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## Fundamentals of Mössbauer Spectroscopy

### A.1 Recoil-free resonant gamma-ray absorption

All nuclei possess excited states, some of which are accessible from the ground state by photon absorption. Often the excited states of the absorber are long-lived and the range of photon energies which will resonantly excite the absorption is extremely narrow. If strong absorption is to be observed, a significant fraction of the energy of the source radiation must be within this range. Such a source may obviously consist of excited nuclei of the same isotope as the absorber. The excited nuclei may be decay products of appropriate parent nuclei. It was once thought that conservation of momentum requires the recoil of the emitting nucleus and that the photon would not have the full transition energy and hence would not resonantly excite the absorber. If the nucleus is free, the recoil momentum and energy are taken by the nucleus itself. In a solid the momentum and energy go into lattice vibrations, i.e., phonons. The temperature dependence of the absorption cross-section of  $\text{Ir}^{191}$  led Mössbauer (1958) to be the first to realize that a photon could be emitted with the entire solid recoiling as one rigid mass. The energy lost to the recoil in this situation is negligible and the emitted photon may resonantly excite the absorber.

### A.2 Nuclear Physics of $\text{Fe}^{57}$

The isotope with the strongest recoilless resonant absorption is  $\text{Fe}^{57}$ . Since the vast majority of the work reported in the Mössbauer literature is for iron, we restrict our discussion to that isotope. Figure 1 shows the decay of  $\text{Fe}^{57}$  from its parent  $\text{Co}^{57}$ . Of all the excited  $\text{Fe}^{57}$  nuclei, about 10% will emit a 14.4 keV gamma ray via a magnetic dipole transition from the metastable  $I = 3/2$  state to the  $I = 1/2$  ground state ( $I$  is the nuclear spin). The ratio of recoil-free 14.4 keV photons to all the 14.4 keV photons emitted is  $f$ , the recoil-free fraction of the source.  $f$  varies with the properties of the solid and decreases monotonically with increasing temperature. The linewidth of the emitted radiation is limited in theory by  $t$ , the mean life of the  $I = 3/2$  state. In  $\text{Fe}^{57}$ ,  $t = 1.4 \times 10^{-7}$  sec, and the energy distribution is given by a Lorentzian with a fullwidth at half maximum of  $\Gamma_{\text{nat}} = 4.7 \times 10^{-9}$  eV (Lang, 1970). The intensity per unit energy of the Mössbauer radiation is many orders of magnitude greater than the background radiation, and we shall henceforth refer to the gamma beam as if it were 100% Mössbauer radiation unless we specifically note otherwise. We shall also assume that the nuclear levels of the source are not split, and the energy distribution of the beam is given by a single Lorentzian.

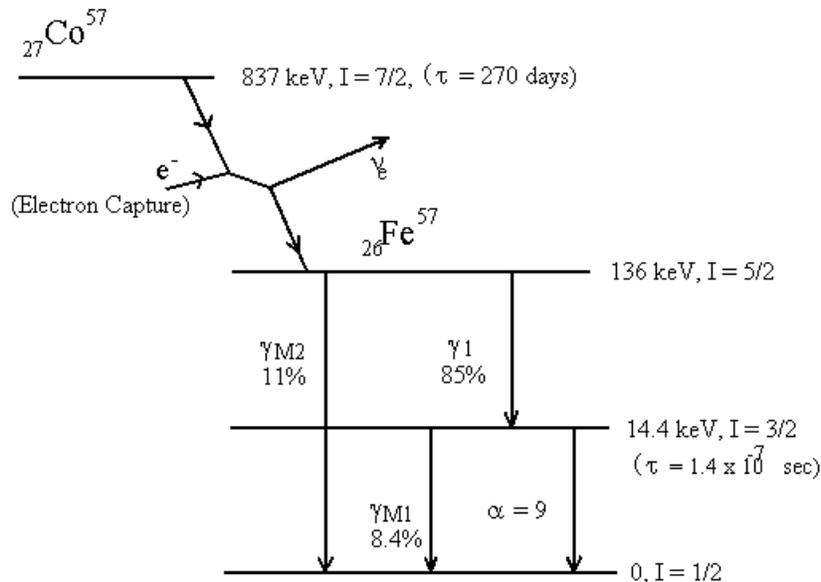


Figure A1 Energy level scheme of  $\text{Fe}^{57}$ . Mössbauer spectroscopy involves the 14.4 keV transition. Intensities are given in % of decays.

To use our Mössbauer source as a spectroscopic tool we must be able to vary its energy over a significant range. This is accomplished by Doppler shifting the energy of the gamma beam. Moving the source at a velocity of 1 mm/sec toward the sample will increase the energy of the photons by 14.4 keV  $(v/c) = 4.8 \times 10^{-8}$  eV or ten natural linewidths. The "mm/sec" is a convenient Mössbauer unit and is equal to  $4.8 \times 10^{-8}$  eV for  $\text{Fe}^{57}$ . A Mössbauer spectrometer consists of a source which may be moved relative to the sample and a counter to monitor the intensity of the beam after it has passed through the sample. The Mössbauer spectrum is a plot of the counting rate against the source velocity, i.e., the beam energy. If the sample nuclear levels are not split and the  $I = 3/2$  to  $I = 1/2$  transition

energy equals that of the source, then the effective cross-section for absorption is a function of gamma energy as given by [Fraunfelder\(1963\)](#)

(eq A1)

$$\sigma_{\text{eff}} = [(2I^*+1)/(2I+1)] [\lambda^2 / 2\pi] [f' / 2(1+\alpha)] \{ \Gamma_{\text{nat}}^2 / [(E-E_\gamma)^2 + \Gamma_{\text{nat}}^2] \}$$

where  $I = 1/2$  and  $I^* = 3/2$  are the ground and excited nuclear spins,  $\alpha = 9.0$  is the internal conversion coefficient (ratio of betas to gammas in the 14.4 keV decay),  $\lambda = 8.61 \times 10^{-9}$  cm is the wavelength of the radiation,  $(E-E_\gamma)$  is the difference between mean incident and resonant gamma energy,  $\Gamma_{\text{nat}}$  is the energy width of the excited nucleus, and  $f'$  is the probability of recoilless absorption. The spectrum will be a single Lorentzian centered at  $\nu = 0$  with a linewidth (FWHM) of  $2\Gamma_{\text{nat}} = 0.19$  mm/sec. The linewidth is  $2\Gamma_{\text{nat}}$  since the observed line arises from the convolution of the source energy distribution and absorber cross section. As discussed below, the hyperfine interactions will split the nuclear levels of the sample and complicate the Mössbauer spectrum.

## A.3 Hyperfine Interactions

### A.3.1 Isomer Shift

The nucleus and its electrons interact in several ways, the most obvious being the electrostatic attraction. If the Fe<sup>57</sup> nuclear charge distribution were the same for the  $I = 1/2$  ground state and the  $I = 3/2$  excited state, then the electrostatic energy of the system of electrons plus nucleus would be the same for both states. In fact the excited Fe<sup>57</sup> nucleus is 0.1% smaller in radius than the ground state nucleus, which causes the Mössbauer transition energy to depend on the electron density at the nucleus. This effect produces the so-called isomer shift of the Mössbauer spectrum, which may be written as

(eq A2)

$$\delta = K \{ \sum_s |\psi(0)|^2 - \sum_a |\psi(0)|^2 \}$$

where  $\delta$  is the isomer shift,  $K$  is a positive constant depending on the change in the nuclear radius,  $\sum_s |\psi(0)|^2$  is the electron density at the source nucleus, and  $\sum_a |\psi(0)|^2$  is the electron density at the absorber nucleus.

To allow isomer shifts to be measured independently of the nature of the source, the centroid of the room temperature spectrum of metallic iron has been adopted as the zero of energy and all shifts are measured relative to it. This convention yields

(eq A3)

$$\delta = K_0 - K \sum_a |\psi(0)|^2$$

where  $K_0$  is a constant. Calculations of  $\delta$  are difficult to perform, hence its most valuable application is classifying various compounds according to oxidation state, degree of covalency, and coordination number. The 1s and 2s electron density at the nucleus is independent of the chemical environment of the Fe ion. However, the 3d electrons shield the 3s electrons and cause a decrease in the electron density at the nucleus. The more delocalized the 3d electrons, the smaller the isomer shift. However, this picture is complicated by the presence of Fe 4s character in the bonding orbitals. The 4s character also reduces the isomer shift, and it is not always clear which of the two effects is dominant ([Greenwood and Gibb, 1971](#)). The electronic contribution to the isomer shift is essentially temperature independent and the observed decrease at high temperatures is due to the relativistic second order Doppler shift. This effect decreases the isomer shift approximately  $6 \times 10^{-4}$  mm/sec for a 1 K increase in  $T$  when the temperature is above the Debye temperature ([Lang and Marshall, 1966](#)).

### A.3.2 Electric Quadrupole Interaction

The excited ( $I = 3/2$ ) state of the Fe<sup>57</sup> nucleus possesses an electric quadrupole moment, and the presence of a low symmetry electric field will tend to orient the nuclear spin. The interaction may be written as

(eq A4)

$$H_Q = - (Q/6) \underline{I} \underline{V} \underline{I}$$

where  $Q$  is the nuclear quadrupole moment,  $\underline{I}$  is the nuclear spin, and  $\underline{V}$  is the electric field gradient (efg) tensor. The elements of the efg tensor are

(eq A5)

$$V_{ij} = \delta^2 V / \delta x_i \delta x_j$$

$i, j = x, y, z$

where  $V$  is the potential due to all charges outside the nucleus and the derivatives are evaluated at the nuclear site. The  $V_{ij}$  are the coefficients of the quadratic terms of a power series expansion of the potential about the nuclear site and are given in their principal axis system by

(eq A6)

$$V_{zz} = \int \rho(r) (3z^2 - r^2) r^{-5} dr$$

and similar expressions.  $\rho(r)$  is the total charge density and the integral is taken over all space outside the nucleus. Also,  $\underline{V}$  is real, symmetric, and traceless. Hence in the frame in which  $\underline{V}$  is diagonal,

(eq A7)

$$H_Q = (Q/4) V_{zz} [I_z^2 - 5/4 + (\eta/3)(I_x^2 - I_y^2)]$$

$$h = (V_{xx} - V_{yy})/V_{zz}$$

where  $x$ ,  $y$ , and  $z$  denote the principal axes of the efg and  $\eta$  is called the asymmetry parameter. By convention,  $x$ ,  $y$ , and  $z$  are chosen so that  $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ , which forces  $0 \leq \eta \leq 1$ . Note,  $V$  has five independent elements. Two of these are  $V_{zz}$  and  $\eta$  and the other three are the Euler angles locating the efg principal axis system relative to some experimental frame.

Reversal of the sign of the nuclear spin will not change the nuclear charge distribution; therefore the efg will not completely lift the fourfold degeneracy of the  $I = 3/2$  states. The quartet will be split into two doublets, while the  $I = 1/2$  states will remain degenerate. Since two transition energies are now possible, two absorption peaks will appear in the Mössbauer spectrum. Diagonalizing H<sub>Q</sub>, we find that the difference in energy of the two peaks to be

(eq A8)

$$\Delta E = (Q/2) V_{zz} (1 + \eta/3)^{1/2}$$

If the recoil-free fraction does not depend on the orientation of the  $\gamma$ -beam relative to the Fe site, a sample with randomly oriented sites in zero applied field will produce a symmetric quadrupole pair. Since the sign of  $\Delta E$  can not be determined from such a spectrum, the absolute value of  $\Delta E$  is usually called "the quadrupole splitting." The sign of  $\Delta E$  is usually referred to as "the sign of  $V_{zz}$ " and is more difficult to measure than the quadrupole splitting.

### A.3.3 Magnetic Hyperfine Interaction

The Fe<sup>57</sup> nucleus possesses a magnetic moment and its energy levels will be perturbed by the local magnetic field. In the presence of a field  $H$ , the interaction is

(eq A9)

$$HM = -g_N \beta_N I H$$

where  $\beta_N$  is the nuclear magneton and  $g_N$  is the nuclear gyromagnetic ratio.  $g_N$  has the values  $0.1806 \pm 0.0014$  and  $-0.1033 \pm 0.0008$  in the ground and excited states, respectively (Lang, 1970).  $H$  will be the sum of an applied field with the internal field of the unpaired electrons. Depending on the magnetic properties of the sample, the internal field may or may not equal zero in the absence of the applied field. A more explicit expression of the magnetic interaction is

(eq A10)

$$HM = P \sum_k \{ |k I + 3(r_k s_k)(r_k I) - (s_k I) - \kappa(s_k I) \} - g_N \beta_N I H_{app}$$

$$P = 2 g_N \beta_N \langle r^{-3} \rangle_{eff}$$

where the sum is over the unpaired electrons,  $|k$  is the orbital angular momentum on the  $k$ th electron and  $\beta$  is the electron magneton. It is convenient to think of  $HM$  in terms of an effective field acting on the nuclear moment. The effective field is

(eq A11)

$$H_{eff} = H_{app} + (p/g_N \beta_N) \sum \{ |k + 3(r_k s_k)r_k - s_k - \kappa s_k \}$$

$$= H_{app} + H_{int}$$

The first term of  $H_{eff}$  is the applied field. The second is the field at the nucleus due to the orbital motion of the electrons. The third and fourth describe the field due to the dipole moment of the electrons. The last term is the Fermi contact term which accounts for any net polarization of the electronic spin at the nucleus. The polarization of  $s$  electron spin at the nucleus stems from the exchange interaction between the 3d electrons and the  $s$  electrons. Any admixture of 4s character into the 3d wave functions would also contribute to the contact field. To a good approximation the net spin at the nucleus will be proportional to  $\sum_k \langle s_k \rangle$ , the sum being taken over 3d electrons.

$P$  and  $\kappa$  depend on the radial part of the wave functions and on shielding effects which are difficult to calculate. Values have been determined empirically for many complexes. Lang and Marshall (1966) quoted values of  $P/g_N \beta_N = -620$  kG and  $\kappa = 0.35$  for high- and low-spin ferric heme complexes.  $P\kappa/g_N \beta_N$  is the effective field per unit spin due to the contact term. For the ferric heme complexes it would be -220 kG. For a variety of high-spin ferrous inorganic compounds the survey of Varret (1976) shows  $P\kappa/g_N \beta_N$  to be approximately -250 kG. Edwards, et al. (1967) found  $P\kappa/g_N \beta_N$  for high-spin ferrous tetrahedral compounds to be reduced to -160 kG by covalency effects.

### A.4 Experimental Setup

The Mössbauer spectra are usually recorded in the transmission geometry using a constant acceleration spectrometer operated in connection with a multi-channel analyzer in the time scale mode. The source is kept at room temperature and consists of approximately 20 mCi of Co<sup>57</sup> diffused into rhodium or palladium foil. The spectrometer is calibrated against a metallic iron foil and zero velocity is taken as the centroid of its room temperature Mössbauer spectrum. In such calibration spectra, linewidths of about 0.23 mm/s were normally observed. The duration of a typical run is a few hours for non-biological compounds and 24 hours for proteins. A typical spectrometer is depicted schematically in Figure A2.

As shown in Figure A2, both the source velocity and the address of the active channel of the multichannel analyzer (MCA) are controlled by the master oscillator. The oscillator synchronizes the source acceleration and the sweep of the memory registers, causing the active channel address to be a linear function of the velocity. In other words, the pulses counted while the source is at a particular velocity are always stored in a particular register.

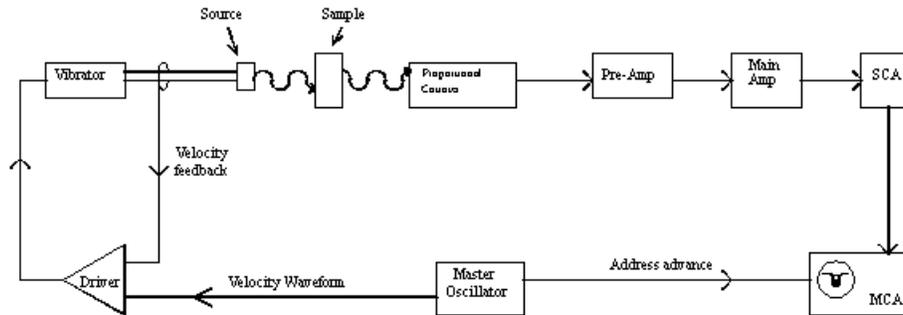


Figure A2 -- Schematic diagram of the Mössbauer spectrometer.

The master oscillator output is a rounded sawtooth or triangular wave and is applied to one of the driver inputs. The driver is essentially a difference amplifier with its output applied to the vibrator. A pick-up coil on the vibrator supplies a voltage proportional to the velocity of the source and is connected to the second input of the driver. The driver and vibrator form a tightly coupled, electro-mechanical, negative feedback loop, forcing the source velocity to be directly proportional to the master oscillator signal. The desired velocity range is selected by scaling the master oscillator signal before it is applied to the driver.

The gas proportional counter contains primarily krypton or argon plus a small amount of methane quench gas. A 14.4 keV photon entering the chamber through the mylar window ionizes some of the Ar or Kr atoms, the creation of each ion/electron pair requiring about 30 eV. The positive ions drift to the outer wall and the electrons to the center wire. The accelerating electrons ionize more atoms, the effective gas gain being approximately 1000. The methane suppresses the random motion of the electrons, thus shortening the travel time to the center wire and the rise time of the signal pulse. The overall efficiency of a Harwell Argon counter is 60% at 14.4 keV, and a 14.4 keV photon will cause about  $10^6$  ion pairs to be created. The 122 keV and 136 keV photons entering the counter Compton scatter and produce a broad background of lower energy signals. The single channel analyzer (SCA) discriminates against most of these, but about 20% of the pulses falling in the 14.4 keV window of the SCA are from this Compton background.

The charge pulse from the counter is amplified and differentiated by the preamp which is mounted as close to the counter as possible. Further amplification of the pulse is provided by the main amplifier and its output is applied to a single channel analyzer. The SCA is set to discriminate against the non-14.4 keV signals. The signals accepted by the SCA are added to the current channel of the MCA.

The observed linewidths are larger than the intrinsic width of 0.19 mm/s since some broadening is always introduced by inhomogeneity of the environment of the iron in the source and sample. Additional broadening arises from imperfections in the source driving mechanism. Even so, typical observed linewidths obtainable in the lab are 0.23 mm/s which is close to the minimum predicted by the uncertainty principle.

We now consider the time required to record a Mössbauer spectrum. A typical sample will have 1 mg/cm<sup>2</sup> of iron in the gamma-ray beam. For purposes of illustration, we assume the spectrum has two absorption peaks. If the Fe<sup>57</sup> is present in its natural 2% abundance, there will be  $2 \times 10^{17}$  Fe<sup>57</sup> nuclei/cm<sup>2</sup>. The peak resonant cross section is approximately  $2 \times 10^{-18}$  cm<sup>2</sup> (Frauenfelder, 1963). We divide this value by 8 because of the finite source linewidth, the two absorption peaks of the spectrum, and the estimated product of the recoil free fraction of the source and absorber. The observed intensity will be 5%. The spectrometer will typically divide the velocity scale into 256 channels. For a 20 mCi source the total counting rate is usually about 20,000 counts/s of which about 85% will be 14.4 keV radiation. The spectrometer duty cycle is about 66% and  $r$ , the 14.4 keV counting rate per channel, is typically 44 counts/s/channel. The signal-to-noise ratio,  $S/N$ , is given by

(eq A12)  

$$S/N = a_p [r T]^{1/2}$$

where  $a_p$  is the peak absorption intensity and  $T$  is the running time. If we want a  $S/N$  of 40, then, for  $a_p = 0.05$ ,  $T$  will be 14,500 s or 4 hours. For a given  $S/N$ , the run time is inversely proportional to the square of the peak absorption.