FIG. 10. α versus X .

While the data do not permit one to fix the value either of α or of X , we can state that they should be related to each other as shown. For values of α less than about $-0.28 a_0^3 \text{ mm/sec}$ (that is greater in magnitude than this number), X is positive which corresponds to transfer of electrons from the s to the d part of the conduction band with increasing pressure. Alternatively, the values for α suggested by Siminek and Sroubec (1967) or by Gol'danski (1963) or Danon (1966) would correspond to relatively large d to s transfer. Stern (1955) has found that as the volume decreases the d band lowers in energy with respect to the s band, making an s to d transfer energetically favourable. Unless one establishes a serious error in Stern's calculation, this is strong evidence in favour of a smaller, that is a more negative, value of α .

In Fig. 10 are also plotted values of α versus X for vanadium, copper, and titanium. Vanadium has the b.c.c. structure while the other two are close packed (b.c.c. and h.c.p. respectively). These are typical of the results for the classes of systems. In general, the close-packed systems exhibit a stronger tendency for s to d transfer than do the b.c.c. metals. This illustrates the basic difference in the effect of pressure on the band structure of these two classes of metals.

2. Ionic Compounds

Figure 11 shows isomer shifts as a function of pressure for a series of typical high spin ferrous and ferric compounds. Insofar as the classification is meaningful, these would be classified as "ionic", and from the figure several facts are apparent. All compounds show a measurable

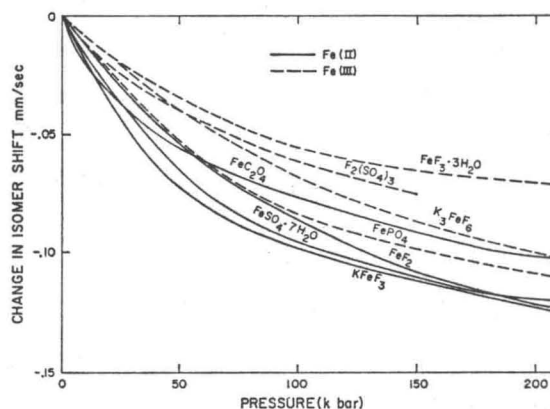


FIG. 11. Isomer shift versus pressure—high spin ferrous and ferric compounds.

increase in electron density at the iron nucleus with increasing pressure. On the average, the ferrous compounds show a measurably larger effect than do the ferric which is almost certainly not due to any consistent difference in compressibility. The effect in the ferrous ion is some 10–12% of the difference between normal ferrous and ferric ions in 150 kb, which represents a significant change in electronic configuration in this range.

In both cases these compounds and other relatively ionic materials such as FeCl_3 and FeBr_3 group into two quite narrow ranges. If the change with pressure were due primarily to electron transfer between ligand and metal, one would expect a much larger variation from ligand to ligand than is observed. It therefore seems reasonable to attribute the pressure effect to deformation of the metal ion wave functions. Simanek and Sroubec (1967) attribute the change with pressure for the ferrous ion entirely to compression of the " s " electrons, increasing the nuclear overlap. Champion *et al.* (1967) attribute the change for both ferrous and ferric ions to reduced shielding of the $3s$ electrons due to the spreading of the $3d$ orbitals discussed earlier. The ferric ions show a smaller change because there are only five $3d$ electrons in this case.

It seems most probable that neither of these factors is negligible. At present there is no apparent way to establish with certainty which is more important. The Simanek and Sroubec approach used as the sole