

Fig. 1. Variation of enthalpy of formation ( $\Delta H_f^{\circ}$ ) 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 ± 5 kcal/mole;
Ti-O <sub>6</sub>	-217 ± 10 kcal/mole (CaTiO <sub>3</sub> omitted because of an unreliable bulk modulus);
Si-O <sub>4</sub>	-154 ± 9 kcal/mole;
Si-O <sub>6</sub>	≈ -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.

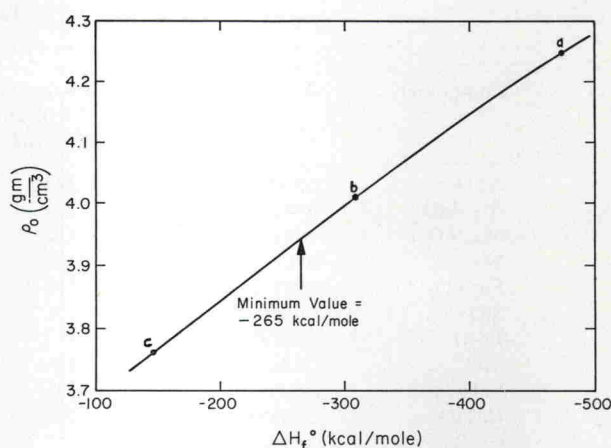


Fig. 2. Relation between calculated ionic enthalpy of formation and density for  $\text{MgSiO}_3$  (perovskite). Arrow indicates minimum permissible value for this high pressure phase. Perovskites (a) and (b) are not stable.