

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>3+</sup> O <sub>3</sub>	perovskite	-3931		3318 <sup>(9)</sup>	579	≈ -137 <sup>(9)</sup>	-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) Sealed 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).