

due to covalent bonds. For crystals whose enthalpy of formation (ΔH_f°) is known, the difference between calculations based on ionic theory and the measured (known) value of ΔH_f° 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, α -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 SiO_2 (stishovite), TiO_2 (rutile), and Al_2O_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 Al_2O_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 ⁽²⁾	2
SiO_2	α -quartz	37.672	3.352	9.168 ⁽³⁾	0.374 ⁽⁴⁾	4
SiO_2	rutile	23.269	2.855	7.7219	3.627 ⁽⁵⁾	4
TiO_2	rutile	31.225	3.149	7.7191 ⁽⁶⁾	2.125 ⁽⁷⁾	4
Al_2O_3	corundum	42.466	3.489	45.7726	2.505 ⁽⁴⁾	1
Cr_2O_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 ⁽⁴⁾	1
$\text{Fe}_2^{3+}\text{O}_3$	perovskite	45.716 ⁽⁵⁾	3.576	44.5549	3.814 ⁽⁵⁾	1
$\text{Fe}^{2+}\text{Fe}^{4+}\text{O}_3$	perovskite	45.716 ⁽⁵⁾	3.576	12.3775	3.814 ⁽⁵⁾	4
MgSiO_3 - (a)	perovskite	39.225 ⁽⁵⁾	3.398	12.3775	4.188 ⁽⁵⁾	4
MgSiO_3 - (b)	perovskite	40.957	3.4	12.3775	3.49 ⁽⁵⁾	4
MgSiO_3 - (c)	perovskite	44.36	3.54	12.3775	2.6 ⁽⁵⁾	4
SrTiO_3	perovskite	59.558	3.905	12.3775	1.787 ⁽⁸⁾	4
CaTiO_3	perovskite	55.8325	3.822	12.3775	1.633 ⁽⁹⁾	4
Al_2MgO_4	spinel	65.939	4.040	67.535	1.95 ⁽¹⁰⁾	1
Mg_2SiO_4	spinel	65.817	4.038	71.99	2.02 ⁽⁹⁾	1
Fe_2SiO_4	spinel	69.782	4.117	72.225	2.12 ⁽²⁾	1
Ni_2SiO_4	spinel	65.0376	4.0215	72.1 (est.)	2.11 ⁽¹¹⁾	1
$\text{Fe}_2\text{Cr}_2\text{O}_4$	spinel	73.455	4.188	64.30	1.87	1
Fe_2TiO_4	spinel	76.766	4.25	68.25	1.76	1
Fe_3O_4	spinel	73.982	4.198	65.475	1.872	1

⁽¹⁾ WADDINGTON, J. C. (1959) *Advan. Inorg. Chem. Radiochem.* **1**, 157.

⁽²⁾ MAO, H. (1967) Ph.D. thesis, Univ. Rochester, N.Y.

⁽³⁾ J. SHIMIN (1966) *Konstanta Madelunga dlia α -kvartsa*, Lietuvos Fiz. Rink., **VI** (3), 383.

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

⁽⁵⁾ Estimated from Hugoniot data, AHRENS *et al.* (1969).

⁽⁶⁾ KINGSBURY (1968).

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

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

⁽⁹⁾ Estimated from ANDERSON's (1967) seismic equation of state.

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

⁽¹¹⁾ 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 ΔH_f° 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 ΔH_f° 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 ρ/R which could presumably give ΔH_f° 's slightly less than the observed, e.g. in Cr_2O_3 .)

For minerals with known heats of formation (e.g. FeO , MgAl_2O_4) we find that the calculated ΔH_f° is almost always greater than the observed value. With the exception of α -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 ⁽²⁾ ionization	Anions ⁽³⁾ ionization	Crystal field	Heat of formation	
							calculated ⁽⁴⁾	observed ⁽⁵⁾
FeO	halite	-877		651	193	-13	-46	-54
SiO ₂	α -quartz	-2182		2469	386	—	+670	-217
	rutile	-2880	-62 ⁽⁶⁾	2469	386	—	-101	-206
TiO ₂	rutile	-2560	-51 ⁽⁷⁾	2224	386	—	-1	-226
Al ₂ O ₃	corundum	-3513	-25 ⁽⁸⁾	2615	579	—	-344	-399
Cr ₂ O ₃	corundum	-3366		2620	579	-120	-287	-273
Fe ₂ ³⁺ O ₃	corundum	-3325		2708	579	—	-45	-197
Fe ₂ ³⁺ O ₃	perovskite	-3587		2708	579	—	-307	> -197 ⁽⁹⁾
Fe ²⁺ Fe ⁴⁺ O ₃	perovskite	-3931		3318 ⁽⁹⁾	579	$\approx -137^{(9)}$	-181	> -197 ⁽⁹⁾
MgSiO ₃ - a	perovskite	-4086		3031	579	—	-476	> -370 ⁽⁹⁾
MgSiO ₃ - b	perovskite	-3958		3031	579	—	-348	> -370 ⁽⁹⁾
MgSiO ₃ - c	perovskite	-3755		3031	579	—	-145	-370 ⁽⁹⁾
SrTiO ₃	perovskite	-3413		2646	579	—	-189	-397 ⁽¹⁰⁾
CaTiO ₃	perovskite	-3397		2687	579	—	-130	-397 ⁽¹⁰⁾
Al ₂ MgO ₄	spinel	-4447		3177	772	—	-507	-553
Mg ₂ SiO ₄	spinel	-4714		3593	772	—	-349	-512
Ni ₂ SiO ₄	spinel	-4761		3869	772	-58	-176	-328 ⁽¹⁰⁾
Fe ₂ SiO ₄	spinel	-4724		3771	772	-23	-204	-350
FeCr ₂ O ₄	spinel	-4171		3271	772	-131	-259	-342 ⁽²⁾
Fe ₂ TiO ₄	spinel	-4325		3526	772	-19	-46	-356
Fe ₃ O ₄	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 TiO₂ 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).