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

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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 ($CaTiO_3$, $SrTiO_3$, $MgSiO_3$, $Fe_2^{3+}O_3$, $Fe^{2+}Fe^{4+}O_3$). 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, Fe^{3+}–O_6, Cr^{3+}–O_6, Fe^{3+}–O_4 and Fe^{2+}–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 amd 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:

$$(Mg, Fe)_2SiO_4 \text{ (olivine)} \rightarrow (Mg, Fe)_2SiO_4 \text{ (spinel)}, \quad \text{(I)}$$

$$2(Mg, Fe)SiO_3 \text{ (pyroxene)} \rightarrow (Mg, Fe)_2SiO_4 \text{ (spinel)} + SiO_2 \text{ (stishovite)}. \quad \text{(II)}$$

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

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