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

$$\text{(Mg, Fe)}_2\text{SiO}_4 \text{ (olivine)} \rightarrow \text{(Mg, Fe)}_2\text{SiO}_4 \text{ (strontium plumbate or potassium nickel fluoride structure)}, \tag{IIIa}$$

$$\text{Al}_2\text{MgO}_4 \text{ (spinel)} \rightarrow \text{Al}_2\text{MgO}_4 \text{ (calcium ferrite structure or calcium titanite structure)}, \tag{IIIb}$$

$$\text{(Mg, Fe)SiO}_3 \text{ (pyroxene)} \rightarrow \text{(Mg, Fe)SiO}_3 \text{ (ilmenite or prerovskite strucutre)}, \tag{IV}$$

$$\text{Fe}_2\text{O}_3 \text{ (hematite)} \rightarrow \text{Fe}_2\text{O}_3 \text{ (perovskite or } \beta\text{-rare earth structure)}. \tag{V}$$

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 twelvefold 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.,

$$\text{M(std.st.)} + \text{X(std.st)} \rightarrow \text{M}^+\text{(ideal gas)} + \text{X}^-\text{ (ideal gas)}, \tag{1}$$

$$\text{M}^+\text{(ideal gas)} + \text{X}^-\text{(ideal gas)} \rightarrow \text{M}^+\text{X}^-\text{(crystal)}. \tag{2}$$

The enthalpy of formation of $M^+$ (ideal gas) which consists of vaporization and ionization enthalpies is obtained from standard thermochemical tables (e.g. ROSSINI *et al.* (1952)). The enthalpy of formation of the anion, such as that of $O^=$, 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

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

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

$$\frac{R_0}{\rho} = \frac{9R_0VK_T}{\alpha_R q^2} + 2. \tag{4}$$

### 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