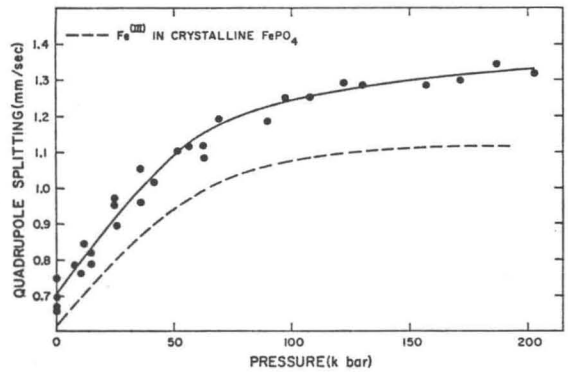

FIG. 27. Quadrupole splitting *versus* pressure—Fe^{III} in phosphate glass.

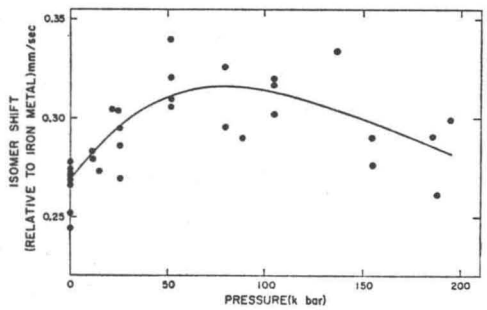

FIG. 28. Isomer shift *versus* pressure—Fe^{III} in silicate glass.

pressure region, a maximum at about 60 kb, and a decrease at higher pressures. The rather low initial value is consistent with a high degree of covalency. Apparently, in the low pressure region changes in orbital occupation dominate, while at high pressure the deformation of the wave functions controls and gives an increase in electron density at the nucleus with increasing pressure. The quadrupole splitting increases very rapidly with pressure, especially at lower pressures, indicating that substantial changes in site symmetry and/or electronic structure occur in the lower pressure region. No tendency for Fe^{III} to reduce to Fe^{II} was observed.

The ferrous ion, in a loose octahedral site, shows virtually no change in isomer shift with pressure. The quadrupole splitting behaves in an unusual manner as shown in Fig. 29; at low pressure there is a small but distinct drop, then a rise. Obviously there is a combination of site compression, change of symmetry, and electron redistribution at these sites. A run was also made with radioactive ^{57}Co introduced as cobaltous ion in silicate glass, and it, of course, does decay to ferrous ion. As can be seen in Fig. 29, the quadrupole splitting behaved

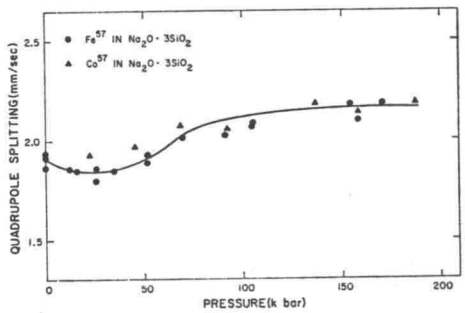

FIG. 29. Quadrupole splitting *versus* pressure—Fe^{II} in silicate glass.

identically to the ordinary ferrous ion, while the isomer shift parallels the behaviour of ordinary ferrous ion but at considerably higher electron density. The only apparent difference was that the cobalt formed a very dilute solution, while the iron was present in about 5% concentration.

In summary, it can be said that both Fe^{III} and Fe^{II} sites in phosphate glass behave very much like those in crystalline phosphates. In silicate glass the Fe^{III} sites exist in tetrahedral sites with considerable covalency and undergo significant change in orbital occupation in the low pressure region. At the ferrous sites, which are of open octahedral symmetry, there is considerable distortion with increasing pressure.

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