

of the metal energy levels vis-à-vis the ligand is apparently due primarily to the spreading of the $3d$ orbitals mentioned above. It can be shown (Vaughan, 1968) that it is possible in principle to reduce this difference by several electron volts using this mechanism. A second factor which tends to stabilize the t_{2g} orbitals is an increase in π bonding of these orbitals with excited ligand orbitals. Since the π bonding is usually considerably smaller than the σ bonding at one atmosphere, it could be expected to increase relatively more. Lewis and Drickamer (1968a) have shown that this is probably a significant factor, but not the controlling one. All of these observations will be important in the interpretation of various aspects of high pressure Mössbauer spectra for iron in ionic and covalent compounds.

To understand the Mössbauer spectrum of iron metal and of iron as a dilute solute in transition metals, a knowledge of the band structure of these materials is important. A review of even simple band structure is beyond the scope of this article, and the transition metals are far from simple, as the relevant electrons are neither completely bound nor almost free. There is, however, evidence (Slater, 1965) that all of the b.c.c. transition metals have very similar band structure, while the close packed members of the series (especially the f.c.c. metals) are very much like each other, but significantly different from the b.c.c. metals. In both cases the conduction band has a mixture of $3d$ and $4s$ character, with different emphasis in different parts of reciprocal lattice space. The relative degree of s and d character may change with pressure. We shall here assume that Stern's (1955) calculations for iron are qualitatively correct.

In the study of magnetism in transition metals, the controversy as to whether the magnetic electrons are primarily tightly bound or itinerant is a long and complex one, with outstanding proponents on each side. High pressure Mössbauer studies have so far contributed in only a minor way to the solution of this problem.

Figure 5 shows the range of isomer shifts for ^{57}Fe in different environments, relative to metallic b.c.c. iron. According to the convention used, the larger the isomer shift, the lower the electron density at the nucleus. Several facts are immediately evident.

(1) Iron as a dilute solute in a series of transition metals shows a relatively narrow range of isomer shifts although the solvent atoms have from 1–9 d electrons in their outer d shell—this would indicate that $3d$ electrons of the iron are not completely integrated into the solvent d band, although, as shall be seen later, they are closely associated with it.

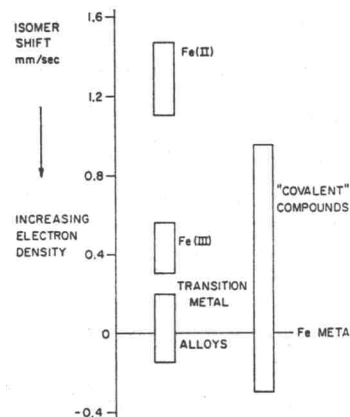


FIG. 5. Isomer shift ranges for iron and compounds.

(2) Ferrous ions typically exhibit a very low electron density. Since their outer configuration is nominally $3d^64s^0$, this can be attributed to the shielding of the $3s$ electrons by the $3d$.

(3) Ferric ions exhibit a significantly higher electron density than do ferrous ions. In both cases typical compounds fall in a range of electron densities, but the two ranges do not come close to overlapping. The ranges shown cover almost all the high spin compounds from the essentially completely ionic such as the fluorides to those with large covalent components such as the acetylacetonate, as long as they can be classified as ferrous or ferric. There is evidence that ferric compounds are generally more covalent than ferrous, and this would indicate some back donation from the ligands to the metal, so that the traditional $3d^54s^0$ ferric configuration is an oversimplification. In view of the narrow range of isomer shifts exhibited by the ferric compounds, however, the viewpoint taken here is that the major difference between the observed ferrous and ferric electron densities (~ 0.9 mm/sec) is due to the reduced shielding of the $3s$ electrons in the latter case.

(4) While the classification "covalent" is ambiguous in that all compounds exhibit some covalency, there are a number of compounds which involve a very high degree of electron sharing. Such compounds as ferrocene and potassium ferro- and ferricyanide fit this description. In addition there are compounds like FeSe_2 , FeTe_2 , FeP , FeP_2 , FeAs