally and perhaps inevitably to the shortening of shared polyhedral edges, just the opposite is true in the spinel structure". As we can see from a comparison of the lengths of shared and unshared edges in the Mg_2SiO_4 structures (Table 5) the forsterite structure is unique in this respect (except for those spinel structures which have relatively large tetrahedral cations). An inspection of the total numbers of shared edges and corners (Table 5) shows however that forsterite is not unique with regard to the number of shared polyhedral elements. According to Pauling's third rule concerning the destabilizing influence of shared polyhedral edges and faces at least model II is energetically just as favorable as forsterite. The difference between model II and olivine is that in the latter the shared edges contract simultaneously and naturally because of the adjustment of the polyhedra to each other, while in model II the shared edges remain long, thus bringing the cations into close contact. The shortening of shared polyhedral edges in polyhedral network structures should not be viewed solely as a consequence of the electrostatic repulsion of cations. Instead one can say that:

> Ionic structures with shared polyhedral edges and faces can only be stable if their geometry allows the shortening of the shared polyhedral edges. When adjustment stresses force a shared edge to be long, this is a particularly destabilizing feature of the crystal structure.

This extension and amendment of Pauling's third rule is proposed on the basis of few data (Table 5). Before it can be fully accepted we need further studies of the kind performed here on the Mg_2SiO_4 polymorphs.

Crystal structures with shared polyhedral edges and faces in which

all shared edges can simultaneously contract cannot be easily invented. Models I, II, and III fail in this regard because the oxygen atoms are in such positions that the shortening of one shared edge results in the lengthening of another shared edge. The geometric feature of the olivine structure which facilitates simultaneous shortening of all shared edges is the *L*-tetrahedron (*L* for "leer") the importance of which was pointed out by Hanke (1965) and Kamb (1968). The six edges of the *L*-tetrahedron contain all the edges shared in the olivine structure between different coordination polyhedra. The central site of the *L*-tetrahedron is not occupied. A movement of oxygen atoms toward the center of the *L*-tetrahedron contracts all shared edges simultaneously. Models I, II, and III have also *L* tetrahedra, but in the case of I and III, there are additional shared edges outside of the *L*-tetrahedra, so that a concerted adjustment of all shared edges is not possible. In model II all shared edges are concentrated in an *L*-tetrahedron, but simultaneous contraction of all shared edges nevertheless cannot be achieved, presumably because the arrangement of the *L*-tetrahedra relative to each other is not favorable.

Since the O–Si–O and O–Mg–O angles are partly functions of the O–O distances, these angles will be distorted from their ideal values in response to the adjustment stresses as the O–O distances change. Therefore it would seem that bond angle theories of the kind proposed by Gillespie (1963) could not be extended to such polyhedral framework structures as we are treating here, but instead should be tested on isolated coordination polyhedra only. However the question arises whether or not a coordination polyhedron observed in a crystalline substance can be considered to be sufficiently isolated from any of its neighbors to be really unperturbed by them. Possibly the only state in which we could observe the unperturbed influence of the electronic structure on polyhedral geometry is the gaseous state.

Petrologic Implications

Phases of a bulk composition close to $(Mg_{0.9}Fe_{0.1})_2SiO_4$ are thought to be a major component of the mantle (Ringwood, 1970). Therefore it is of considerable geochemical interest to discuss the meaning of the calculated densities and formula volumes for the different hypothetical Mg_2SiO_4 polymorphs (Table 1). It must be emphasized again that all volumes discussed here pertain to zero pressure, even when a hypothetical high pressure phase is discussed. Some of the arguments made could be invalidated in case that similar interatomic distances respond in a different manner in different structure types to the same kind of external pressure.

All polymorphs considered here have smaller formula volumes than

the forsterite-type. Model II, which appears to be energetically favorable both in regard to the number of shared edges and the fact that at least the shared tetrahedral edges are shorter than the unshared edges (Table 5), has a volume which is only 4 percent smaller than the volume of the low pressure olivine phase. It is therefore no surprise that β-Mg_2SiO_4 which has a volume 8 percent smaller than olivine is the preferred high density phase. Model I has a higher density than model II, but is energetically even more unfavorable because it has more shared edges (Table 5). Model III has the smallest formula volume of all structures considered here (except for the Sr_2PbO_4 and K_2MgF_4-type) but is also energetically most unfavorable in terms of the number and length of its shared edges. Since no attempt was made to try the impossible and enumerate all possible Mg_2SiO_4 polymorphs the comparison of these three models with the observed structures does not prove anything beyond the fact that a reasonable interpretation can be offered why these three types have not been observed yet. It is conceivable, though not likely, that a hypothetical model IV can be constructed which obeys Pauling's rules and the "shared edge length" criterion better than the models discussed here. Such a model would be of interest especially if its formula volume should calculate to be less than 66 Å^3, because this would be a potential post-spinel phase. Incidentally: should any of the three models be subsequently observed in an actual crystal structure I would expect it to be model II.

Cubic close packed and hexagonal close packed arrangements of oxygen atoms have different properties in regard to shared polyhedral elements when their voids are filled with cations, a point which has been discussed by Moore and Smith (1970). For the case of the Mg_2SiO_4 stoichiometry c.c.p. allows arrangements in which no edges are shared between the Si-tetrahedra and the Mg-octahedra. In h.c.p. however the tetrahedra must share edges with the octahedra. Once we get into high pressure phases, which are more dense than olivine, but also have unfavorably long shared edges, c.c.p. structures (β and γ-Mg_2SiO_4) appear to be more stable than the h.c.p. structures because the long shared edges involve only the magnesium coordination octahedra and not both octahedra and tetrahedra as in models I, II, and III (Table 5). The inverse spinel structure $(MgSi)^{[6]}Mg^{[4]}O_4$, which would have the advantage of shorter shared edges, has however so far not been reported to occur for Mg_2SiO_4 at high pressures. The reason for this may be that its formula volume is larger than β-Mg_2SiO_4 or normal γ-Mg_2SiO_4 (Table 1) and that Si and Mg would be sharing octahedral edges. The β-Mg_2SiO_4 and the γ-Mg_2SiO_4 types occur both

at high pressures in stable phases despite the fact that the shared polyhedral edges in these structures are long. Apparently the free energy change resulting from the decreased volume of these phases is greater than the destabilizing influence of the long shared edges (as already pointed out for spinel by Kamb, 1968).

Reid and Ringwood (1970) and Ringwood (1970) have suggested that Mg_2SiO_4 may crystallize at high pressures over 200 kbar with the strontium plumbate structure type or (less likely) the K_2MgF_4 type. The *D*-structure of Mg_2SiO_4 in the strontium plumbate type indeed is very reasonable both in terms of the formula volume which is 17 percent below the volume of forsterite, as predicted by Reid and Ringwood (1970), and in regard to the calculated interatomic distances (Table 6). Even the rather short distance O(1)–O(1) of 2.30 Å occurring in the edge shared by two Si coordination octahedra fits well into our knowledge of six coordinated silicon. The corresponding shared edge in stishovite (rutile-type SiO_2) has a length of 2.29 Å (Baur and Khan, 1971). The edge shared SiO_6 octahedra forming chains of composition SiO_4 are a common feature of both stishovite and strontium plumbate type Mg_2SiO_4. In both structures the chains extend parallel to the crystallographic *c*-direction. In stishovite each SiO_4 chain is connected via common corners to four neighboring chains, while in strontium plumbate type Mg_2SiO_4 the SiO_4 chains are isolated from each other by intervening edge shared chains of Mg coordination

Table 6. Mg_2SiO_4 in Sr_2PbO_4- and K_2MgF_4- types. DLS-input and DLS-results.

Sr_2PbO_4-type	Input	Result		Input	Result
4xSi-O(1)	1.780Å	1.79Å	Mg-O(1)	2.600Å	2.64Å
2xSi-O(2)	1.780	1.78	2xMg-O(2)	2.110	2.08
2xO(1)-O(1)	2.592	2.75	2xMg-O(2)	2.110	2.09
2xO(1)-O(1)[Si]	2.447	2.30	O(1)-O(1)[M]	2.809	2.93
4xO(1)-O(2)[M]	2.447	2.49	2xO(1)-O(2)	2.959	2.85
4xO(1)-O(2)	2.592	2.56	2xO(2)-O(2)[M]	2.809	2.75
2xSi-Si		2.75	2xO(2)-O(2)[M]	2.809	2.70
4xSi-Mg		2.90	2xMg-Mg		2.75
Mg-O(1)	2.110	2.12	2xMg-Mg		2.89
Mg-O(1)	2.110	2.13	Mg-Mg		3.07
K_2MgF_4-type	Input	Result		Input	Result
4xSi-O(1)	1.760Å	1.76Å	4xMg-O(1)	2.180Å	2.20Å
2xSi-O(2)	1.720	1.72	Mg-O(2)	2.180	2.19
4xO(1)-O(1)	2.475	2.48	4xMg-O(2)	2.490	2.52
8xO(1)-O(2)	2.475	2.46	Mg-Mg		2.64
8xSi-Mg		2.81			

polyhedra. Six Mg polyhedral chains surround every SiO_4 chain and share with it polyhedral corners. The arrangement of the chains (not of the oxygen atoms) is close packed when viewed along *c*, and there are twice as many Mg chains as SiO_4 chains. The geometric analogy between stishovite and this hypothetical Mg_2SiO_4 phase is encouraging, not so much because it would supply direct evidence for the existence of the strontium plumbate type at higher pressures, but because it is aesthetically pleasing and may be a hint towards a completely new high pressure silicate crystal chemistry based on the condensations of silicon coordination octahedra through corners and edges. Another hint is provided by the high pressure transformation of $KAlSi_3O_8$ into the hollandite type structure (Ringwood, 1970).

The *D*-structure of Mg_2SiO_4 in the K_2MgF_4 type has a volume only 12 percent smaller than the volume of forsterite. Reid and Ringwood (1970), who compared relative volumes of many substances in the K_2MgF_4 type with the volumes of the constituent oxides, suggested that the volume should be 25 percent smaller. The reason for this discrepancy has to be sought in the relatively small size of the magnesium atom in nine coordination and in the particular geometry of the K_2MgF_4 type. Since the *a* cell constants are determined by the Si–O(1) distances ($a = 2d$(Si–O)) the Mg–O(2) distance which occurs four times must be about 2.49 Å (or $0.5a\sqrt{2}$). In order to reduce the average Mg–O distance to 2.31 Å, the five remaining individual Mg–O distances had to be reduced in the DLS input to 2.18 Å. The result of that is an improbably close approach (2.64 Å) of two Mg atoms across a shared square face of the Mg coordination polyhedra. The *c*-cell constant could be only shortened, and the volume decreased, by making this Mg–Mg distance even shorter. Therefore the K_2MgF_4 structure type appears to occur only for chemical compounds in which the 9-coordinated cation is large enough to have nine contacts to oxygen atoms of approximately the same length. It does not seem to be a likely structure for Mg_2SiO_4 under any conditions.

The difficulty in finding a structure type (or types) for Mg_2SiO_4, which has a volume smaller than the volumes of the constituent oxides (periclase and stishovite) may be indicative of a deeper seated problem (no pun intended). While a substantial decrease in volume can be attained easily by going from four to six coordination the same is not true for going from six to eight coordination. A hypothetical MgO in the sphalerite-type structure would have a formula volume of 23.0 $Å^3$, the halite type periclase has a volume of 18.8 $Å^3$ (which is a reduction of 18 percent). A change to the CsCl type, based on an Mg–O distance of 2.31 Å in eight coordination, would leave the formula volume es-

sentially unchanged at 19.0 Å. The reason for the constant volume is the increase in bond length with higher coordination and, more importantly, the fact that the oxygen atoms in periclase are cubic closed packed (12 neighbors at 2.98 Å) while in the CsCl-type, a less efficient simple cubic packing occurs (6 neighbors at 2.67 Å). A contraction could be achieved however in going from stishovite to CaF_2-type SiO_2. Assuming the distance Si–O to be 1.83 Å, the volume for SiO_2 would be 18.9 $Å^3$ (as compared to 23.3 $Å^3$ for stishovite). This is a small change if compared with the formula volume of 34.3 $Å^3$ in coesite type SiO_2. Therefore an Mg_2SiO_4 composition consisting of NaCl type MgO and CaF_2 type SiO_2 would have a formula volume of 56.5 $Å^3$ or 7 percent below the volume of periclase plus stishovite (60.8 $Å^3$). A change to the coordination numbers 9, 10, or 11 does not give promise of close packed arrangements either, as the experience with the K_2MgF_4 type shows us. A coordination number of 12 could not be attained for a stoichiometry Mg_2SiO_4 because it is too cation-rich and would involve cation-cation contact (unless of course the bonding character would change under high pressures so drastically as to allow cation-cation contacts). Of most promise would be 8-coordinated structures but it is a curious fact that no $M_2^{[8]}X^{[6]}O_6$ or $M_2^{[8]}X^{[8]}O_4$ structures seem to be known at present. This may be related to the inefficiency of packing of 8-coordinated polyhedra. The volume of 56.5 $Å^3$ is 23 percent below the volume of forsterite. Since it is difficult to envision much closer packed atomic arrangements it has to be assumed that further compressions must be achieved by a reduction in the lengths of the distances between the atoms. A volume 23 percent lower than the volume of olivine seems therefore to be near the limiting volume which can be achieved by a rearrangement of coordination numbers. It appears possible that Mg_2SiO_4 phases at pressures higher than the assumed stability limit of the hypothetical strontium plumbate type return to arrangements based on oxygen close packing but with appreciably shortened oxygen-oxygen and cation-oxygen distances. This should imply that density increases with increasing pressure will be smaller for the post strontium plumbate phases than for smaller pressures and is consistent with the smaller seismic velocity-depth gradients assumed in the lower mantle (see discussion by Ringwood, 1970).

Conclusion

The work reported above shows that it is possible to predict certain details of complete crystal structures by starting with chemically reasonable interatomic distances and adjusting these distances to each other by distance least squares refinement. This method makes use of

a computer for the modeling of crystal structures and allows therefore a rapid application of the type of geometric analysis which was performed by Kamb (1968) for olivine and γ-Mg_2SiO_4. The crystal structures investigated here are all of the same type: they represent rather dense polyhedral linkages with extensive sharing of polyhedral edges and corners. Meier and Villiger (1969) had investigated (under a very different viewpoint) the open tetrahedral frameworks, mostly of feldspars and zeolites, where only corner-sharing is occurring. Shoemaker and Shoemaker (1967) applied the method to an intermetallic compound. The approach should be extended to further classes of compounds. It could also be refined by allowing explicitly for electrostatic interactions. This could be done either by straight electrostatic calculations, or by introducing pseudo-electrostatic terms into the DLS-refinement: for instance the Mg–Mg repulsion could be approximated by an input distance d(Mg–Mg) which is deliberately chosen at a larger value than actually observed in known crystal structures.

The fact that the DLS-refinement method allows us to investigate crystal structures geometrically without recourse to any bonding models is its strength rather than a weakness. This is so because different investigators may disagree (and do disagree very often) about the bonding theory applicable to a given crystal structure. There can be however very little disagreement about the lengths of observed interatomic distances even when the interpretations in terms of bonding models do differ. Therefore the use of the geometric refinement method may be termed crystal chemical positivism. In this application the positivism has proved to be fruitful. In our present state of knowledge, neither the ionic theory (electrostatic potential calculation) nor the covalent approach would have allowed the calculation of unit cell constants and positional coordinates of the Mg_2SiO_4 polymorphs.

The simulation of crystal structures by computer opens the way for the investigation of crystal structures at simulated conditions under which their study is experimentally difficult or impossible. It may aid in deciding between different models for a particular structure when the experimental evidence is inconclusive. Structure simulation will also allow the testing of hypothetical structures or of hypotheses about the behavior of crystal structures under varying conditions. It may help in predicting which isomorphic substitutions in a particular structure should be possible and even more, at which point a structure should become unstable and show a transition. In short: crystal structure simulation appears to have many potentially interesting and/or useful applications.

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