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

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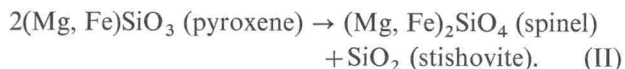
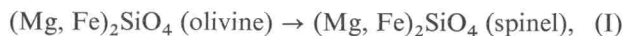
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Shock wave and static high pressure data for mantle minerals have indicated that at high pressures a series of denser polymorphs form whose crystal structures can at present only be inferred from calculated densities and crystal chemical arguments. In order to determine the admissibility of some of these proposed structures theoretical Madelung lattice energies are calculated for several oxides (FeO , Al_2O_3 , Cr_2O_3 , Fe_2O_3 , SiO_2 , TiO_2) spinels (Al_2MgO_4 , Mg_2SiO_4 , Fe_2SiO_4 , Ni_2SiO_4 , FeCr_2O_4 , Fe_2TiO_4 , Fe_3O_4) and perovskites (CaTiO_3 , SrTiO_3 , MgSiO_3 , $\text{Fe}_2^{3+}\text{O}_3$, $\text{Fe}^{2+}\text{Fe}^{4+}\text{O}_3$). Comparison of calculated enthalpies

of formation with measured values yield approximate values for the effects of covalency on enthalpies of formation for Al-O_6 , Ti-O_6 , Si-O_4 , 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 (MgSiO_3) can not enter a perovskite with a density greater than about 3.9 g/cm^3 and that the high pressure phase of Fe_2O_3 can be a perovskite only if the Fe^{3+} disproportionates into Fe^{2+} and 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:



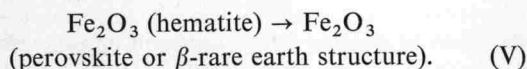
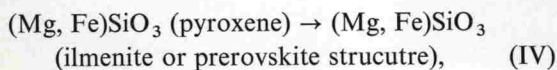
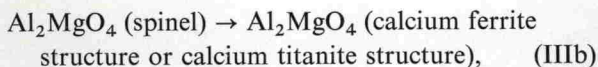
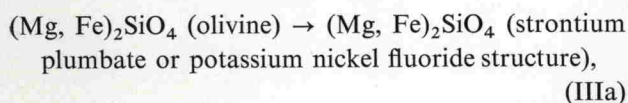
Because both reactions (I) and (II) involve large increases in elastic moduli and hence elastic velocities,

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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 Mg^{++} or Fe^{++} and of 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 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



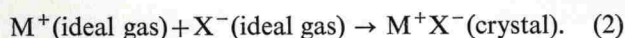
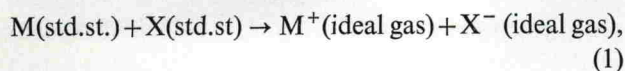
In the analysis of the shock wave data for the high pressure phases, the zero-pressure bulk modulus and density were calculated using ANDERSON's (1967) seismic equation of state. The probable structures of the high pressure phases were inferred on the basis of the calculated densities, crystal-chemical 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 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 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, λ and ρ are repulsive force constants, R is some scale length (we use the cube root of the molecular volume), and α_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 ρ 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 ρ is obtained from empirical data. The largest contribution to non-ionic lattice energy is