R. Pauthenet : Nous pensons maintenant que ces résultats expérimentaux peuvent recevoir une meilleure interprétation dans le cadre de la théorie de M. Néel sur les propriétés magnétiques des grains fins antiferromagnétiques: Sauf pour les alliages concentrés ou mal trempés, la formation de grains superparamagnétiques est ici très réduite.

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The Isomer Shift in Fe^{57}

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The positions of the energy levels of a nucleus incorporated into an atom or an ion are influenced by the electrostatic monopole interaction of the nuclear charge and the surrounding electrons. The displacement of any level from its value for a bare nucleus will be proportional to the *s*-electron density at the nucleus and the constant of proportionality will depend upon the nuclear charge distributions. The energy of a γ-ray emitted between two levels with different charge distributions must then vary linearly with the prevailing *s*-electron density. In a Mössbauer experiment in which the emitter and absorber are different materials containing the same active nucleus, the difference in γ-ray energies will be observed as a shift of the center of the absorption line proportional to the difference of *s*-electron densities of the active nuclei in emitter and absorber.

For a uniform distribution of nuclear charge a nonrelativistic calculation which includes the distortion of the electron wave function inside the nuclear charge gives for the shift in γ-ray energy:

$$E_{\rm abs}-E_{\rm em}$$
$$=\frac{2\pi Ze^2}{5}[R_{\rm is}^2-R_{\rm gr}^2][\Psi(0)_{\rm abs}|^2-|\Psi(0)_{\rm em}|^2]$$

where Z is the nuclear charge, $R_{\rm is}$ and $R_{\rm gr}$ the radii of the isomeric and ground states and $|\Psi(0)_{\rm abs}|^2$ and $|\Psi(0)_{\rm em}|^2$ are the total *s*-electron densities at the nucleus for a point nucleus in the absorber and emitter. In practice relativistic corrections are included.

A series of experiments has been made on the Fe^{57} 14 keV γ-ray in which the emitting nuclei were in stainless steel and the absorbing nuclei in a variety of divalent and trivalent iron compounds, or in iron dissolved in various metals. The measured shifts in the Mössbauer absorption line furnish a measure of the *s*-electron density at the absorber nuclei relative to that at the nuclei in stainless steel.

The observed shifts may be classified in the following way: the divalent compounds have the largest shifts and the more ionic the compound the larger the shift; the trivalent compounds have the next largest shifts and are also arranged by ionicity; the metal solutions all have small shifts. It is to be noted that such a simple classification does not exist for similar data on tin (Kistner).

It must be concluded for the divalent and trivalent compounds that the *s*-electron density at the nucleus is primarily determined by the $3d$ configuration involved. The effect is one of shielding; the greater the number of $3d$'s the lower the *s*-density. The dispersion of the shifts for different compounds of the same valency is due to the addition of $4s$-electron density in covalent bonds and from an augmentation effect pointed out by Marshall and by Clogston. This is the change in effective number of $3d$'s arising from the mixing of $3d$ wave functions with ligand wave functions. For configurations whose electrons have all the same spin the number of $3d$'s is increased and the s-density should therefore decrease. The observed increase in s-density with increased covalency seems to imply that in iron the augmentation is less important than s-admixture.

An attempt has been made to give a tentative quantitative interpretation of the observed shifts. It is assumed that the shifts for the most ionic divalent and trivalent compounds can be identified with those for pure $3d^6$ and $3d^5$ configurations; further, the difference of these shifts is associated with the difference of the total s-electron density at the nucleus as obtained from R. E. Watson's Hartree-Fock calculations for the various configurations of Fe. This calibrates the shifts in terms of electron density and yields predicted shifts for other $3d$ configurations.

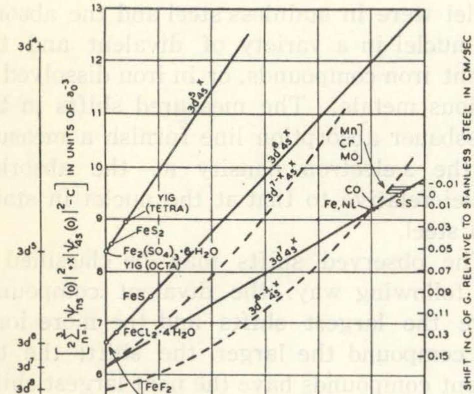

Fig. 1. Total s-electron density at the iron nucleus as a function of s-electron contribution for various configurations. The constant C has the value $-11{,}873\ a_0^{-3}$.

Ignoring the augmentation effect we need to know the effect of adding fractions of a $4s$-electron to the $3d$ configurations. This has been estimated by use of the Fermi-Segrè formula. This gives the density at the nucleus of an s-electron outside closed shells in terms of the observed term values of the s-electron. We use it outside incomplete $3d$ shells, but it seems unlikely that the errors are more than about 20%. By suitable interpolation we apply the formula also to configurations with fractional numbers of $3d$ electrons; together with Watson's data this procedure gives us total s-electron densities for configuration such as $3d^y\ 4s^x$.

Fig. 1 shows the result of such estimates. The total s-density at the nucleus is plotted vertically and the amount of added $4s$-electron is shown horizontally. A number of lines are shown giving s-densities for configurations with integral numbers of $3d$ electrons and integral total numbers of electrons. In the absence of augmentation the observed divalent and trivalent compounds have been assigned to the $3d^6\ 4s^x$ and $3d^5\ 4s^x$ curves.

Considering now the data on iron in various metals it is clear that the small spread in observed shifts is most naturally interpreted as indicating that iron in metallic solution assumes essentially the same electronic configuration independent of the solvent. From the fact that iron "in solution" in iron must have a total of eight electrons we may place it on the curve for $3d^{8-x}\ 4s^x$. The observed shift then implies that the prevalent configuration is very near to $3d^7\ 4s^1$. Despite the looseness of some of the calculations it is clear that this estimate is fairly reliable. Recent band calculations for iron by Wood appear to lead also to the prediction of about one s-electron below the Fermi level.

DISCUSSION

C. G. SHULL: May I comment that recent neutron diffraction studies have suggested a $4s$ electron spin polarization in iron with a magnetization contribution of $-0.2\mu_B$? This then leads to the configuration $3d^{7.6}4s^{0.4}$.

L. R. WALKER: It would be impossible, I think, to reconcile our interpretation of the isomer shift with the configuration $3d^{7.6}4s^{0.4}$.