1968; *Wang*, 1967; *Ahrens et al.*, 1969]. In this study two approaches were followed: (1) the most probable garnet hpp structure was inferred from analog studies, and the density was defined by using crystal chemical systematics; and (2) recovery measurements were attempted, and the products were examined by using X ray techniques.

There are essentially two modes by which garnet may achieve a higher density state: (1) transformation of the basic ABO_3 compound into a single mineral component involving a structural modification or an increase of coordination of the A and/or B cations or both; or (2) a disproportionation reaction in which two or more high-pressure mineral components are the products. In the second case, analog studies present several possibilities. Breakdown of the $(Fe, Mg, Ca, Mn)_3Al_2Si_3O_{12}$ garnet into its component oxides is a primary consideration. The calculated density of the component oxides of the Salida garnet sample is 4.66 g/cm^3, which represents an 11.5% increase over the initial garnet density. The offset of the Hugoniot data in Figure 4 above the extrapolated garnet isentrope is approximately 5%, if small corrections for thermal pressure and the energy of transition are neglected. Therefore disproportionation into component oxides does not appear likely. A disproportionation reaction into $Al_2O_3 + 3(Fe, Mg, Ca, Mn)SiO_3$, where the latter reactant may occur in the pyroxene, ilmenite, or perovskite structures, is also a possibility. However, none of these combinations is compatible with the observed density increase. Moreover, with regard to such disproportionation reactions *Ahrens et al.* [1969] have pointed out that the type of transformation that actually occurs under shock conditions will be determined by both thermodynamic and kinetic factors. In the submicrosecond duration of the passage of a shock wave, kinetic factors will favor transformation into a single homogeneous phase if a suitable structure exists. For these reasons a disproportionation reaction has been abandoned in favor of transition into a single high-pressure mineral phase.

Precedents for the transformations of ABO_2 compounds, based on analog studies of germanates and related materials [e.g., *Ringwood*, 1970], have been discussed in the introduction. The most probable are the ilmenite and perov-skite structures. In addition, less likely possibilities are A and B rare earth structures. Again, when the approximate density increase of 5% indicated by the Hugoniot data is considered, the excessive density increases associated with a garnet–B rare earth (7–9%) or a garnet-perovskite (16–18%) transformation as estimated from analog studies [e.g., *Ringwood*, 1970; *Reid and Ringwood*, 1969] appear to preclude these transitions as explanations of the present data. Therefore the most probable transformation consistent with the garnet Hugoniot data involves a high-pressure phase in the ilmenite or corundum structures. For the almandine-garnet under consideration, because of the differences in the ionic radii of the primary Fe^{2+}, Al^{3+}, and Si^{4+} cations, an ordered relationship would be expected among the cations within an approximate hexagonal close-packed oxygen anion framework. However, because of the short duration of the shock transformation, long-range disorder would be more likely. Therefore the degree to which the structure actually produced under shock conditions is more 'ilmenitelike' or 'corundumlike' is not clear. Because the ilmenite structure is most probable under equilibrium conditions and is therefore to be associated with possible application to the mantle, we prefer an ilmenitelike structure as the most reasonable alternative.

As was previously discussed, the reduction methodology used in analyzing the garnet hpp Hugoniot data requires specification of the initial density. An estimate of the density of compounds of ABO_3 stoichiometry is provided by molar volume relationships. *Reid and Ringwood* [1969] have prepared graphs of average metal-oxygen (octahedral) bond length versus molar volume for a number of ABO_3 and M_2O_3 compounds in their appropriate structural forms. The relevant data for compounds in ilmenite and corundum structures have been plotted in Figure 6. These data have been fit by least squares to a quadratic equation, the locus of which also is indicated in Figure 6. The average octahedral cation-anion bond length for $(Fe_{0.79}, Mg_{0.14}, Ca_{0.04}, Mn_{0.03})_3Al_2Si_3O_{12}$ garnet hpp was estimated from the component simple oxides. The result, $M—O_{avg} = 1.946$ A, in conjunction with the quadratic fit to the corundum-ilmenite data, yields a value of 44.6 ± 0.8 A^3 for the volume per formula unit of garnet
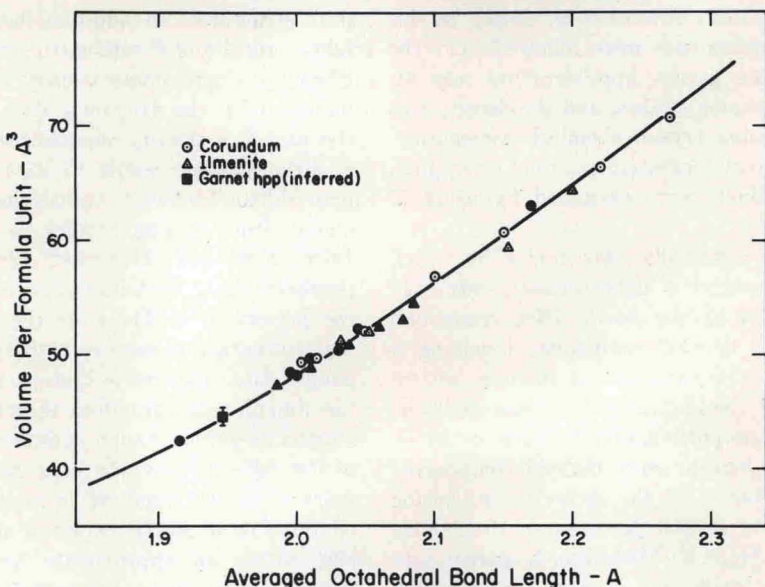
Fig. 6. Averaged octahedral bond lengths versus volume per formula unit for M_2O_3 and ABO_3 compounds having corundum and ilmenite structures [after *Reid and Ringwood*, 1969]. Solid symbols refer to bond lengths determined from atomic coordinates, and open symbols to bond lengths estimated from simple oxides. The inferred volume per formula unit for ilmenite-like garnet hpp also is indicated.

hpp. The gram formula weight of the sample is 120.62 grams. Therefore the calculated density of the garnet hpp phase is 4.48 ± 0.08 g/cm³. In addition, a similar relation involving the molar volume and the ionic radii of the individual A and B cations in ilmenite compounds was used by *Ahrens and Graham* [1972] to arrive at an estimated density of approximately 4.41 g/cm³.

To clarify and refine the density and the structure of the high-pressure phase, an attempt was made to recover shocked specimens of garnet hpp. Although some question has been raised about the relation of shock-induced phase changes to the recovered material [*Wang*, 1967], the recovery of shock-induced stishovite from quartz by J. D. Kleeman (personal communication, 1971) suggests the possible application of this technique to other materials. The method is explained in some detail by *Hörz and Ahrens* [1969] and *Gibbons and Ahrens* [1971]. Essentially, it involves embedding small disks of the sample (4.75 mm in diameter and 0.15 mm thick) within large stainless-steel 304 target holders, which, in turn, are impacted by

high-velocity flyer plates. The sample itself is encapsulated within a smaller stainless-steel 304 cylindrical container that releases intact from the target holder after the passage of the shock wave. The shocked specimen may then be removed from the steel container and examined by using X ray and optical methods. Peak pressure within the specimen may be determined by an impedance match solution based on the flyer plate velocity and the release adiabat characteristics of both the target holder and the flyer plate materials [e.g., *Gibbons and Ahrens*, 1971]. For the garnet work, tungsten flyer plates were launched at the target in 20-mm Lexan projectiles fired from a smooth-bore solid propellant gun.

The recovered samples of garnet, shocked to approximately 400–500 kb, were examined optically and by standard Debye-Scherrer X ray powder diffraction methods using FeK_α radiation and a Mn filter. Optical examination of the recovered samples indicated no suggestion of mineral phases other than the original garnet. However, the individual grains showed many characteristics of intense deformation. Particu-