For the 3–3 perovskite we calculate a heat of formation 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_2O_3 as a 2–4 perovskite presents some problems. The heat of formation of Fe^{4+} 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 determine. There are no measured values for this quantity. We have estimated it as follows: Fe^{4+} has four 3d electrons and is isoelectronic with Mn^{3+} and Cr^{2+}. The crystal field splitting of the energy levels in Mn^{3+} is about 6000 cm^{-1} greater than in Cr^{2+}. Other pairs of isoelectronic ions (V^{4+}–Ti^{3+}, Cr^{3+}–V^{2+}, Fe^{3+}–Mn^{2+}, Co^{3+}–Fe^{2+}) behave similarly with the higher charge ion having a splitting of ≈ 6000 cm^{-1} more than the lower charges ion. We therefore assume that the splitting for Fe^{4+} 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 $3d^4$ ions and this will destabilize them. We have therefore considered only the spin-paired case because it is both probable and more tractible. 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^{4+} has only four valence electrons for six bonds so it should be nearly ionic. For Fe^{2+} in twelve coordination bonding will likewise be nearly ionic. (The long bond lengths (≈ 2.5 Å) accompanying this high coordination will make crystal field effects on Fe^{2+} negligible.) It seems therefore subject to our estimations about the energetics of Fe^{4+}, that the heat of formation of $Fe^{2+}Fe^{4+}O_3$ (perovskite) is slightly larger than that of hematite and that it therefore is an admissible high-pressure structure.

5. Conclusions

The above calculations lead to the following conclusions:

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 compressibility such as quartz.

3. For nearly ionic bonds the energy due to covalency of a particular bond is nearly constant in minerals with the same coordination (e.g. Fe_2SiO_4–Mg_2SiO_4; Al_2O_3–Al_2MgO_4).

4. Covalency in a particular bond appears to decrease as coordination increases (e.g. Mg_2SiO_4 (spinel)–SiO_2 (stishovite)).

5. If enstatite converts to the perovskite structure at high pressure, it should have an equivalent zero-pressure density of ≈ 3.9 g/cm^3.

6. Hematite does not form a perovskite at high pressures unless the Fe^{3+} disproportionates into Fe^{2+} and Fe^{4+}. 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 predict solid–solid transition pressures, this type of calculation permits bounds to be placed on the density and bulk modulus of proposed high-pressure structures.

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