

and FeSb to which it is difficult to assign a definite valence. As one might expect, this rather amorphous group of compounds has a large range of isomer shifts.

Ingalls (1967) found a linear correlation between the maximum of the square of the radial portion of the $3d$ wave function and the $3s$ electron density at the nucleus using Hartree-Fock free ion wave functions. A variational calculation, the purpose of which was to establish the effect of change of the shape of the $3d$ orbitals in going from the free ion to the metal on the $3s$ density at the nucleus, indicates that the correlation is still good for the bond wave functions, even though some of these have large electron densities in the tail of the wave function.

Thus, in trying to interpret isomer shift data in terms of covalency, it is necessary to remember that the isomer shift may not be sensitive to electron density located between the metal ion and the ligand, which is a usual criterion for covalency, but primarily to the change of $3d$ density on the ion.

As was indicated earlier in the paper, the measured difference in isomer shift between source and absorber involves a constant α . There has been a considerable controversy about the value of α , and thus of $\Delta R/R$, although it is agreed that α is negative, that is that the radius of the nucleus in the excited state is less than that in the ground state. Walker *et al.* (1961) assigned the difference in isomer shift between ferrous and ferric ion entirely to the difference in shielding of the $3s$ electrons due to the presence of one more $3d$ electron (that is they assumed configurations $3d^6 4s^0$ and $3d^5 4s^0$). Using Watson's (1959) free ion wave functions they obtained the value

$$\alpha = -0.47 a_0^3 \text{ mm/sec} \quad (4)$$

where a_0 is the Bohr radius.

Simanek and Stroubec (1967) however assign the difference in isomer shift between ferrous and ferric ion entirely to a difference in occupation of the $4s$ level, that is they assume that the ferrous ion, at least in compounds like the fluoride, is completely ionic, while the ferric ion has the configuration $3d^5 4s^{0.2}$. They consider overlap distortion as the only significant factor in changing $\Delta\epsilon$ with pressure, and, using published data on the oxide and fluoride, obtain a considerably smaller value of about -0.12 for α .

Gol'danski (1963) and Danon (1966) also estimate a relatively small value for α . The value of α must be considered in discussing the effect of pressure on the isomer shift in metallic iron, and in iron as a dilute solute in transition metals.

II. PRESSURE EFFECTS

A. ISOMER SHIFT

The factors which affect the electron density at the nucleus as a function of pressure (interatomic distance) are of two types: (a) deformation of the wave functions, and (b) transfer of electrons between orbitals. This can take the form of transfer of electrons between, say, the $3d$ and $4s$ orbitals of an iron atom or ion, or transfer of electrons between the $3d$ and $4s$ parts of the conduction band of a metal, or of transfer of electrons between metal and ligand orbitals, either bonding or non-bonding. The process by which the electron density changes with interatomic distance is a complex one, so that any description given here is, at best, an approximation and must be regarded as tentative. We shall first discuss metals and alloys for which at least a reasonably quantitative theory has been developed, and then discuss the significant factors governing the behaviour of compounds.

1. Iron and Alloys

The isomer shift of ^{57}Fe in b.c.c. iron has been investigated by a number of people including Pound *et al.* (1961), Nicol and Jura (1963), Pipkorn *et al.* (1964), and Moyzis and Drickamer (1968a). Figure 6 is a composite of results, largely from the last two papers. The isomer shift decreases with increasing pressure, corresponding to an increase of

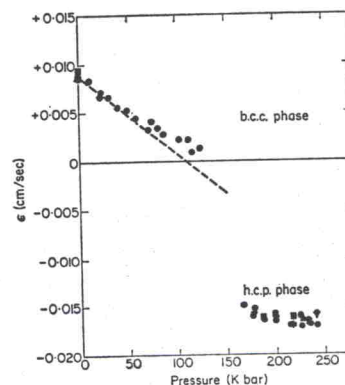


FIG. 6. Isomer shift of metallic iron versus pressure.