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Phases and Stresses in Ferrous Metals by Mössbauer Spectroscopy†

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Abstract—Mössbauer spectroscopy is based on resonant absorption of gamma rays by nuclei. Of the several dozen isotopes for which the Mössbauer effect has been measured, iron is by far the easiest. A spectrometer consists of a gamma-ray source, the substance under study, a detector and electronics for sorting and storing the received pulses, and a Doppler shift mechanism for sweeping the energy of the gamma rays. An extra, resonant absorption occurs for discrete energies of the gamma rays. The major phases of iron yield distinct spectra: ferrite has six widely spaced lines, iron carbide has six lines less widely spaced, and austenite yields a single line. Corrosion products, too, can be identified. The effect of stress in the magnitudes normally encountered is subtle—the center of the pattern and the magnitude of the splitting change slightly. There is reason to believe that the experimental techniques are now becoming adequate to this measurement, and that surface stress can be determined to a precision of 10,000 psi in about 30 min.

1. Introduction

The Mössbauer effect is now 10 years old.(1) Conceived by nuclear physicists, and utilized brilliantly in sophisticated experiments involving relativity(2) and solid state theory,(3) the chemical and analytical consequences are now being widely appreciated. Useful applications are being, and have been, found in chemistry, biochemistry, metallurgy, and geology.

Superficially, a Mössbauer spectrometer bears little resemblance to an optical spectrometer. The major components consist of a radioactive source, selective detector of gamma rays, a Doppler scanning device, and pulse-handling electronics (Fig. 1). Radioactive processes are ordinarily insensitive to the state of chemical combination. The extraordinary purity of the Mössbauer gamma rays reveals something of the chemical environment of the nuclide under study, even though the actual "chemical effect" changes the nuclear energy levels by only a few parts in 10^{11}.

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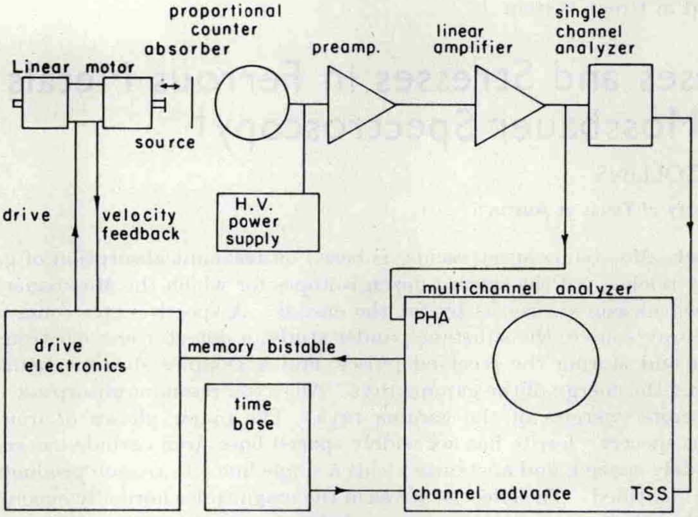

Figure 1. Block diagram of a Mössbauer spectrometer. The multichannel analyzer is operated in the PHA (pulse height analysis) mode for set-up of the single channel analyzer, then switched to TSS (time sequence scaling) for data aquisition.

Many of the heavier elements exhibit the Mössbauer effect.(4) Most of the chemical applications have involved ^{57}Fe and ^{119}Sn, as these combine ease of experiment with chemical interest. These are stable isotopes. Only the source is radioactive, in general. This paper will concentrate on ^{57}Fe, and metallurgical aspects in particular.

2. Theory

Mössbauer spectroscopy is based on the discovery of Rudolph Mössbauer that certain gamma rays emitted in the course of radioactive decay are extremely pure. Nuclei, like atoms or molecules, can often exist in energy states other than the ground state. Transitions between these states typically occur with emission or absorption of gamma rays with energies of 10–100 kev or more. An excited nuclear state will chemically resemble the ground nuclear state, since the atomic number is unchanged. The excited state differs in spin, size, and of course energy (Fig. 2).

The excitation of a ground state nucleus into an excited state occurs readily when stimulated by a gamma ray having the correct energy. Such gamma rays might be thought to occur upon the de-excitation of the excited state in another nucleus, which had been placed in this excited state by radioactive decay or by Coulomb excitation. This effect is well known in optical spectroscopy as resonance fluorescence. Before Mössbauer's discovery, knowledgable physicists were certain that nuclear resonance fluorescence could not take place. They knew that energy and momentum must be conserved. The gamma ray carries off a momentum $p = h\nu/c$, and the recoiling nucleus carries off this same momentum. The energy imparted to the recoiling nucleus is $E = p^2/2m$. Conservation of energy required that the energy of the nuclear transition be divided into two parts: most of the energy is carried away by the gamma ray, and the rest is carried away by the recoiling nucleus. Mössbauer showed, however, that for nuclei in solids, some of the gamma rays carry the full energy of the nuclear transition. In a solid, a nucleus

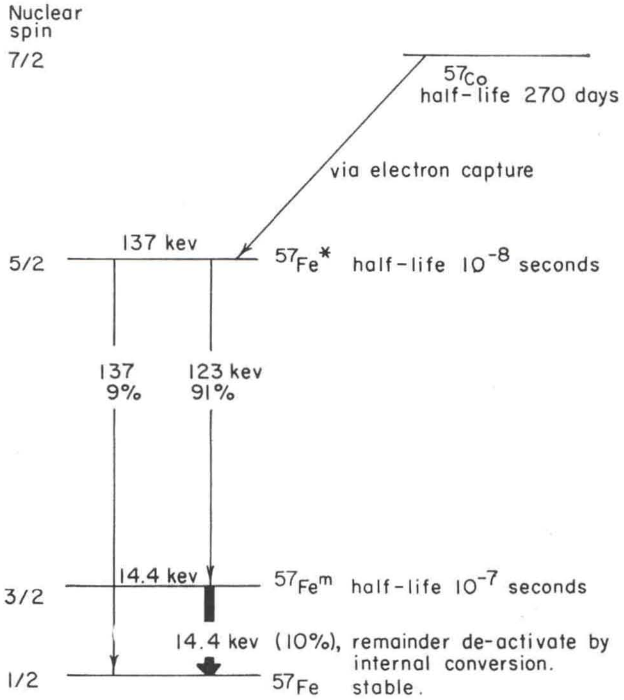

Figure 2. Decay scheme of ^{57}Co. The shaded transition includes the Mössbauer radiation.

is not free to recoil with arbitrary energy. Since the recoil energy is insufficient to break the chemical bonds which hold the nucleus, the question becomes one of creating, or not, a lattice phonon. Radiation of the nominal transition energy is hence composed of two components. One of these is slightly shifted and broadened by having created simultaneously a lattice phonon, and the other (recoilless, or Mössbauer, fraction) carried the full energy of the transition. The spread of energies of this Mössbauer radiation is limited only by the uncertainty principle, which means that the radiation from long-lived (metastable) nuclear levels can be sharp indeed. Mössbauer spectroscopy is concerned only with this recoilless fraction—the remainder represents unwanted background noise.

3. What can be learned?

A Mössbauer spectrum consists of the relative transmission of a sample as the energy of the Mössbauer gamma rays is varied. The variation of energy is not large. Doppler motion of the source up to a few centimeters per second ordinarily suffices to cover the region of interest. The relative energy shift is the ratio of the Doppler velocity to the velocity of light.

The Mössbauer spectrum may consist of one, two, or more lines. Probably the most striking effect on the spectrum is that caused by a large magnetic field.(5) In metallic iron, the magnetic field spontaneously present at the iron nucleus at room temperature is 330 kG. This splits the ground state ($I = \frac{1}{2}$) into two levels and the excited state ($I = \frac{3}{2}$) into four levels. Six of the eight possible transitions are allowed by the magnetic dipole selection rules, $\Delta m = \pm 1, 0$. The $3:2:1:1:2:3$ intensity ratio of the lines is a consequence of the change of sign of the gyromagnetic ratio in the ground and excited states, plus an application of the Clebsch–Gordan coefficients, taken over a random orientation of the magnetic field.

The spacing of these six lines measures the magnetic field (Fig. 3). Mössbauer spectroscopy has been used to follow the decreasing internal magnetic field as the temperature is increased toward the Curie temperature. Internal magnetic fields exist in a number of iron phases and compounds. These differ appreciably at room temperature for alpha iron (also known as ferrite), martensite, and

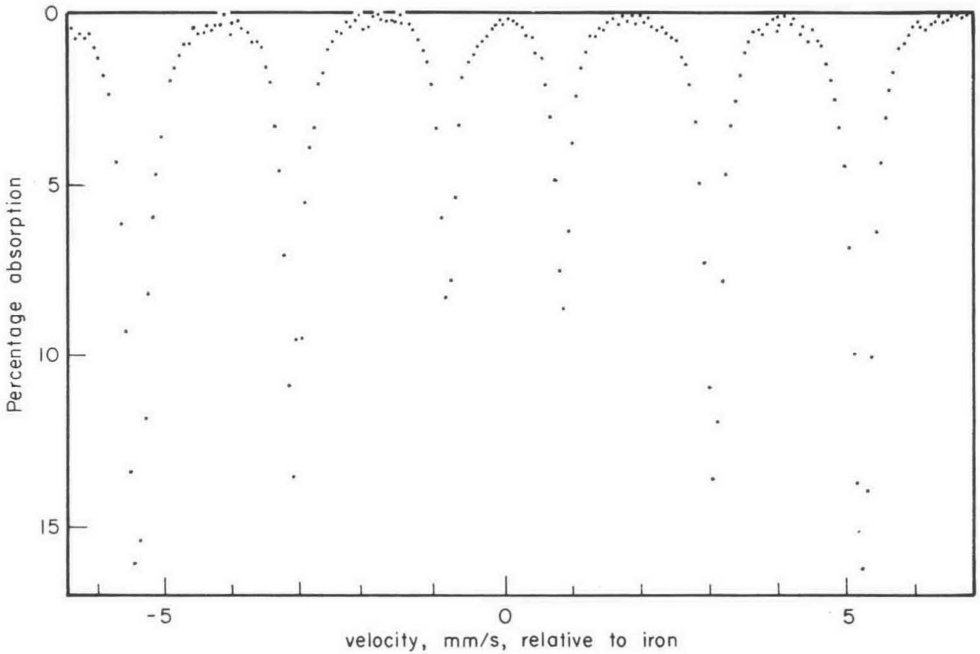

Figure 3. ^{57}Fe Mössbauer spectrum of 0.001″ shim steel at room temperature. The splitting of these lines arises from the internal magnetic field of 330 kilogauss.

iron carbide, and vanish for austenite. The technology of steels comprises an expanding field for the Mössbauer technique. A compound need not be ferromagnetic for the existence of large internal magnetic fields. Paramagnetic compounds below the Neél temperature become magnetically ordered. The local field at the nucleus may be quite large, although the net external field is essentially zero. Hematite (Fe_2O_3) is antiferromagnetic at room temperature. The internal magnetic field is 510 kG.(6) Magnetite (Fe_3O_4) has a spine structure, with ferrous and ferric iron atoms in octahedral and tetrahedral sites. The internal magnetic fields differ for these different kinds of iron, and the Mössbauer technique is being used for the study of such materials (Fig. 4).

Another readily measured parameter is the position of the center of the spectrum, relative to some fixed energy. This has been termed " isomer shift ", and arises in part from chemical differences of bonding. Specifically, the isomer shift measures the " s " electron density at the iron nucleus. This varies with valence state, as well as ligand configuration and strength. The isomer shift also depends on temperature in a very interesting way.(7,8) The energy of the gamma ray measured in the rest frame of the nucleus is a constant. A consequence of special relativity is that a moving clock appears to keep time more slowly than does a stationary clock. Atoms move faster as the temperature is raised. The Mössbauer radiation from a hot source is accordingly lower in energy when measured in the laboratory frame of reference, and it must have an additional Doppler velocity added to achieve a given resonance.

Most spectra of diamagnetic iron compounds consist of two lines. The splitting arises from the interaction between the quadrupole moment of the excited nuclear state and the asymmetric distribution of charge about the nucleus.(6) The ground state has no nuclear quadrupole moment. The electric field gradient tensor measures the deviation of the charge cloud about the nucleus from spherical symmetry. This distortion may be prolate (football shaped) or oblate (pancake-shaped), or may even lack axial symmetry. Two sources of the electric field gradient tensor may be present in a given structure. The ligand asymmetry, weighted according to ligand strength, is one factor. Non-spherical distributions of electrons, such as uncompensated 3*d* electrons, also contribute. Experience

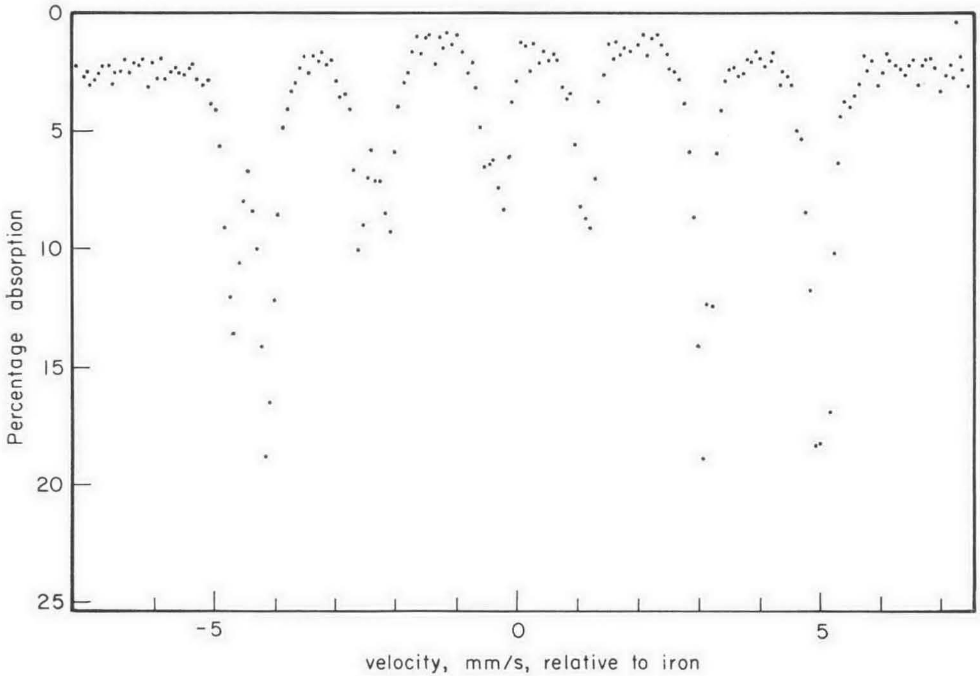

Figure 4. ^{57}Fe spectrum of synthetic magnetite, Fe_3O_4, at room temperature. Note the evidence for at least two different iron sites, with different magnetic fields and isomer shifts.

has shown that when ligands are adequately weak that the compound is " high-spin ", the ligands do not contribute importantly to the electric field gradient tensor. Very strong ligands, such as cyanide, overshadow the uncompensated 3*d* electron contribution.

The electric field gradient contains information concerning structure and bonding. The gradient of a vector is a tensor, which in this case has nine components:

$$\text{e.f.g.} = -\begin{pmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{pmatrix}$$

Only two independent components remain after rotation into the principal axes, plus the consideration that the trace vanishes. The axes are then re-named such that the absolute values of the diagonal elements decrease in the order, zz, yy, and xx. The parameters are then chosen as V_{zz} and η,(9) which ranges from zero for axial symmetry to a maximum value of one. The quadrupole splitting is proportional to $V_{zz}(1+\eta^2/3)^{1/2}$, so that a measurement of this splitting measures neither parameter. The only generally promising method for the extraction of both parameters is the magnetic perturbation method.(10) A large magnetic field is used to split the degeneracies remaining after quadrupole splitting. Even with a powder sample, characteristic distortions are produced and these enable the determination of the parameters of the electric field gradient tensor.(11)

The identification and measurement of corrosion products is quite practical. The usual lack of well-formed crystallites, which hinders X-ray evaluation, is less of a burden for Mössbauer analysis. There is an observable effect of stress on the Mössbauer spectrum, too. The stress change " s " electron density at the nucleus, and so shifts the spectrum. Compression shifts the spectrum to lower energy, -5.43×10^{-8} mm/s/psi.(12) A second and smaller effect is that the magnetic splitting varies with stress:

$$\frac{1}{H}\left(\frac{\partial H}{\partial P}\right)_T = -1.15 \times 10^{-8}/\text{psi}$$

These effects are small and require care to measure with any precision. The line width of the ^{57}Fe Mössbauer line is nominally

0.3 mm/s, and this amounts to a shift only 2% of a line width for 100,000 psi.

4. Instrumentation

The basic elements of a Mössbauer spectrometer are the source, velocity transducer, absorber (normally the substance under study), energy-selective gamma ray detector, and pulse-handling electronic apparatus. The Mössbauer spectrum consists of a plot of the energy-selected gamma ray counts received vs. Doppler velocity of the source relative to the absorber.

The radioactive source depends on the isotope under study. For iron studies, ^{57}Co is the source. The quantity of material in the source is typically so small that it can neither be seen nor weighed. It is diffused into another metal for handling ease, to provide a preferred chemical environment (e.g., to provide a single narrow line), and for enhancement of the Mössbauer fraction.

Most velocity transducers are now designed for constant-acceleration motion. This gives a linear velocity variation with time, which is equivalent to a linear frequency sweep. The displacement is then parabolic. Mechanical drives have been used, particularly where large masses must be moved. Extreme mechanical precision is essential to avoid velocity noise. The trend in drives has been toward electromagnetic units; the motion is caused by a current-carrying coil in a magnetic field. A desired velocity vs. time waveform is created electronically, and this voltage is compared continuously with the velocity feed-back signal. The difference signal is amplified and drives the motor in such a sense as to reduce the error. Advantages of the electromagnetic drive include flexibility of waveform, velocity range, freedom from precise machine work, and virtual freedom from wear.

The selective detector will be a proportional counter or possibly a photomultiplier coupled to a scintillation crystal. For optimum signal/noise in the Mössbauer spectrum, the gamma rays containing the Mössbauer fraction must be separated cleanly from the others present. In addition, a fast count rate capability is essential since the signal/noise ratio is proportional to the square root of the number of counts in any velocity interval. The detector emits pulses sized according to the energy contained in each detected gamma ray. After amplification and shaping, the desired height pulses are selected with a single-channel analyzer.

The counts are stored in a multichannel analyzer (MCA) of 400 or more channels. This MCA is best operated in the multiscaling mode, such that each channel gross-counts pulses for a selected time before switching the input to the next channel. The velocity of the transducer is slaved to this scan rate, such that each channel address corresponds uniquely to a definite velocity interval. The motion is of course cyclical, the sense of the acceleration being reversed periodically. The scan rate through the entire 400 or so channels is normally between 1 and 50 per sec. Exposure times range from an hour to several tens of hours, depending on the difficulty of the sample and the precision required.

Transmission geometry cannot be used for most metallurgical studies, since the sample can be only 0.001 in. thick. Mössbauer spectra have been obtained(13) in the back-scatter mode, in which the gamma rays strike the accessable surface of the sample and the consequences of resonant capture are detected from the same side. These consequences are (1) 6.5 keV Fe X-rays which arise from internal conversion of the excited ^{57}Fe nucleus, (2) Auger electrons also arising from internal conversion, and (3) 14 keV radiation re-emitted from the excited nuclei. The depth range of (1) and (3) is about 0.001 in., while in (2) the range is two orders of magnitude less. If the scattered 14 keV gammas are detected, care is needed that lead be excluded. Lead has a 14 keV X-ray which interferes, so that other shielding is required.

In the one-sided spectra shown here (Fig. 5), the 6.5 keV Fe X-rays were detected. The geometry is inherently poor. A wide solid angle is preferred for speed, but the " cosine broadening " effect can be troublesome. Consider gamma rays from source to detector in transmission geometry. Those passing along the central axis are doppler shifted by ν/c. Those emerging at an angle α relative to the velocity vector are shifted by $\nu \cos \alpha/c$. This " smears " the spectrum, whether it is taken in transmission or back-scatter, so long as a Doppler motion is used for the scanning mechanism.

A thermal drive is stable, but is limited in range. It is unaffected by the cosine broadening, and much better geometry is possible.

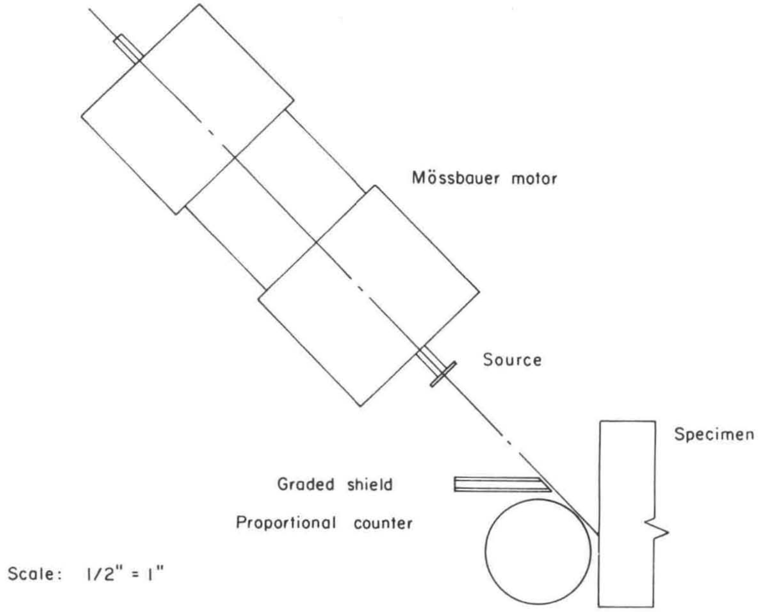

Figure 5. 45° geometry for front-surface Mössbauer spectroscopy.

5. Phases of Steels

Several spectra of steels are shown next, taken in back-scatter mode (Fig. 6–11). This results in spectra which point up, as in emission, rather than absorption. Note the effect of rust on the cast-iron sash weight. There are many different kinds of rust—this one is β-FeOOH.

6. Effect of Pressure

Pressure shifts the center of the Mössbauer spectrum to the left (lower energy). The amount of this shift is small for realizable stresses. At 100,000 psi, the shift is 2% of a line width. Such a small shift can be measured with scanning spectrometers, but with marginal accuracy. As we seek to determine stresses to 10,000 psi and less, a better experimental approach is required.

The count rate vs. stress is most sensitive when one sits on the

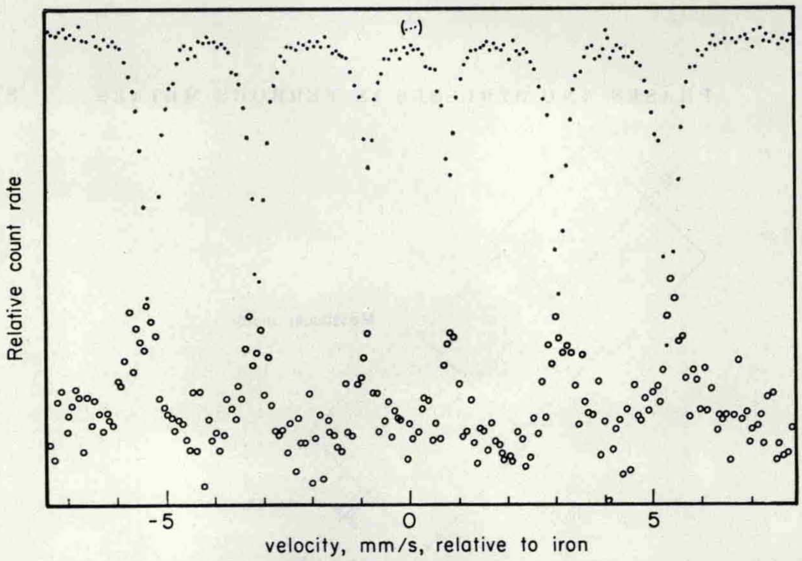

Figure 6. Relative speed of data acquisition, transmission vs. front-surface techniques. Upper: 0.0005″ iron in transmission. Lower: 0.5″ iron, front surface. Time: 53 minutes each.

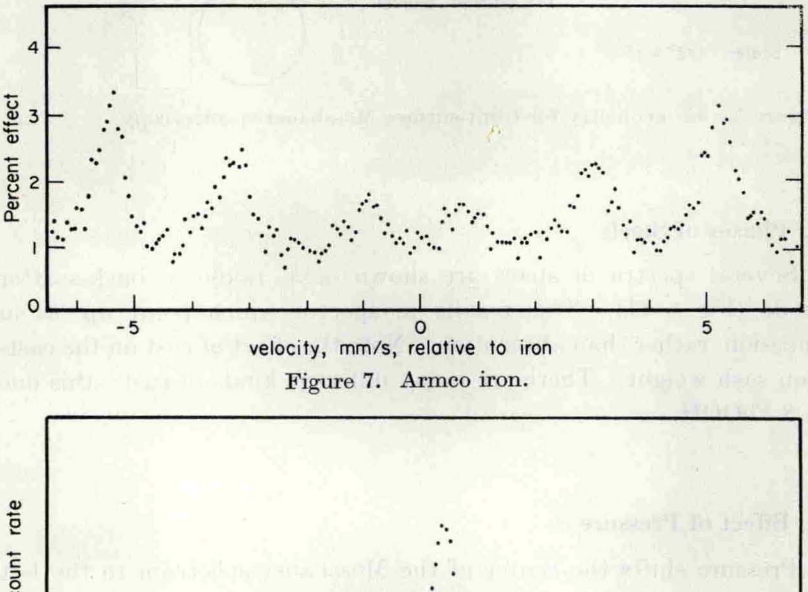

Figure 7. Armco iron.

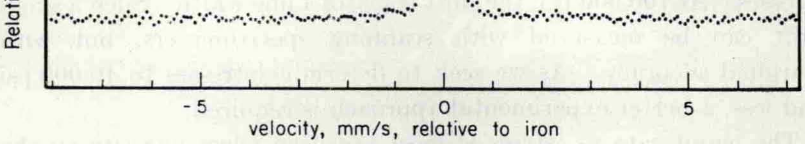

Figure 8. 304 stainless steel.

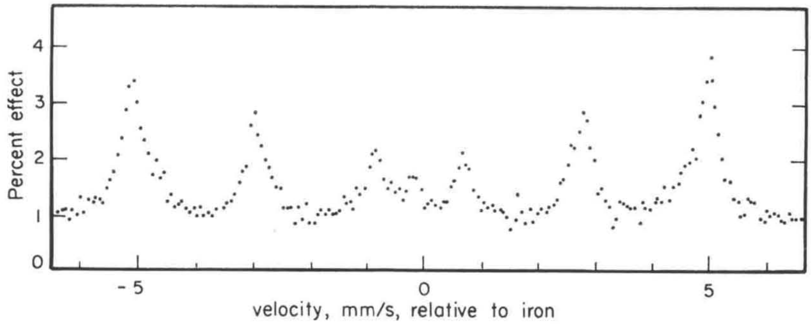

Figure 9. 4340 steel, austenitized at 1,550 °F., cleaned of surface scale with wet sandpaper.

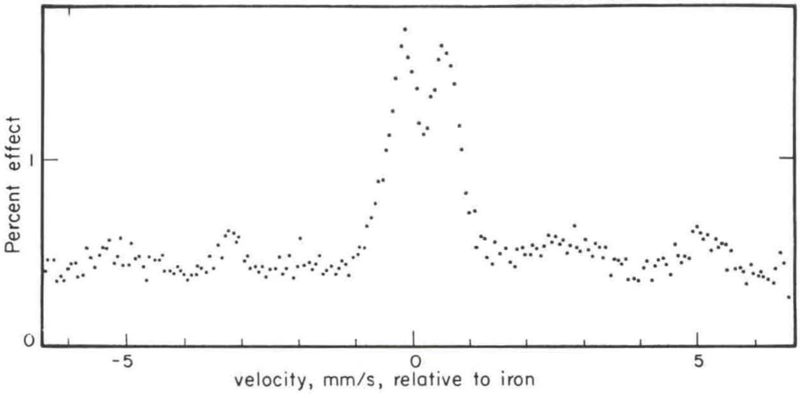

Figure 10. Rusty window-sash weight.

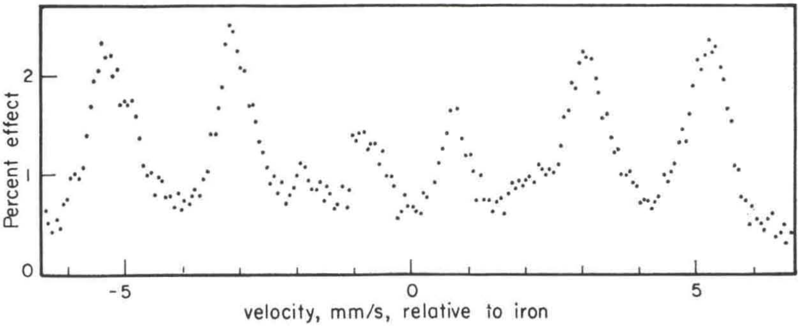

Figure 11. Window-sash weight, fresh-cut surface.

flanks of the resonance. Stress then increases one count rate and decreases the other, as is shown in Fig. 12.

7. Theory

A theoretical description is needed, in order that the changed count rates be converted into stress. Consider the use of transmission geometry and assume the Lorentzian line shape (Fig. 13).

The most sensitive spots, C and B, are those for which the slope is a maximum. This occurs at $x - \delta = \pm 0.5774(\Gamma/2)$. Literature compressibility data[2] indicate that, for ferrite,

$$\frac{1}{\nu}\left(\frac{\partial \nu}{\partial P}\right)_T = -2.6 \times 10^{-18}/\text{Kg/cm}^2$$

which leads to a shift for the center of the resonance of -0.00565 mm/sec for 100 K psi. We now define ϵ_T as:

$$\epsilon_T = \frac{N(T)_p - N(T)_0}{N(T)_0}$$

That is, ϵ_T is the relative change of count rate, at any point along the resonance as determined by the temperature of the source, due to the applied stress.

8. Experimental

Stress tests within the Mössbauer apparatus were conducted with 99.99% Fe foil, 0.0005 in. × 1.00 in., in uniaxial tension. A plot of $\epsilon_{100} - \epsilon_{-80}$ vs. tension is shown next. Each point represents one or more counting period of 2,000 sec (Fig. 14).

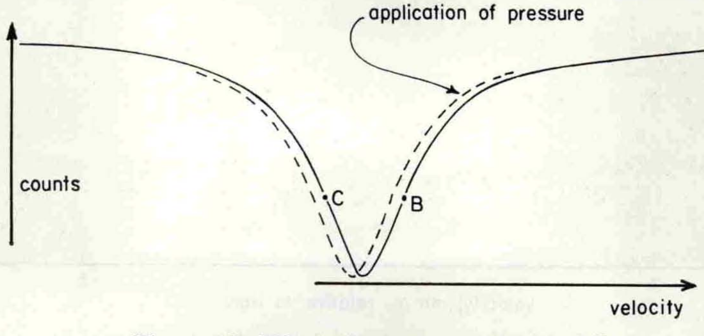

Figure 12. Effect of pressure on isomer shift.

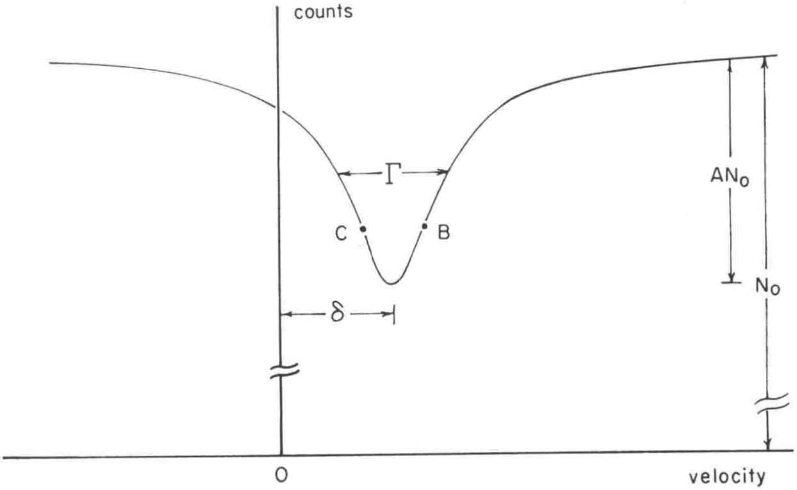

Figure 13. Analytical parameters to be considered.

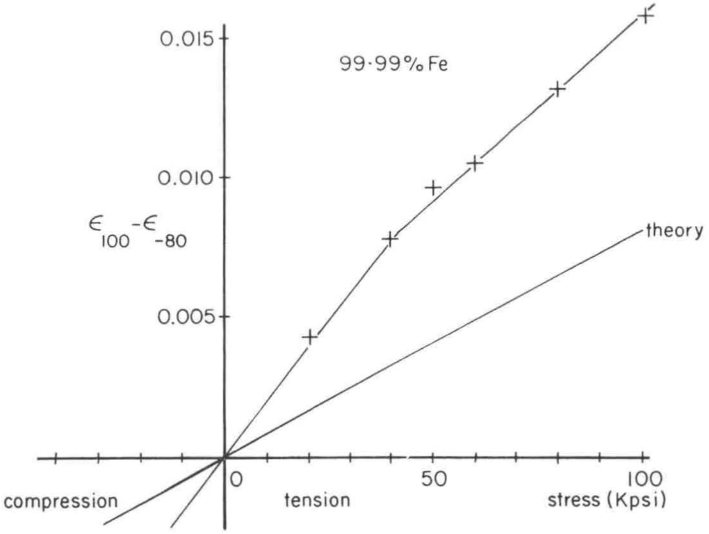

Figure 14. Relative count rates vs stress, ferrite.

Unexpectedly, the plot is not a simple straight line. The theoretical line is also indicated. This theoretical sensitivity requires a knowledge of the parameters A, $\Gamma/2$, and $\mathrm{d}x/\mathrm{d}T$. These were determined for the source and absorber as follows:

Absorber Temperature	Γ, mm/s	dx	A
− 80 C	0.270	+ 0.0528 mm/s	.186
25 C	0.251	0	.185
100 C	0.274	− 0.0400 mm/s	.173

The "theory" line is derived as follows, assuming $\delta = 0$ (source and absorber lattices identical):

$$N(x) = N_0\left(1 - \frac{A}{1+\left(\frac{x-\delta}{\Gamma/2}\right)^2}\right)$$

$$\epsilon_T = \frac{\mathrm{d}N_T}{N_0} = \frac{A\cdot 2\cdot\frac{x_T}{\Gamma/2}\frac{1}{\Gamma/2}\,\mathrm{d}x}{\left[1+\left(\frac{x}{\Gamma/2}\right)^2\right]^2}$$

$$\mathrm{d}x = -\,0.0000565\ \mathrm{mm/s/K\ psi}^2$$

$$\epsilon_{100} = \frac{0.173\cdot 2\cdot\frac{0.0400}{0.274/2}\,\frac{2}{0.274}\cdot\mathrm{d}x}{\left[1+\left(\frac{0.0400}{0.274/2}\right)^2\right]^2}$$

$$= 0.0000350/\mathrm{k\ psi}$$

$$\epsilon_{-80} = -\,0.0000461/\mathrm{k\ psi}$$

Note that $x = x(T)$, but that dx is the response to stress.

The net result of several runs at 100 °C is shown in Fig. 15 and the break seems to always be there. It is always pleasant to find that Mother Nature *can* be generous, with greater sensitivity than expected at the low end of this scale.

A carbon steel foil, 99.9% Fe, 0.001 × 1.00 in. was also examined (i.e., a 1010 steel). The results are quite different, as is shown in Fig. 16. Note, however, that the ϵ_T value at which the foil breaks is nominally the same in both foils. Interesting!

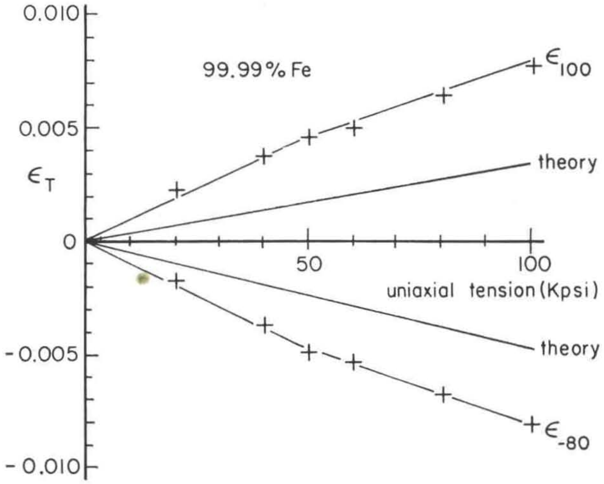

Figure 15. Relative count rate vs stress, at 100 °C and at −80 °C, separately.

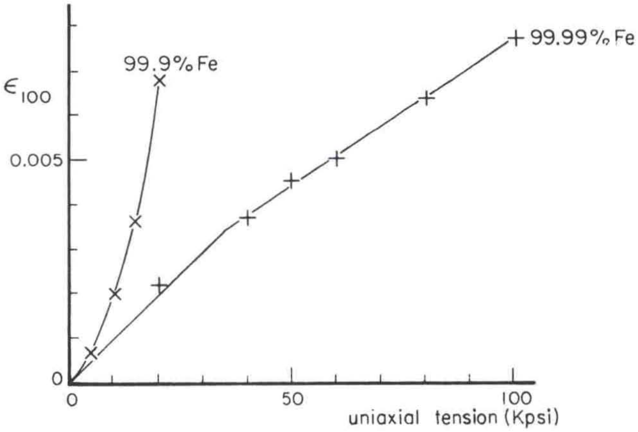

Figure 16. Response of ferrite and of a low carbon steel.

9. Where do we go from here?

In the actual problem of measuring a stress existing in a piece of metal, we have additional problems. We cannot simply follow the count rate vs. applied stress—the stress is already there. Further, the line width and center of the resonance may be changed by alloying conditions. Hopefully, even welds will be measureable, despite the migration of alloying elements. And, the measurement must utilize the one-sided technique, since specimens of interest are usually thicker than foils.

These unknown factors are tentatively treated as requiring additional data points—four will probably suffice. The sensitivity of count rate to geometry is simplified for flat surfaces by setting at the distance which gives a broad maximum in count rate. Curved surfaces will be more troublesome.

Acknowledgements

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REFERENCES

1. Mössbauer, Rudolf L., *A. Physik*, **151,** 124 (1958); *Z. Naturforsch*, **14A,** 211 (1959).
2. Pound, R. V. and Rebka, G. A. Jr., *Phys. Rev. Letters*, **4,** 337 (1960).
3. Maradudin, A. A. and Flinn, P. A., *Phys. Rev.*, **126,** 2059 (1962).
4. Muir, A. H. Jr., Ando, K. J. and Coogan, H. M., " Mössbauer Effect Data Index," issue 3, North American Science Center, Thousand Oaks, California (1965).
5. Preston, R. S., Hanna, S. S. and Heberle, J., *Phys. Rev.*, **128,** 2207 (1962).
6. Kistner, O. C. and Sunyar, A. W., *Phys. Rev. Letters*, **4,** 412 (1960).
7. Pound, R. V. and Rebka, G. A. Jr., *Phys. Rev. Letters*, **4,** 274 (1960).
8. Josephson, B. D., *Phys. Rev. Letters*, **4,** 341 (1960).
9. Cohen, M. M. and Reif, F., *Solid State Physics*, **5,** 324 (1957) (Academic Press, New York, N.Y.).
10. Ruby, S. L. and Flinn, P. A., *Rev. Mod. Phys.*, **36,** 351 (1964).
11. Collins, R. L. and Travis, John C., " The Electric Field Gradient Tensor," to be published in the Third Mössbauer Methodology Symposium (1967).
12. Pipkorn, D. N., Edge, C. K., DeBrunner, P., De Pasquali, G., Drickamer, H. G. and Frauenfelder, H., *Phys. Rev.*, **135,** A1604 (1964).
13. Terrell, J. H. and Spijkerman, J. J., *Applied Physics Letters*, **13,** 11 (1968).