HIGH PRESSURE MÖSSBAUER STUDIES

electron density at the nucleus, but the rate of increase decreases markedly at high pressure. As Moyzis has shown, $\Delta \epsilon$ is not linear in either pressure or volume. The experimental results can be expressed in the form :

$$\Delta \epsilon = -8.1 \times 10^{-4}P + 1.65 \times 10^{-6}P^2 \tag{5a}$$

$$= 1.38 \frac{\Delta V}{V} + 2.7 \left(\frac{\Delta V}{V}\right)^2 (\text{mm/sec})$$
(5b)

where P is in kb.

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At about 130 kb there is a first-order phase transition in iron from the b.c.c. to the h.c.p. structure, with a large decrease in isomer shift of the order of -0.24 mm/sec. The isomer shift in the high pressure h.c.p. phase decreases relatively slowly with increasing pressure or density, which, as shall be seen, is characteristic of close-packed metals.

Figures 7-9 show the isomer shift for iron as a dilute solute in a series of transition metals, plotted versus $\Delta V/V$ for the host. The solid line



FIG. 7. Isomer shift versus $\Delta V/V$ —b.c.c. metals.

represents the low pressure slope for b.c.c. iron. In Fig. 7 are shown the b.c.c. metals and in Figs 8 and 9 close-packed systems. These results are from the work of Pipkorn *et al.* (1964), Edge *et al.* (1965), Drickamer *et al.* (1965), and Moyzis and Drickamer (1968b). The feature which is immediately apparent is that the change of isomer shift with compression is much greater in the former than in the latter.

Ingalls (1967) has presented an analysis of the isomer shift of iron which can also be applied qualitatively to the dilute alloys (Ingalls et al., 1967; Moyzis and Drickamer, 1968a, 1968b).





FIG. 8. Isomer shift versus $\Delta V/V$ —f.c.c. metals.

In iron the 4s electrons exist in a relatively broad band, such that they can be characterized as "nearly free". This overlaps the much narrower 3d band. The other transition metals have a qualitatively similar structure, but within each group, b.c.c., f.c.c. and h.c.p., the similarities are much stronger than they are between groups.



FIG. 9. Isomer shift versus $\Delta V/V$ —h.c.p. metals.

In the first order, one can divide the effects of changing pressure (or volume) into two parts: the effect of compression of the 4s band $d(\Delta\epsilon)_L$, and the effect of transfer of electrons into or out of s-like states in the s-d conduction band $d(\Delta\epsilon)_B$. From the calculations of Walker et al. (1961) one can estimate the first effect:

$$\frac{d (\Delta \epsilon)_L}{d \ln V} = 1.4 \text{ mm/sec.}$$
(6)

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