

Walker L R, Wertheim G K & Jaccarino V. Interpretation of the Fe<sup>57</sup> isomer shift. *Phys. Rev. Lett.* 6:98-101, 1961.  
[Bell Telephone Laboratories, Murray Hill, NJ]

This paper presented a systematic study of the isomer shift of the Fe<sup>57</sup> Mössbauer line in various atomic environments and gave a quantitative theoretical analysis of this effect. It also estimated the radius of the excited nuclear state responsible for the gamma ray. [The SC<sup>1</sup>® indicates that this paper has been cited in over 525 publications since 1961.]

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"The Mössbauer effect, or resonant absorption of recoil free nuclear gamma rays, was discovered in 1958.<sup>1,2</sup> It was realized immediately that these gamma rays could provide the most 'sharply tuned' electromagnetic radiation available. In addition to such exciting possibilities as the measurement of the gravitational red shift, it appeared that there might be fruitful applications to solid-state physics. As in nuclear magnetic resonance, one might use the nucleus as a probe of the magnetic and electric environment. One of the first isotopes in which the Mössbauer effect was observed was Fe<sup>57</sup>. This has a very narrow natural line width and the nuclear magnetic hyperfine splitting was quickly observed and measured in metallic iron and a variety of iron compounds.

"At Bell Laboratories, while studying the hyperfine splitting and electric quadrupole effects in oriented single crystals of iron fluoride, we became interested in what we called the 'isomer shift,' which had recently been noted by Kistner and Sunyar.<sup>3</sup> What is observed is that the Mössbauer resonance is displaced if the emitter and absorber are

situated in different atomic environments. This effect has its origin in the fact that the charge radius of the excited state of Fe<sup>57</sup> which emits the gamma ray differs from that of the ground state. So if the nuclear charge density interacts with the surrounding electronic charge density, this interaction is different in excited and ground states. The gamma ray energy is evidently shifted by an amount proportional to the s-electron charge density at the nucleus. The isomer shift then measures the difference between the s-electron density in emitter and absorber.

"In iron the 3s and 4s electrons are the ones whose densities at the nucleus have significant variations. The 3s density is determined primarily by the shielding in the various 3d configurations. Here we were lucky to have available R.E. Watson's<sup>4</sup> recent Hartree-Fock calculations of iron wave functions for various configurations. We established a calibration for the Fe isomer shift by identifying two compounds as purely ionic, that is, pure 3d<sup>5</sup> and 3d<sup>6</sup>, using Watson's data combined with experiment. By use of the Fermi-Segre-Goudsmit formula and Charlotte Moore's tables,<sup>5</sup> we found a recipe to give the effect of 4s admixtures on the density at the nucleus. In this way, we were able to put together a map for relating isomer shift to chemical or ionic state.

"At the same time, the isomer shifts in the two pure ionic states tell us the difference in charge radii of the Fe<sup>57</sup> excited and ground states. It is fascinating that the excited state radius is smaller than that of the ground state. This is now understood since the excited state appears to be identifiable with the ground state in the shell-model.

"The considerable number of citations to this paper can be traced to two things. First, the paper was a pioneering effort, coordinating and clarifying a lot of rather new and unfamiliar material and seems to have been substantially correct. Second, the paper was of considerable interest to chemists, which meant that its potential readership was far greater than that of the normal physics paper. A recent discussion of the subject of isomer shifts may be found in *Mössbauer Isomer Shifts*.<sup>6</sup>

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2. .... Kernresonanzabsorption von Gammastrahlung in Ir.<sup>191</sup> *Naturwissenschaften* 45:538-9, 1958.
3. Kistner O C & Sunyar A W. Evidence for quadrupole interaction of Fe<sup>57m</sup>, and influence of chemical binding on nuclear gamma-ray energy. *Phys. Rev. Lett.* 4:412-15, 1960.
4. Watson R E. *Iron series Hartree-Fock calculations*. Cambridge, MA: Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, 15 June 1959. Technical Report No. 12. 258 p.
5. Moore C E. *Atomic energy levels as derived from the analyses of optical spectra*. Washington, DC: US Government Printing Office, 1952. Vol. II. NBS Circular 467.
6. Shenoy G K & Wagner F E, eds. *Mössbauer isomer shifts*. Amsterdam: North-Holland, 1978. 956 p.