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 modeling lattice energies and calculated for several oxides (FeO, Al2O3, Cr2O3, Fe2O3, SiO2, TiO2) spinels (Al2MgO4, Mg2SiO4, Fe2SiO4, Ni2SiO4, Fe2CrO4, Fe2TiO4 Fe3O4 and perovskites (CaTiO3, SrTiO3, MgSiO3, Fe2+Fe3+O3). Comparison of calculated enthalpies of formation with measured values yield approximate values for the effects of covacency on enthalpies of formation for Al-O, Si-O, Si-O, Fe2+-O2, Cr3+-O, Fe3+-O, and Fe3+-O. The 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 (MgSiO3) cannot enter a perovskite with a density greater than about 3.9 g/cm3 and that the high pressure phase of Fe2SiO4 can be a perovskite only if the Fe3+ disproportionate into Fe3+* and Fe2+* and the 3d electrons in the latter are spin paired.

1. Introduction

Recent seismological studies (Johnson, 1968), Archambault 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 that 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), Arimoto and Fujisawa (1968), Selkar (1964) and thermochemical studies (Airens and Smyo (1967) and Airens (1967)) have shown that the probable mantle minerals, olivine and pyroxene, transform near 100 kb to denser structures according to the reactions:

\[(\text{Mg, Fe})_{2}\text{SiO}_4 \text{ (olivine)} \rightarrow (\text{Mg, Fe})_{2}\text{SiO}_4 \text{ (spinel)} \]

\[(\text{Mg, Fe})_2\text{SiO}_4 \text{ (pyroxene)} \rightarrow (\text{Mg, Fe})_2\text{SiO}_4 \text{ (spinel)} \]

\[+\text{SiO}_3 \text{ (stishovite)} \]

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 2.4 Mb. Although there is a large increase in mean bulk modulus and density ("10^2") in both reactions (I) and (II), the coordination of Mg** or Fe** and of Si** is octahedral and tetrahedral, respectively, in both olivine and spinel. In reaction (I) 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 700 km or "post-spinel" transition zone (Anderson, 1967), presumably involves a transition of all the Si** to octahedral coordination and perhaps of the divalent metals to 8 or higher coordination with oxygen. The available shock-wave data have been analyzed by McQueen et al. (1967), also quoted in Brinch (1966) for some of the likely mantle minerals and some of their structural analogs display stronger 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 Airens et al. (1969) in order to obtain the density and equation of state parameters of the shock-induced high pressure.
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.,

\[ M_{(\text{ideal gas})} + X_{(\text{std})} \rightarrow M^+_{(\text{ideal gas})} + X^-_{(\text{ideal gas})} \]

\[ M^+_{(\text{ideal gas})} + X^-_{(\text{ideal gas})} \rightarrow M^+X^-_{(\text{crystal})} \]  

(1)

(2)

The enthalpy of formation of \( M^+ \) (ideal gas) which consists of vaporization and ionization energies 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 \( NCG^*T \), where \( N \) is the number of moles of ionic gas per mole of solid. Assuming that the ionic gas is an ideal gas, \( C_p = \frac{T}{R} \), 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

\[ U_j = z_i \exp(-R_j/R) - z_i^2/R \]

where \( z \) is the number of nearest neighbors, \( i \) and \( j \) are repulsive force constants, \( R \) is some scale length (we use the cube root of the molecular volume), and \( z_i \) is the Madelung constant for the same scale length. Using the equilibrium lattice dimensions we can eliminate \( z_i \) and summing over the lattice we get the lattice energy

\[ W_L = -N \frac{\epsilon}{R_0} \left[ 1 + \frac{1}{R_0} \right] \]

(3)

where \( N \) is Avogadro’s number. The parameter \( \rho \) is evaluated using the relation with the bulk modulus, \( K_B \):

\[ \rho = 3R_0K_B \frac{3/2}{Z^2} + 2. \]

(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 dipoles 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 1 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
due to covalent bonds. For crystals whose enthalpy of formation (ΔHf) is known, the difference between calculations based on ionic theory and the measured (known) value of ΔHf gives 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 modulus used to calculate the ionic enthalpy do not 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, a-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 SiO2 (stishovite), TiO2 (rutile), and Al2O3 (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 TiO2 it is 51 kcal/mole (Kingsbury (1968) and for Al2O3 multipole interactions account for about 25 kcal/mole (Hafner and Raymond (1965)).

3. Results

Equations (3) and (4) were used to calculate the lattice energies of a number of common oxides. The resulting values are listed in Table 1. The data in Table 1 have been calculated using a lattice model that includes both ionic and covalent contributions. The Table 1 Data for calculation of lattice energies

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>P(10^12)</th>
<th>R(Å)</th>
<th>E(MB)</th>
<th>e^2/ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>halite</td>
<td>20.197</td>
<td>1.273</td>
<td>2.2018</td>
<td>1.427</td>
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<tr>
<td>SiO2</td>
<td>a-quartz</td>
<td>37.672</td>
<td>3.352</td>
<td>9.668</td>
<td>0.374</td>
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<tr>
<td>SiO2</td>
<td>rutile</td>
<td>23.569</td>
<td>2.855</td>
<td>7.7219</td>
<td>3.627</td>
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<td>TiO2</td>
<td>rutile</td>
<td>31.225</td>
<td>3.149</td>
<td>7.1719</td>
<td>2.122</td>
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<tr>
<td>Al2O3</td>
<td>corundum</td>
<td>42.466</td>
<td>3.489</td>
<td>47.726</td>
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<td>Cr2O3</td>
<td>corundum</td>
<td>48.30</td>
<td>3.44</td>
<td>45.282</td>
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<td>Fe3+ Fe4+ O2+</td>
<td>corundum</td>
<td>30.268</td>
<td>3.691</td>
<td>45.679</td>
<td>2.026</td>
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<td>Fe3+ Fe4+ O2+</td>
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<td>45.716</td>
<td>3.576</td>
<td>45.549</td>
<td>3.812</td>
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<tr>
<td>Fe4+ Fe4+ O2+</td>
<td>perovskite</td>
<td>45.716</td>
<td>3.576</td>
<td>12.775</td>
<td>3.812</td>
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<td>MgSiO3 (-a)</td>
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<td>39.225</td>
<td>3.398</td>
<td>12.775</td>
<td>4.187</td>
</tr>
<tr>
<td>MgSiO3 (-b)</td>
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<td>3.44</td>
<td>12.775</td>
<td>3.891</td>
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<td>44.36</td>
<td>3.54</td>
<td>12.775</td>
<td>2.61</td>
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<td>1.95</td>
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<td>4.25</td>
<td>68.25</td>
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<td>73.982</td>
<td>4.198</td>
<td>65.475</td>
<td>1.872</td>
</tr>
</tbody>
</table>

117 Estimated from Hugoniot data, ARBENZ et al. (1958).
118 Kingsbury (1968).
119 Average value from G. Simmons (1965) J. Geol. Res. Center 34, 1.
121 Estimated from Anderson's (1967) seismie equation of state.


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. stilbite and cordierite) we have estimated multipole contributions to $W_i$. 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 calculation of a value of $\Delta H_f$; this is more than the observed value in most cases explained by an appreciable covariant contribution to ionic energy. If on the other hand a value of $\Delta H_f$ is calculated to be considerably less than that which is thermochronically measured we must conclude that substantial covariant 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 lastent 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 $\mu R$ which could presumably give $\Delta H_f$'s slightly less than the observed, e.g. in Cr$_2$O$_3$.)

For minerals with known heats of formation (e.g. FeO, MgAl$_2$O$_4$) we find that the calculated $\Delta H_f$ 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 covariant bond energies. Also there are small contributions from multipole forces in the cases for which they have not been included. We conclude

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>$W_1$</th>
<th>Multipole terms</th>
<th>Ionic contribution</th>
<th>Crystal field</th>
<th>Heat of formation calculated</th>
<th>Heat of formation observed</th>
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<tbody>
<tr>
<td>FeO</td>
<td>halite</td>
<td>-877</td>
<td>651</td>
<td>193</td>
<td>-13</td>
<td>-46</td>
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<td>SiO$_2$</td>
<td>quartz</td>
<td>-2182</td>
<td>2469</td>
<td>386</td>
<td>-670</td>
<td>-217</td>
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<td>TiO$_2$</td>
<td>rutile</td>
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<td>2469</td>
<td>386</td>
<td>-101</td>
<td>-206</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>corundum</td>
<td>-3513</td>
<td>2615</td>
<td>579</td>
<td>-344</td>
<td>-599</td>
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<tr>
<td>Cr$_2$O$_3$</td>
<td>corundum</td>
<td>-3366</td>
<td>2620</td>
<td>579</td>
<td>-287</td>
<td>-273</td>
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<tr>
<td>Fe$_{1+y}$O$_2$</td>
<td>corundum</td>
<td>-3125</td>
<td>2708</td>
<td>579</td>
<td>-45</td>
<td>-197</td>
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<td>Fe$_{1-y}$O$_2$</td>
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<td>2708</td>
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<td>-307</td>
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<td>3118</td>
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<td>-348</td>
<td>-170</td>
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<td>3031</td>
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<td>-165</td>
<td>-170</td>
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<td>2546</td>
<td>579</td>
<td>-189</td>
<td>-197</td>
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<td>2546</td>
<td>579</td>
<td>-150</td>
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<td>spinel</td>
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<td>3177</td>
<td>772</td>
<td>-307</td>
<td>-553</td>
<td></td>
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<td>N$_2$SiO$_4$</td>
<td>spinel</td>
<td>-4761</td>
<td>3177</td>
<td>772</td>
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<td>-553</td>
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<td>Fe$_2$SiO$_4$</td>
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<td>3771</td>
<td>772</td>
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<td>-170</td>
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<td>Fe$_2$SiO$_4$</td>
<td>spinel</td>
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<td>3771</td>
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<td>-204</td>
<td>-170</td>
<td></td>
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<td>Fe$_2$TiO$_4$</td>
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<td>3526</td>
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<tr>
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<td>3526</td>
<td>772</td>
<td>-109</td>
<td>-267</td>
<td></td>
</tr>
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</table>

1) Calculated from eq. (2) in the text.
4) From equations (1) and (6).
6) Scaled from data of Kingbury (1968) for FeO$_2$ according to $\mu_{\alpha}=\mu_{\beta}$.005$.
7) Kingbury (1968).
8) Hauser and Raymond (1968).
9) See text.
that if the structure is known our estimates will not be extremely low even if non-ionic bonding is important.

The enthalpy calculated for α-quartz is in much poorer agreement with the observed heat of formation than any of the above compounds. This possibly arises from its low bulk modulus (which may in itself result from covalency). If however the 160 kcal/mole covalent contribution of Si–O bond determined from the silicate spinels is valid for tectosilicates then very little of the almost 900 kcal/mole discrepancy in quartz can be attributed to covalency. We conclude that the lattice energy calculated as we have done it is not valid for oxides in fourfold coordination which are as covalent as quartz.

Table 3 lists the differences between calculated and measured enthalpies of formation for several of the compounds. There are five cases in which a particular coordination is represented by more than one compound: Al–O₆, Ti–O₆, Fe²⁺–O₆, Fe³⁺–O₆, and Si–O₆. For both corundum and spinel (MgAl₂O₄) the apparent enthalpy of covalency is about 50 kcal/mole; for three silicate spinels it is about 160 kcal/mole and for rutile and two titanates it is about 235 kcal/mole. The second case shows that for different compounds in the same structure the same ion pairs have nearly identical enthalpies of covalency. The other cases show that this holds even for different structures if the coordination is the same. However, comparison of stishovite and the silicate spinels shows that this is now true if there is a coordination change. Therefore the following list of enthalpies of covalency can be inferred for future use: Al–O₆ = 25 ± 5 kcal/mole; Ti–O₆ = 217 ± 10 kcal/mole (CaTiO₃ omitted because of an unreliable bulk modulus); Si–O₆ = 154 ± 9 kcal/mole; Si–O₆ = 105 kcal/mole.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Enthalpy of formation (kcal/mole) observed calculated</th>
<th>Apparent enthalpy of covalency (kcal/mole)</th>
<th>Predominant covalent bond</th>
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</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>corundum</td>
<td>-399</td>
<td>-344</td>
<td>Al–O₆</td>
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<tr>
<td>Al₂MgO₄</td>
<td>spinel</td>
<td>-553</td>
<td>-507</td>
<td>Al–O₆</td>
</tr>
<tr>
<td>Mg₂SiO₄</td>
<td>spinel</td>
<td>-512</td>
<td>-349</td>
<td>Al–O₆, Mg–O₆</td>
</tr>
<tr>
<td>Ni₂SiO₄</td>
<td>spinel</td>
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<td>-176</td>
<td>Al–O₆, Ni–O₆</td>
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<td>spinel</td>
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<td>-204</td>
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<tr>
<td>SiO₂</td>
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<td>-206</td>
<td>-101</td>
<td>Si–O₆</td>
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<tr>
<td>Fe₂O₃</td>
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<td>Fe³⁺–O₆</td>
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<td>-267</td>
<td>-108</td>
<td>Fe³⁺–O₆, Mg–O₆</td>
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</tbody>
</table>

* See text.
FeO
\textsuperscript{2+} \cdot O\textsubscript{2-} \approx 80 \text{ kcal/mole} \text{ (see further discussion below for FeO}_3\text{).}
FeO
\textsuperscript{2+} \cdot O\textsubscript{2-} \approx 88 \pm 5 \text{ kcal/mole}
FeO
\textsuperscript{2+} \cdot O\textsubscript{2-} \approx 110 \text{ kcal/mole}

(The quoted uncertainties represent the total spread between values calculated for different compounds.)

The relative cova lency of stishovite and the silicate spinels is as one would expect. In stishovite each Si\textsuperscript{4+} is bonded to six O\textsuperscript{2-} ions at a distance of \(\approx 1.77\ \text{Å}\), whereas in the spinels each Si is bonded to only four O\textsuperscript{2-} at \(\approx 1.62\ \text{Å}\). The lower coordination will favor covalent bonding more than the higher. Similarly shorter bonds may also favor cova lency. This relation between cova lency and coordination also holds for the two iron ions, Fe\textsuperscript{2+} and Fe\textsuperscript{3+}.

The energies for hematite indicate a rather large cova lency contribution of about 150 kcal/mole. How ever, a closer examination of the isostructural Al\textsubscript{2}O\textsubscript{3} indicates that such an estimate is much too high. The multipole term in general is due primarily to dipole effects with a smaller effect due to quadrupoles. However, in Al\textsubscript{2}O\textsubscript{3} the dipole terms are negligible and the quadrupole terms dominate (Hafner and Raymond (1968)). This is not required by the general corundum lattice but only by the specific one for Al\textsubscript{2}O\textsubscript{3}. We should expect therefore that for Fe\textsubscript{2}O\textsubscript{3} as for most oxides the dipole terms would be larger than the 25 kcal/mole in Al\textsubscript{2}O\textsubscript{3}. This will decrease the cova lency contribution (probably to less than 100 kcal/mole).

For the compounds whose heat of formation and structure is unknown we can use the arguments given at the beginning of this section to evaluate the correctness of the proposed structure. If our calculated heat of formation is much less than that of a stable phase we conclude that the structure is not correct in some respect.

Ahrens et al. (1969) have proposed several possible shock-induced high-pressure structures for Mg\textsubscript{2}SiO\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3}. The high-pressure equation of state as well as zero-pressure pressure-density of Mg\textsubscript{2}SiO\textsubscript{4} (\(\approx 4.25\ \text{g/cm}^3\)) is poorly known. This severely limits the accuracy of our calculation.

For Mg\textsubscript{2}SiO\textsubscript{4} the high-pressure phase proposed for the shocked state was either a perovskite structure or an ilmenite structure. The latter was favored because it gives a density which is closer to that inferred from the shock data. Our calculation for Mg\textsubscript{2}SiO\textsubscript{4} (perovskite) for a density of 4.25 g/cm\(^3\) gives a heat of formation about 100 kcal/mole less than that of the natural phase, enstatite. In addition, Si\textsuperscript{4+} in six-fold coordination with oxygen should contribute about \(- 150\ \text{kcal/mole}\) to heat of formation (cf. stishovite) making Mg\textsubscript{2}SiO\textsubscript{4} (perovskite) much more stable than Mg\textsubscript{2}SiO\textsubscript{4} (enstatite). We know that this can not be true, so we conclude that either this proposed structure or the density is incorrect. A density of 4.07 g/cm\(^3\) gives a heat of formation about 20 kcal/mole less than that of enstatite even after including the cova lency effects (see fig. 2). A density of 3.95 g/cm\(^3\) gives an enthalpy of formation which would be consistent with the perovskite structure. The reported shock data for enstatite (McQueen and Marrin (1966)) are not sufficiently de finite to exclude this value. Unfortunately no Made lump constant is available for ilmenite so we can not check that structure.

Ahrens et al. (1969) also proposed that Fe\textsubscript{2}O\textsubscript{3} which has the corundum structure at low pressure, goes into a perovskite structure at high pressures. We have in vestigated two cases: the first in which the iron remains trivalent (forming a 3–2 perovskite) and the second in which an electron is transferred from one iron ion to the other yielding one divalent and one tetravalent ion for each pair of Fe\textsuperscript{2+} (forming a 2–4 perovskite (Reid and Wingwood, 1969)). The latter case leads to some major difficulties which will be discussed after considering the first, simpler case.

Fig. 2. Relation between calculated (top) enthalpy of formation and density for Mg\textsubscript{2}SiO\textsubscript{4} (perovskite). Arrow indicates minimum permissible value for this high pressure phase. Perovskites 1a and 1b are not stable.
For the 3-3 perovskite we calculate a heat of forma-
tion of \(-307\) kcal/mole or 110 kcal/mole less than that of
hematite. This energy is probably even lower when we
allow for the covalence of the octahedrally coordinated
Fe\(^{3+}\) and for multipole terms. We therefore conclude
that a 3-3 perovskite is not a reasonable high-pressure
phase of hematite.

Evaluation of the heat of formation of Fe\(_2\)O\(_3\) as a
3-4 perovskite presents some problems. The heat of
formation of Fe\(^{3+}\) is given by Allen in *Astrophysical
Quantities* (1963), but the precision is poor and may be
as uncertain as \(-200\) kcal/mole. The effect of crystal
fields on the heat of formation is also difficult to deter-
mine. There are no measured values for this quantity.
We have estimated it as follows: Fe\(^{3+}\) has four 3d
electrons and is isoelectronic with Mn\(^{3+}\) and Cr\(^{3+}\).
The crystal field splitting of the energy levels in Mn\(^{3+}\)
is about 6000 cm\(^{-1}\) greater than in Cr\(^{3+}\). Other pairs
of isoelectronic ions (V\(^{3+}\), Ti\(^{3+}\), Cr\(^{2+}\), V\(^{2+}\), Fe\(^{2+}\),
Mn\(^{2+}\), Co\(^{2+}\), Fe\(^{2+}\)) behave similarly with the higher
charge ion having a splitting of about 6000 cm\(^{-1}\) more
than the lower charged ion. We therefore assume that
the splitting for Fe\(^{3+}\) is about 6000 cm\(^{-1}\) greater than for
Mn\(^{3+}\). This leads to a crystal field energy of about
\(-46\) kcal/mole if the electrons are not paired in the 3d
orbitals or about \(-139\) kcal/mole if they are paired. It
seems probable that the splitting of the energy levels is
sufficient to induce such pairing. If such pairing does not
occur we must be cautious because Jahn-Teller
distortion can be very large in 3d ions and this will
destabilize them. We have therefore considered only
the spin-paired case because it is both probable and
more tractable. In this case the enthalpy of formation is
calculated to be \(-181\) kcal/mole, only 16 kcal/mole
above that of hematite.

Contributions due to covalency are probably quite
small for this structure. Fe\(^{3+}\) has only four valence
electrons for six bonds so it should be nearly ionic.
For Fe\(^{3+}\) in twelve coordination bonding will likewise
be nearly ionic. (The long bond lengths (\(\geq 2.5\) A) ac-
companying this high coordination will make crystal
field effects on Fe\(^{3+}\) negligible.) It seems therefore
subject to our estimations about the energetics of
Fe\(^{3+}\), that the heat of formation of Fe\(^{3+}\)-Fe\(^{3+}\) O\(_2\) (per
ovskite) is slightly larger than that of hematite and
that it therefore is an admissible high-pressure struc-
ture.

5. Conclusions

The above calculations lead to the following con-
clusions:

1. In most cases lattice energy calculations suitably
corrected for permanent multipole energies will give a
good estimate of the covalency of a compound.

2. This is not true for oxides with very high com-
pressibility such as quartz.

3. For nearly ionic bonds the energy due to coval-
ency of a particular bond is nearly constant in minerals
with the same coordination (e.g. Fe\(_3\)SiO\(_4\)-Mg\(_2\)SiO\(_4\);
Al\(_2\)O\(_3\)-Al\(_2\)MgO\(_4\)).

4. Covalency in a particular bond appears to de-
crease as coordination increases (e.g. Mg\(_2\)SiO\(_4\) (spinel)-
SiO\(_2\) (cristobalite)).

5. If enstatite converts to the perovskite structure at
high pressure, it should have an equivalent zero-pres-
sure density of \(\neq 3.8\) g/cm\(^3\).

6. Hematite does not form a perovskite at high pres-
sures unless the Fe\(^{4+}\) disproportionates into Fe\(^{3+}\)
and Fe\(^{2+}\). If the d electrons in the latter would be spin
paired under the conditions of its formation, then a
2-4 perovskite structure appears compatible with the
properties of the high pressure phase inferred from the
shock data.

Although it is not possible to calculate a theoretical
enthalpy of formation with sufficient accuracy to pre-
dict solid-solid transition pressures, this type of calcula-
tion permits bounds to be placed on the density and
bulk modulus of proposed high-pressure structures.

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