

Reprinted from:

1970, *Phys. Earth Planet. Interiors* 3, 205-212. North-Holland Publishing Company, Amsterdam

Printed in the Netherlands

## STABILITY OF MANTLE MINERALS FROM LATTICE CALCULATIONS AND SHOCK WAVE DATA\*

EDWARD S. GAFFNEY and THOMAS J. AHRENS

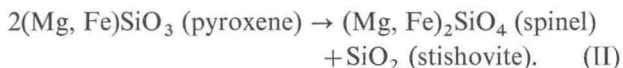
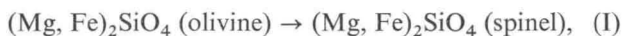
*Seismological Laboratory, California Institute of Technology  
Pasadena, California, U.S.A.*

Shock wave and static high pressure data for mantle minerals have indicated that at high pressures a series of denser polymorphs form whose crystal structures can at present only be inferred from calculated densities and crystal chemical arguments. In order to determine the admissibility of some of these proposed structures theoretical Madelung lattice energies are calculated for several oxides ( $\text{FeO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ) spinels ( $\text{Al}_2\text{MgO}_4$ ,  $\text{Mg}_2\text{SiO}_4$ ,  $\text{Fe}_2\text{SiO}_4$ ,  $\text{Ni}_2\text{SiO}_4$ ,  $\text{FeCr}_2\text{O}_4$ ,  $\text{Fe}_2\text{TiO}_4$ ,  $\text{Fe}_3\text{O}_4$ ) and perovskites ( $\text{CaTiO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{MgSiO}_3$ ,  $\text{Fe}_2^{3+}\text{O}_3$ ,  $\text{Fe}^{2+}\text{Fe}^{3+}\text{O}_3$ ). Comparison of calculated enthalpies

of formation with measured values yield approximate values for the effects of covalency on enthalpies of formation for  $\text{Al-O}_6$ ,  $\text{Ti-O}_6$ ,  $\text{Si-O}_4$ ,  $\text{Si-O}_6$ ,  $\text{Fe}^{3+}\text{-O}_6$ ,  $\text{Cr}^{3+}\text{-O}_6$ ,  $\text{Fe}^{3+}\text{-O}_4$  and  $\text{Fe}^{2+}\text{-O}_4$ . This effect is seen to be very similar for the same ion pair in the same coordination but in different compounds. The calculations indicate that enstatite ( $\text{MgSiO}_3$ ) can not enter a perovskite with a density greater than about  $3.9 \text{ g/cm}^3$  and that the high pressure phase of  $\text{Fe}_2\text{O}_3$  can be a perovskite only if the  $\text{Fe}^{3+}$  disproportionates into  $\text{Fe}^{2+}$  and  $\text{Fe}^{4+}$  and the 3d electrons in the latter are spin paired.

### 1. Introduction

Recent seismological studies (JOHNSON (1968), ARCHAMBEAU *et al.* (1969)) have shown that the marked increase in elastic velocity, long known to occur in the C-region of the earth at a depth between 200 and 900 km arises from at least two distinct zones within this range which are approximately 50 km thick. The seismological data indicate the velocity increases sharply at about 375 km in the shallow zone, and again at about 700 km in the deeper zone. The results of both static high pressure studies (RINGWOOD (1970), AKIMOTO and FUJISAWA (1968), SCLAR (1964)) and thermochemical studies (AHRENS and SYONO (1967) and ANDERSON (1967)) have shown that the probable mantle minerals, olivine and pyroxene, transform near 100 kb to denser structures according to the reactions:



Because both reactions (I) and (II) involve large increases in elastic moduli and hence elastic velocities,

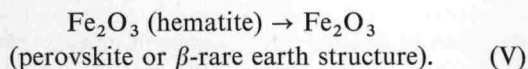
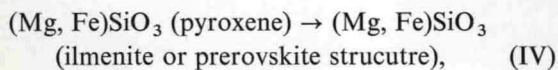
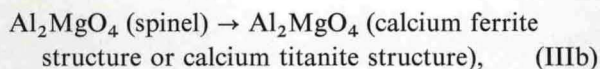
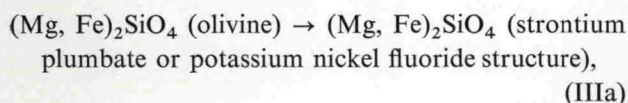
\* Contribution No. 1625, Division of Geological Sciences, California Institute of Technology.

ANDERSON (1967) has suggested that these take place in the upper transition zone. In the case of reaction (I), the bulk modulus increases from about 1.2 Mb to about 2.1 Mb. Although there is a large increase in mean bulk modulus and density ( $\approx 10\%$ ) in both reactions (I) and (II), the coordination of  $\text{Mg}^{++}$  or  $\text{Fe}^{++}$  and of  $\text{Si}^{+4}$  is octahedral and tetrahedral, respectively, in both olivine and spinel. In reaction (II) one half of the silicon ions go from tetrahedral to octahedral coordination (in stishovite) with oxygen ions. Reactions (I) and (II) thus represent relatively large increases in density without large accompanying changes in ion coordination.

In contrast to the upper transition zone, the lower 750 km or "post-spinel" transition zone (ANDERSON, 1967), presumably involves a transition of all the  $\text{Si}^{+4}$  to octahedral coordination and perhaps of the divalent metals to 8 or higher coordination with oxygen. The available shock-wave Hugoniot data (MCQUEEN *et al.* (1967), also quoted in BIRCH (1966)) for some of the likely mantle minerals and some of their structural analogs display strong evidence of transition to the so-called post-spinel phases. These shock-wave data have been analyzed by MCQUEEN *et al.* (1967), WANG (1968), ANDERSON and KANAMORI (1968), and AHRENS *et al.* (1969) in order to obtain the density and equation of state parameters of the shock-induced high pressure



phases. Ahrens *et al.* have suggested that, at least in the shock-wave case, the so-called "post-spinel" transformations might correspond to the following reactions



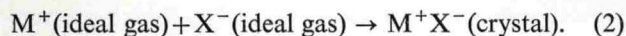
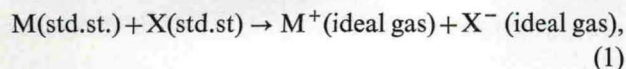
In the analysis of the shock wave data for the high pressure phases, the zero-pressure bulk modulus and density were calculated using ANDERSON'S (1967) seismic equation of state. The probable structures of the high pressure phases were inferred on the basis of the calculated densities, crystal-chemical arguments, and the results of static high pressure experiments on analog compounds. In all of the proposed high-pressure phases, silicon is in sixfold coordination and the other cations are in six, eight, or twelfold coordination with oxygen.

In order to determine the admissibility of one or more of the proposed high-pressure structures, and to evaluate the heats of formation and types of bonding involved in these polymorphs, we have calculated theoretical lattice energies for some of the pertinent simple oxides, spinels, and perovskites. These polymorphs are presumably present in the mantle. A modified Born-type calculation for ionic bonding in the crystals is used with the available data for bulk moduli and density (lattice parameters) in calculating theoretical enthalpies of formation.

## 2. Theory

### 2.1. Born-Haber cycle

The Born-Haber cycle may be used to calculate the heat of formation of an essentially ionic crystal if the lattice energy is known, viz.,



The enthalpy of formation of  $\text{M}^+$  (ideal gas) which consists of vaporization and ionization enthalpies is obtained from standard thermochemical tables (e.g. ROSINI *et al.* (1952)). The enthalpy of formation of the anion, such as that of  $\text{O}^-$ , the principal anion of interest to the study of the mantle, must be calculated theoretically (GAFFNEY and AHRENS (1969)). The enthalpy change associated with eq. (2) is just equal to the lattice energy  $W_L$  (discussed below) plus  $NC_pT$  where  $N$  is the number of moles of ionic gas per mole of solid. Assuming that the ionic gas is an ideal gas,  $C_p = \frac{5}{2}R$ , where  $T$  and  $R$  have their usual meanings.

### 2.2. Calculation of the lattice energy

The lattice energy  $W_L$  is the energy change of (2) above. The Born-Mayer form of the potential is

$$U_j = z\lambda \exp(-R/\rho) - \frac{\alpha_R}{R},$$

where  $z$  is the number of nearest neighbors,  $\lambda$  and  $\rho$  are repulsive force constants,  $R$  is some scale length (we use the cube root of the molecular volume), and  $\alpha_R$  is the Madelung constant for the same scale length. Using the equilibrium lattice dimensions we can eliminate  $z\lambda$  and summing over the lattice we get the lattice energy

$$W_L = - \frac{N_A \alpha_R q^2}{R_0} \left( 1 - \frac{\rho}{R_0} \right). \quad (3)$$

where  $N_A$  is Avagadro's number. The parameter  $\rho$  is evaluated using the relation with the bulk modulus,  $K_T$ :

$$\frac{R_0}{\rho} = \frac{9R_0 V K_T}{\alpha_R q^2} + 2. \quad (4)$$

### 2.3. Other forces

In the above derivation of the lattice energy  $W_L$  we have considered a "purely ionic" crystal with only two kinds of forces, coulombic and repulsive. However, there are other forces which may contribute to the lattice energy. Among these are van der Waals forces, covalent bonds and dipole and higher order multipole forces. In addition, there is zero-point and vibrational energy in the lattice. These last two and the van der Waals terms are fairly small, less than about 10 kcal/mole combined (GAFFNEY and AHRENS (1969)) and their omission is somewhat compensated for since the repulsive parameter  $\rho$  is obtained from empirical data. The largest contribution to non-ionic lattice energy is

due to covalent bonds. For crystals whose enthalpy of formation ( $\Delta H_f^\circ$ ) is known, the difference between calculations based on ionic theory and the measured (known) value of  $\Delta H_f^\circ$  give an apparent value for the covalent enthalpy in the lattice. There will, however, be some error in taking the actual enthalpy and the calculated ionic enthalpy equal to the covalent bond energy. This is because the lattice parameters and bulk moduli used to calculate the ionic enthalpy do themselves reflect the actual potentials within the crystal and not just the ionic portion of the potential. Also the "resonance" between ionic and covalent bonding arrangements will contribute to the lattice energy. However, in general the difference between the calculated ionic enthalpy and the actual enthalpy should be a good index of the relative proportion of covalent bonding involved.

In some of the crystal structures considered, notably

rutile,  $\alpha$ -quartz and corundum, non-radially-symmetric electric fields are known to be present at some of the lattice sites. In such cases the charge distribution associated with the ion occupying that site will be deformed into a dipole or higher order multipole. As a result interactions other than monopole interactions should be included in calculating the ionic lattice energy. We have taken such interaction into account only for  $\text{SiO}_2$  (stishovite),  $\text{TiO}_2$  (rutile), and  $\text{Al}_2\text{O}_3$  (corundum). In the first, the permanent dipole effect can be estimated to be about 62 kcal/mole (by analogy with KINGSBURY's (1968) calculation of this same effect in rutile). For rutile it is 51 kcal/mole (KINGSBURY (1968)) and for  $\text{Al}_2\text{O}_3$  multipole interactions account for about 25 kcal/mole (HAFNER and RAYMOND (1968)).

### 3. Results

Equations (3) and (4) were used to calculate the lat-

TABLE I  
Data for calculation of lattice energies

Compound	Structure	$V(\text{\AA}^3)$	$R_0(\text{\AA})$	$\alpha_R^{(1)}$	$K_T(\text{Mb})$	$q^2(e^2)$
FeO	halite	20.197	2.723	2.2018	1.42 <sup>(2)</sup>	2
$\text{SiO}_2$	$\alpha$ -quartz	37.672	3.352	9.168 <sup>(3)</sup>	0.374 <sup>(4)</sup>	4
$\text{SiO}_2$	rutile	23.269	2.855	7.7219	3.627 <sup>(5)</sup>	4
$\text{TiO}_2$	rutile	31.225	3.149	7.7191 <sup>(6)</sup>	2.125 <sup>(7)</sup>	4
$\text{Al}_2\text{O}_3$	corundum	42.466	3.489	45.7726	2.505 <sup>(4)</sup>	1
$\text{Cr}_2\text{O}_3$	corundum	48.30	3.64	45.282	2.237	1
$\text{Fe}_2^{3+}\text{O}_3$	corundum	50.268	3.691	45.679	2.027 <sup>(4)</sup>	1
$\text{Fe}_2^{3+}\text{O}_3$	perovskite	45.716 <sup>(5)</sup>	3.576	44.5549	3.814 <sup>(5)</sup>	1
$\text{Fe}^{2+}\text{Fe}^{4+}\text{O}_3$	perovskite	45.716 <sup>(5)</sup>	3.576	12.3775	3.814 <sup>(5)</sup>	4
$\text{MgSiO}_3$ - (a)	perovskite	39.225 <sup>(5)</sup>	3.398	12.3775	4.188 <sup>(5)</sup>	4
$\text{MgSiO}_3$ - (b)	perovskite	40.957	3.4	12.3775	3.49 <sup>(5)</sup>	4
$\text{MgSiO}_3$ - (c)	perovskite	44.36	3.54	12.3775	2.6 <sup>(5)</sup>	4
$\text{SrTiO}_3$	perovskite	59.558	3.905	12.3775	1.787 <sup>(8)</sup>	4
$\text{CaTiO}_3$	perovskite	55.8325	3.822	12.3775	1.633 <sup>(9)</sup>	4
$\text{Al}_2\text{MgO}_4$	spinel	65.939	4.040	67.535	1.95 <sup>(10)</sup>	1
$\text{Mg}_2\text{SiO}_4$	spinel	65.817	4.038	71.99	2.02 <sup>(9)</sup>	1
$\text{Fe}_2\text{SiO}_4$	spinel	69.782	4.117	72.225	2.12 <sup>(2)</sup>	1
$\text{Ni}_2\text{SiO}_4$	spinel	65.0376	4.0215	72.1 (est.)	2.11 <sup>(11)</sup>	1
$\text{Fe}_2\text{Cr}_2\text{O}_4$	spinel	73.455	4.188	64.30	1.87	1
$\text{Fe}_2\text{TiO}_4$	spinel	76.766	4.25	68.25	1.76	1
$\text{Fe}_3\text{O}_4$	spinel	73.982	4.198	65.475	1.872	1

<sup>(1)</sup> WADDINGTON, J. C. (1959) *Advan. Inorg. Chem. Radiochem.* **1**, 157.

<sup>(2)</sup> MAO, H. (1967) Ph.D. thesis, Univ. Rochester, N.Y.

<sup>(3)</sup> J. SHIMIN (1966) *Konstanta Madelunga dlia  $\alpha$ -kvartsa*, Lietuvos Fiz. Rink., **VI** (3), 383.

<sup>(4)</sup> ANDERSON, O. L., E. SCHREIBER, R. C. LIEBERMANN and N. SOGA (1968) *Rev. Geophys.* **6**, 491.

<sup>(5)</sup> Estimated from Hugoniot data, AHRENS *et al.* (1969).

<sup>(6)</sup> KINGSBURY (1968).

<sup>(7)</sup> Average value from G. SIMMONS (1965) *J. Grad. Res. Center* **34**, 1.

<sup>(8)</sup> BELL R. O. and G. RUPPRECHT (1963) *Phys. Rev.* **129**, 90.

<sup>(9)</sup> Estimated from ANDERSON's (1967) seismic equation of state.

<sup>(10)</sup> LEWIS, M. F. (1966) *J. Acoust. Soc. Am. Letters* **40** (3), 728.

<sup>(11)</sup> MAO, H., T. TAKAHASHI and W. A. BASSETT (1970) *Phys. Earth Planet. Interiors* **3**, 51



tice energy of several mantle minerals using data given in table 1. The cube root of the molecular volume is used as the scale length  $R$ . For the compounds mentioned above (e.g. stishovite and corundum) we have estimated multipole contributions to  $W_L$ . The heats of formation have been calculated by the Born-Haber cycle and are shown, with the other energies in the cycle, in table 2.

#### 4. Discussion

Several of the compounds shown in table 2 have known heats of formation. These serve as a check on the validity of our calculations: a value of  $\Delta H_f^\circ$  that is more than the observed value is in most cases explained by an appreciable covalent contribution to lattice energy. If on the other hand a value of  $\Delta H_f^\circ$  is calculated to be considerably less than that which is thermochemically measured we must conclude that substantial

covalent and/or strong dipole or higher multipole interaction takes place in the mineral, and the simple ionic model is inappropriate. A positive contribution to the lattice energy can arise only from repulsive forces all of which have been included empirically regardless of their mathematical form. (Failure to include all attractive forces will have a small effect on calculation of  $\rho/R$  which could presumably give  $\Delta H_f^\circ$ 's slightly less than the observed, e.g. in  $\text{Cr}_2\text{O}_3$ .)

For minerals with known heats of formation (e.g.  $\text{FeO}$ ,  $\text{MgAl}_2\text{O}_4$ ) we find that the calculated  $\Delta H_f^\circ$  is almost always greater than the observed value. With the exception of  $\alpha$ -quartz discrepancies are from 6 to 280 kcal/mole, and lie mostly between about 50 and 250 kcal/mole. These greater values arise from an omission of covalent bond energies. Also there are small contributions from multipole forces in the cases for which they have not been included. We conclude

TABLE 2  
Born-Haber cycle energies (kcal/mole)

Compound	Structure	$W_L^{(1)}$	Multiple terms	Cations <sup>(2)</sup> ionization	Anions <sup>(3)</sup> ionization	Crystal field	Heat of formation	
							calculated <sup>(4)</sup>	observed <sup>(5)</sup>
FeO	halite	-877		651	193	-13	-46	-54
SiO <sub>2</sub>	$\alpha$ -quartz	-2182		2469	386	—	+670	-217
	rutile	-2880	-62 <sup>(6)</sup>	2469	386	—	-101	-206
TiO <sub>2</sub>	rutile	-2560	-51 <sup>(7)</sup>	2224	386	—	-1	-226
Al <sub>2</sub> O <sub>3</sub>	corundum	-3513	-25 <sup>(8)</sup>	2615	579	—	-344	-399
Cr <sub>2</sub> O <sub>3</sub>	corundum	-3366		2620	579	-120	-287	-273
Fe <sub>2</sub> <sup>3+</sup> O <sub>3</sub>	corundum	-3325		2708	579	—	-45	-197
Fe <sub>2</sub> <sup>3+</sup> O <sub>3</sub>	perovskite	-3587		2708	579	—	-307	> -197 <sup>(9)</sup>
Fe <sup>2+</sup> Fe <sup>4+</sup> O <sub>3</sub>	perovskite	-3931		3318 <sup>(9)</sup>	579	$\approx -137^{(9)}$	-181	> -197 <sup>(9)</sup>
MgSiO <sub>3</sub> - a	perovskite	-4086		3031	579	—	-476	> -370 <sup>(9)</sup>
MgSiO <sub>3</sub> - b	perovskite	-3958		3031	579	—	-348	> -370 <sup>(9)</sup>
MgSiO <sub>3</sub> - c	perovskite	-3755		3031	579	—	-145	-370 <sup>(9)</sup>
SrTiO <sub>3</sub>	perovskite	-3413		2646	579	—	-189	-397 <sup>(10)</sup>
CaTiO <sub>3</sub>	perovskite	-3397		2687	579	—	-130	-397 <sup>(10)</sup>
Al <sub>2</sub> MgO <sub>4</sub>	spinel	-4447		3177	772	—	-507	-553
Mg <sub>2</sub> SiO <sub>4</sub>	spinel	-4714		3593	772	—	-349	-512
Ni <sub>2</sub> SiO <sub>4</sub>	spinel	-4761		3869	772	-58	-176	-328 <sup>(10)</sup>
Fe <sub>2</sub> SiO <sub>4</sub>	spinel	-4724		3771	772	-23	-204	-350
FeCr <sub>2</sub> O <sub>4</sub>	spinel	-4171		3271	772	-131	-259	-342 <sup>(2)</sup>
Fe <sub>2</sub> TiO <sub>4</sub>	spinel	-4325		3526	772	-19	-46	-356
Fe <sub>3</sub> O <sub>4</sub>	spinel	-4228		3359	772	-11	-108	-267

(1) Calculated from eq. (3) in the text.

(2) ROSSINI *et al.* (1952) Nat. Bur. Std. Bull. 500 except as otherwise noted.

(3) GAFFNEY and AHRENS (1969).

(4) From equations (3) and (4).

(5) ROBIE and WALDBAUM (1968) U.S. Geol. Surv. Bull. 1258, except as otherwise noted.

(6) Scaled from data of KINGSBURY (1968) for TiO<sub>2</sub> according to  $r_{\text{TiO}^{2+}}/r_{\text{SiO}^{2+}}$ .

(7) KINGSBURY (1968).

(8) HAFNER and RAYMOND (1968).

(9) See text.

(10) TAYLOR and SCHMALZREID (1964) J. Phys. Chem. 68, 2444, and AKIMOTO, FUJISAWA and KATSURA (1965).

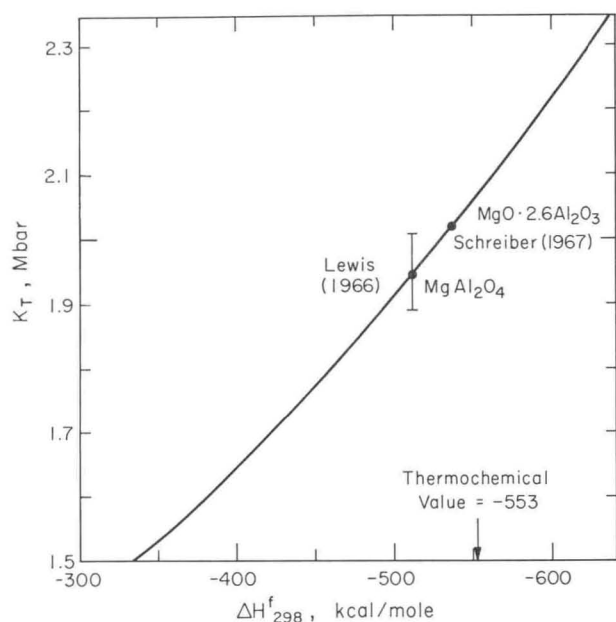


Fig. 1. Variation of enthalpy of formation ( $\Delta H_f^0$ ) of  $\text{Al}_2\text{MgO}_4$  (spinel) with  $K_T$ .

that if the structure is known our estimates will not be extremely low even if non-ionic bonding is important.

The enthalpy calculated for  $\alpha$ -quartz is in much poorer agreement with the observed heat of formation than any of the above compounds. This possibly arises from its low bulk modulus (which may in itself result from covalency). If however the 160 kcal/mole covalent contribution of Si-O bond determined from the silicate

spinel is valid for tectosilicates then very little of the almost 900 kcal/mole discrepancy in quartz can be attributed to covalency. We conclude that the lattice energy calculated as we have done it is not valid for oxides in fourfold coordination which are as compressible as quartz.

Table 3 lists the differences between calculated and measured enthalpies of formation for several of the compounds. There are five cases in which a particular coordination is represented by more than one compound: Al-O<sub>6</sub>, Ti-O<sub>6</sub>Fe<sup>2+</sup>-O<sub>4</sub>, Fe<sup>3+</sup>-O<sub>6</sub> and Si-O<sub>4</sub>. For both corundum and spinel ( $\text{MgAl}_2\text{O}_4$ ) the apparent enthalpy of covalency is about 50 kcal/mole, for three silicate spinels it is about 160 kcal/mole and for rutile and two titanites it is about 235 kcal/mole. The second case shows that for different compounds in the same structure the same ion pairs have nearly identical enthalpies of covalency. The other cases show us that this holds even for different structures if the coordination is the same. However, comparison of stishovite and the silicate spinels shows that this is now true if there is a coordination change. Therefore the following list of enthalpies of covalency can be inferred for future use:

- Al-O<sub>6</sub>  $-25 \pm 5$  kcal/mole;
- Ti-O<sub>6</sub>  $-217 \pm 10$  kcal/mole (CaTiO<sub>3</sub> omitted because of an unreliable bulk modulus);
- Si-O<sub>4</sub>  $-154 \pm 9$  kcal/mole;
- Si-O<sub>6</sub>  $\approx -105$  kcal/mole);

TABLE 3  
Apparent enthalpies of covalency

Compound	Structure	Enthalpy of formation (kcal/mole)		Apparent enthalpy of covalency (kcal/mole)	Predominant covalent bond
		observed	calculated		
Al <sub>2</sub> O <sub>3</sub>	corundum	-399	-344	-55	Al-O <sub>6</sub>
Al <sub>2</sub> MgO <sub>4</sub>	spinel	-553	-507	-46	Al-O <sub>6</sub>
Mg <sub>2</sub> SiO <sub>4</sub>	spinel	-512	-349	-163	Si-O <sub>4</sub>
Ni <sub>2</sub> SiO <sub>4</sub>	spinel	-328	-176	-152	Si-O <sub>4</sub>
Fe <sub>2</sub> SiO <sub>4</sub>	spinel	-350	-204	-146	Si-O <sub>4</sub>
SiO <sub>2</sub>	rutile	-206	-101	-105	Si-O <sub>6</sub>
Fe <sub>2</sub> O <sub>3</sub>	corundum	-197	-45	-80*	Fe <sup>3+</sup> -O <sub>6</sub>
TiO <sub>2</sub>	rutile	-226	-1	-225	Ti-O <sub>6</sub>
SrTiO <sub>3</sub>	perovskite	-397	-189	-208	Ti-O <sub>6</sub>
CaTiO <sub>3</sub>	perovskite	-397	-130	-267	Ti-O <sub>6</sub>
Cr <sub>2</sub> O <sub>3</sub>	corundum	-273	-287	+14	Cr-O <sub>6</sub>
FeCr <sub>2</sub> O <sub>4</sub>	spinel	-342	-259	-83	Fe <sup>2+</sup> -O <sub>4</sub>
Fe <sub>2</sub> TiO <sub>4</sub>	spinel	-356	-46	-310	Ti-O <sub>6</sub> , Fe <sup>2+</sup> -O <sub>4</sub>
Fe <sub>3</sub> O <sub>4</sub>	spinel	-267	-108	-159	Fe <sup>3+</sup> -O <sub>6</sub> , Fe <sup>3+</sup> -O <sub>4</sub>

\* See text.



$\text{Fe}^{3+}-\text{O}_6 \approx -80$  kcal/mole (see further discussion below for  $\text{Fe}_2\text{O}_3$ ).

$\text{Fe}^{2+}-\text{O}_4 = -88 \pm 5$  kcal/mole

$\text{Fe}^{3+}-\text{O}_6 \approx -110$  kcal/mole

(The quoted uncertainties represent the total spread between values calculated for different compounds.)

The relative covalent energy of stishovite and the silicate spinels is as one would expect. In stishovite each  $\text{Si}^{4+}$  is bonded to six  $\text{O}^-$  ions at a distance of  $\approx 1.77$  Å, whereas in the spinels each Si is bonded to only four  $\text{O}^-$  at  $\approx 1.62$  Å. The lower coordination will favor covalent bonding more than the higher. Similarly shorter bonds may also favor covalency. This relation between covalency and coordination also holds for the two iron ions,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ .

The energies for hematite indicate a rather large covalent contribution of about 150 kcal/mole. However, a closer examination of the isostructural  $\text{Al}_2\text{O}_3$  indicates that such an estimate is much too high. The multipole term in general is due primarily to dipole effects with a smaller effect due to quadrupoles. However, in  $\text{Al}_2\text{O}_3$  the dipole terms are negligible and the quadrupole terms dominate (HAFNER and RAYMOND (1968)). This is not required by the general corundum lattice but only by the specific one for  $\text{Al}_2\text{O}_3$ . We should expect therefore that for  $\text{Fe}_2\text{O}_3$  as for most oxides the dipole terms would be larger than the 25 kcal/mole in  $\text{Al}_2\text{O}_3$ . This will decrease the covalent contribution (probably to less than 100 kcal/mole).

For the compounds whose heat of formation and structure is unknown we can use the arguments given at the beginning of this section to evaluate the correctness of the proposed structure. If our calculated heat of formation is much less than that of a stable phase we conclude that the structure is not correct in some respect.

AHRENS *et al.* (1969) have proposed several possible shock-induced high-pressure structures for  $\text{MgSiO}_3$  and  $\text{Fe}_2\text{O}_3$ . The high-pressure equation of state as well as zero-pressure pressure-density of  $\text{MgSiO}_3$  ( $\approx 4.25$  g/cm<sup>3</sup>) is poorly known. This severely limits the accuracy of our calculation.

For  $\text{MgSiO}_3$  the high-pressure phase proposed for the shocked state was either a perovskite structure or an ilmenite structure. The latter was favored because it gives a density which is closer to that inferred from the shock data. Our calculation for  $\text{MgSiO}_3$  (perov-

skite) for a density of 4.25 g/cm<sup>3</sup> gives a heat of formation about 100 kcal/mole less than that of the natural phase, enstatite. In addition,  $\text{Si}^{4+}$  in six-fold coordination with oxygen should contribute about -150 kcal/mole to heat of formation (cf. stishovite) making  $\text{MgSiO}_3$  (perovskite) much more stable than  $\text{MgSiO}_3$  (enstatite). We know that this can not be true, so we conclude that either this proposed structure or the density is incorrect. A density of 4.07 g/cm<sup>3</sup> gives a heat of formation about 20 kcal/mole less than that of enstatite even after including the covalent effects (see fig. 2). A density of  $\approx 3.95$  g/cm<sup>3</sup> gives an enthalpy of formation which would be consistent with the perovskite structure. The reported shock data for enstatite (MCQUEEN and MARSH (1966)) are not sufficiently definitive to exclude this value. Unfortunately no Madelung constant is available for ilmenite so we can not check that structure.

AHRENS *et al.* (1969) also proposed that  $\text{Fe}_2\text{O}_3$ , which has the corundum structure at low pressure, goes into a perovskite structure at high pressures. We have investigated two cases: the first in which the iron remains trivalent (forming a 3-3 perovskite) and the second in which an electron is transferred from one iron ion to the other yielding one divalent and one tetravalent ion for each pair of  $\text{Fe}^{3+}$  (forming a 2-4 perovskite (REID and RINGWOOD, 1969)). The latter case leads to some major difficulties which will be discussed after considering the first, simpler, case.

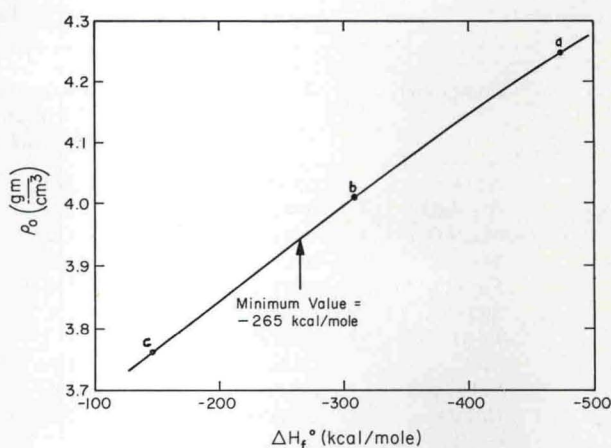


Fig. 2. Relation between calculated ionic enthalpy of formation and density for  $\text{MgSiO}_3$  (perovskite). Arrow indicates minimum permissible value for this high pressure phase. Perovskites (a) and (b) are not stable.



For the 3-3 perovskite we calculate a heat of formation of  $-307$  kcal/mole or  $110$  kcal/mole less than that of hematite. This energy is probably even lower when we allow for the covalence of the octahedrally coordinated  $\text{Fe}^{3+}$  and for multipole terms. We therefore conclude that a 3-3 perovskite is not a reasonable high-pressure phase of hematite.

Evaluation of the heat of formation of  $\text{Fe}_2\text{O}_3$  as a 2-4 perovskite presents some problems. The heat of formation of  $\text{Fe}^{4+}$  is given by Allen in *Astrophysical Quantities* (1963), but the precision is poor and may be as uncertain as  $+200$  kcal/mole. The effect of crystal fields on the heat of formation is also difficult to determine. There are no measured values for this quantity. We have estimated it as follows:  $\text{Fe}^{4+}$  has four 3d electrons and is isoelectronic with  $\text{Mn}^{3+}$  and  $\text{Cr}^{2+}$ . The crystal field splitting of the energy levels in  $\text{Mn}^{3+}$  is about  $6000\text{ cm}^{-1}$  greater than in  $\text{Cr}^{2+}$ . Other pairs of isoelectronic ions ( $\text{V}^{4+}\text{-Ti}^{3+}$ ,  $\text{Cr}^{3+}\text{-V}^{2+}$ ,  $\text{Fe}^{3+}\text{-Mn}^{2+}$ ,  $\text{Co}^{3+}\text{-Fe}^{2+}$ ) behave similarly with the higher charge ion having a splitting of  $\approx 6000\text{ cm}^{-1}$  more than the lower charges ion. We therefore assume that the splitting for  $\text{Fe}^{4+}$  is about  $6000\text{ cm}^{-1}$  greater than for  $\text{Mn}^{3+}$ . This leads to a crystal field energy of about  $-46$  kcal/mole if the electrons are not paired in the 3d orbitals or about  $-139$  kcal/mole if they are paired. It seems probable that the splitting of the energy levels is sufficient to induce such pairing. If such pairing does not occur we must be cautious because Jahn-Teller distortion can be very large in  $3d^4$  ions and this will destabilize them. We have therefore considered only the spin-paired case because it is both probable and more tractable. In this case the enthalpy of formation is calculated to be  $-181$  kcal/mole, only  $16$  kcal/mole above that of hematite.

Contributions due to covalency are probably quite small for this structure.  $\text{Fe}^{4+}$  has only four valence electrons for six bonds so it should be nearly ionic. For  $\text{Fe}^{2+}$  in twelve coordination bonding will likewise be nearly ionic. (The long bond lengths ( $\approx 2.5\text{ \AA}$ ) accompanying this high coordination will make crystal field effects on  $\text{Fe}^{2+}$  negligible.) It seems therefore subject to our estimations about the energetics of  $\text{Fe}^{4+}$ , that the heat of formation of  $\text{Fe}^{2+}\text{Fe}^{4+}\text{O}_3$  (perovskite) is slightly larger than that of hematite and that it therefore is an admissible high-pressure structure.

## 5. Conclusions

The above calculations lead to the following conclusions:

1. In most cases lattice energy calculations suitably corrected for permanent multipole energies will give a good estimate of the covalency of a compound.
2. This is not true for oxides with very high compressibility such as quartz.
3. For nearly ionic bonds the energy due to covalency of a particular bond is nearly constant in minerals with the same coordination (e.g.  $\text{Fe}_2\text{SiO}_4\text{-Mg}_2\text{SiO}_4$ ;  $\text{Al}_2\text{O}_3\text{-Al}_2\text{MgO}_4$ ).
4. Covalency in a particular bond appears to decrease as coordination increases (e.g.  $\text{Mg}_2\text{SiO}_4$  (spinel)- $\text{SiO}_2$  (stishovite)).
5. If enstatite converts to the perovskite structure at high pressure, it should have an equivalent zero-pressure density of  $\approx 3.9\text{ g/cm}^3$ .
6. Hematite does not form a perovskite at high pressures unless the  $\text{Fe}^{3+}$  disproportionates into  $\text{Fe}^{2+}$  and  $\text{Fe}^{4+}$ . If the d electrons in the latter would be spin paired under the conditions of its formation, then a 2-4 perovskite structure appears compatible with the properties of the high pressure phase inferred from the shock data.

Although it is not possible to calculate a theoretical enthalpy of formation with sufficient accuracy to predict solid-solid transition pressures, this type of calculation permits bounds to be placed on the density and bulk modulus of proposed high-pressure structures.

## Acknowledgements

This research was supported by the National Science Foundation, Grant GA-1650. We have profited from discussing this work in various stages with A. E. Ringwood, A. L. Reid and B. Kamb, and from written communication with M. Tosi.

## References

- AHRENS, T. J., D. L. ANDERSON and A. E. RINGWOOD (1969) *Rev. Geophys.*, in press.
- AHRENS, T. J. and Y. SYONO (1967) *J. Geophys. Res.* **72**, 4181.
- AKIMOTO, S. and H. FUJISAWA (1968) *J. Geophys. Res.* **73**, 1467.
- ALLEN, C. W. (1963) *Astrophysical quantities*, 2nd ed. (Athlone Press, London).
- ANDERSON, D. L. (1967) *Science* **157**, 1165.
- ANDERSON, D. L. and H. KANAMORI (1968) *J. Geophys. Res.* **73**, 6477.

- ARCHAMBEAU, C. B., E. A. FLINN and D. G. LAMBERT (1969), in press.
- BIRCH, F. (1966) Compressibility; elastic constants, in: S. P. Clark, ed., *Handbook of physical constants*, Geol. Soc. Am. Mem. 97.
- GAFFNEY, E. S. and T. J. AHRENS (1969) *J. Chem. Phys.*, in press.
- HAFNER, S. and M. RAYMOND (1968) *J. Chem. Phys.* 49, 3570.
- JOHNSON, L. (1969), to be published.
- KINGSBURY, P. I. (1968) *Acta Cryst.* A24, 578.
- KITTEL, C. (1966) *Introduction to solid state physics*, 3rd ed. (Wiley and Sons, New York).
- MCQUEEN, R. G., S. P. MARSH and J. N. FRITZ (1967) *J. Geophys. Res.* 72, 4999.
- REID, A. F. and A. E. RINGWOOD (1969), to be published.
- RINGWOOD, A. E. (1970), *Phys. Earth Planet. Interiors* 3, 109.
- ROSSINI, R. D., D. D. WAGMAN, W. H. EVANS, S. LEVINE and I. JAFFE (1952) *Nat. Bur. Std. (U.S.) Circ.* 500.
- SCLAR, C. B., L. C. CARRISON and C. M. SCHWARTZ (1964) *J. Geophys. Res.* 69, 325.
- WANG, C. (1968) *J. Geophys. Res.* 73, 6459.