CHAPTER II

THE MÖSSBAUER EFFECT

1. Cross-section.

Under general assumptions the energy dependent cross-section for nuclear resonance processes can be expressed by (Breit and Wigner (1936), Kapur and Peierls (1938)).

$$\sigma(E) = \frac{\sigma_o \Gamma^2}{4(E - E_o)^2 + \Gamma^2}$$

where for the case of gamma ray resonant absorption

$$\sigma_\circ = \frac{\lambda^2 (2I_e + 1)}{2\pi(2I_g + 1)}$$

is the maximum absorption cross-section

E_o the energy of the excited state

Γ the natural width of the excited state

$I_e I_g$ the spin of the excited and the ground state

λ the wavelength of the gamma ray

Usually the excited state can decay by several modes, the most predominant one for low lying states being the internal conversion process. The total width is then the sum of the partial widths; i.e.,

$$\Gamma = \Gamma_\gamma + \sum_i \Gamma_{ei} = \Gamma_\gamma (1 + \%)$$

where $\Gamma\gamma$ is the gamma ray partial width and α the internal conversion coefficient.

To get the final cross-section for absorption and scattering experiments $\sigma(E)$ has to be modified depending on the number of emission processes occurring before final detection of the gamma ray; i.e., (Jackson, 1955)

$$\sigma_{abs} = \frac{\Gamma_\gamma}{\Gamma}\sigma(E)$$

$$\sigma_{scatt} = \left(\frac{\Gamma_\gamma}{\Gamma}\right)^2 \sigma(E)$$

The cross-section has a Lorentzian shape with the full width at half maximum equal to Γ. In the case of hyperfine splitting (see Section 2.6, 2.7) each resolved line will exhibit this shape.

Similarly, the normalized source intensity can be expressed by

$$I(E) = \frac{\Gamma}{2\pi}\frac{1}{(E - E_o)^2 + (\Gamma/2)^2}$$

which is just the square of the Fourier analyzed time-dependent wave function of the photon.

2. <u>Lattice Binding</u>.

The amazing feature about the Mössbauer effect is not only that the emission and absorption of the gamma rays occur without recoil, but also that the line is not Doppler broadened and exhibits, under ideal conditions, the natural line width.

The essential aspect of the recoilless effect is readily explained if one considers the radiating nucleus as strongly bound in a crystal such that the momentum is taken up by the crystal as a whole. If, according to the Einstein model of a solid, the recoil energy R is small compared to that required to excite the lattice, the gamma ray will be emitted with the full transition energy E_o. (See next section.)

Classically (Shapiro (1961)) one obtains the unbroadened line by regarding the source atom as bounded in a harmonic oscillator potential such that during an emission of a quantum of frequency $\omega_o = E_o / \hbar$ the thermal vibrations of the atom in the lattice (of frequency Ω) will modulate the source radiation. The resulting frequency spectrum will consist of the fundamental carrier frequency $\omega_\circ$ with side frequencies $\omega_\circ \pm$ n Ω, n=1, 2, 3.... The amplitude of the various components is given by the Bessel function $J_n\left(\frac{x_\circ \omega_\circ}{c}\right)$, where $x_\circ$ is the amplitude of oscillation of the atom. The intensity of the central component, which can be identified with the unshifted Mössbauer line is $f = J_\circ^{\,2}\left(\frac{x_\circ \omega_\circ}{c}\right)$ which, if generalized for a large number of lattice vibrations, can be expanded to give

$$f = \exp\left(-\frac{\langle x^2 \rangle}{\lambda\!\!\!^{-2}}\right);\ \lambda\!\!\!^{-} = \frac{c}{\omega_\circ}$$

$\langle x^2 \rangle$ is the mean square displacement of the nucleus about its equilibrium position. A similar factor is obtained for the absorption mechanism.

The implications of this result have been discussed by Frauenfelder (1962) and Nussbaum (1966) and in more general terms by Lipkin (1960). Even though the classical treatment does account for the unshifted line, it does not account for the shape of the phonon spectrum. In an actual solid the lattice vibration spectrum is a continuum with the individual oscillators interacting with one another. Furthermore in a lattice containing different atoms, variations of the force constants between neighbouring atoms have to be considered.

3. <u>Debye-Waller Factor</u>.

The factor f gives that fraction of the radiation which is emitted and absorbed without recoil. It is very similar to the Debye-Waller factor know from X-ray diffraction work, which describes the temperature variation of the elastically scattered radiation intensity.

Both factors depend on the mean square displacement of the radiating system. To obtain £x^2§ one can assume, to a first approximation, that the crystal obeys the Debye model; i.e., that the frequency spectrum is described by the density function.

$$\mathrm{r}(\omega) = \frac{9N\omega^2}{\omega_D{}^3} \qquad \text{... 3.1.}$$

normalized for the 3N possible modes of vibration, N being the number of atoms in the crystal. ω_D is the maximum vibration frequency with the Debye temperature defined by

$$\theta_D = \frac{\hbar\omega_D}{k_B}$$

In a harmonic potential each mode of oscillation ω_i has associated with it an energy

$$3NM\omega_i{}^2\left\langle x_i{}^2\right\rangle = \hbar\omega_i\left(\frac{1}{e^{\hbar\omega_i/kT}-1}+\frac{1}{2}\right) = \hbar\omega_i\left(n_i+\frac{1}{2}\right)$$

Averaging over all of the frequencies one obtains:

$$\begin{aligned}\frac{\left\langle x^2\right\rangle}{\lambda^2} &= \frac{6R}{\hbar\omega_D{}^3}\int_{\circ}^{w_{\circ}}\left(\frac{1}{2}=\overline{n}\right)\omega d\omega \\ &= \frac{3R}{2k_B\theta_D}\left[1+4\left(\frac{T}{\theta_D}\right)^2\int_{\circ}^{\theta_D/T}\frac{udu}{e^u-1}\right]\end{aligned} \qquad \text{... 3.2.}$$

This integral can be readily evaluated at the limit of low and high temperature

$$f = \exp\left(-\frac{3R}{2k\theta_D}\right) \text{ for T} << \theta_D \qquad \text{... 3.3a.}$$

$$f = \exp\left(-\frac{6RT}{k\theta_D{}^2}\right) \text{ for T} >> \theta_D \qquad \text{... 3.3b.}$$

Even though the integral in Equation 2.3.2 accounts for the predominant temperature dependence of f, an additional factor arises because of the volume dependence of θ_D (Boyle, et al., 1961) which, for crystals with cubic symmetry, can be expressed through the Grüneisen constant $\gamma = -\frac{\partial \ln \theta_D}{\partial \ln V}$.

The effect of thermal expansion is then given by

$$\left(\frac{\partial \theta_D}{\partial T}\right)_P = \theta_D \left(\frac{\partial \ln \theta_D}{\partial \ln V}\right)\left(\frac{\partial \ln V}{\partial T}\right) = \frac{\theta_D \gamma^2 K C_V}{V} \qquad \text{... 3.4.}$$

where C_V is the heat capacity per unit volume and K is the compressibility of the solid. Preston, et al., (1962) find that increasing the temperature of an iron lattice from room temperature to 1000°C decreases θ_D by about 100°K.

Changing the ambient pressure at the lattice has a similar effect on θ_D.

$$\left(\frac{\partial \theta_D}{\partial P}\right)_T = \theta_D \left(\frac{\partial \ln \theta_D}{\partial \ln V}\right)\left(\frac{\partial \ln V}{\partial P}\right) = \theta_D \gamma K \qquad \text{... 3.5.}$$

for iron $\frac{\Delta \theta_D}{\theta_D} \approx 1.0 \times 10^{-6}$ per kg/cm^2 and is therefore negligible for most purposes.

In the foregoing discussion, the characteristic lattice temperature has been assumed to be θ_D. This is, however, not strictly the case, as can be readily seen by writing the integral for the heat capacity (Kittel, 1957).

$$C_v = \frac{3\hbar^2}{\omega^3{}_D k_B T^2} \int_{\circ}^{w_D} \bar{n}^2 w^4 \exp\left(\hbar\omega / kT\right) d\omega \qquad \text{... 3.6.}$$

A comparison of this equation with Equation 2.3.2 shows that different weighting factors have been used in the two frequency integrals, so that the θ_D obtained from specific heat measurements does not necessarily represent the lattice temperature of interest for evaluating f. Whereas C_v accentuates the high frequency part of the spectrum, Equation 2.3.2 puts more weight on the low frequency part.

In a realistic model one would also have to consider the effects of the acoustical and the optical vibration modes in a crystal, and, in the case of impurity atoms in a host lattice, the presence of localized modes. The acoustical modes have a broad frequency band that can be well approximated by the Debye model. The frequency spectra of the optical and the localized modes are more peaked and can be better represented by the Einstein model (Wertheim, 1964) for which

$$\mathrm{f} = \exp\left(-\frac{R}{k\theta_E}\left(3 - \frac{2\theta_E}{T}\right)\right) \text{ for T} << \theta_E \qquad \text{... 3.7a.}$$

$$= \exp\left(-\frac{2RT}{k\theta_E{}^2}\right) \text{ for T} >> \theta_E \qquad \text{... 3.7b.}$$

where $\theta\mathrm{E} = \frac{\hbar\omega_E}{\hbar_B}$ and ω_E is the Einstein frequency.

Comparing Equations 2.3.3 and 2.3.7 for $\theta_D = \theta_E$ one finds that the latter gives a higher value for f, a factor which is enhanced if $\omega_E < \omega_D$ as would be expected for a lightweight impurity in a heavyweight lattice (Montroll and Potts, 1955).

Accurate measurements of the recoilless fraction have given considerable information about the properties of various crystal lattices. Boyle, et al., (1961) have shown that the temperature variation of f for the 24 keV radiation from ^{119}Sn deviates from Equation 2.3.3, which they attribute to anharmonicities in the lattice potential.

The problem of an impurity atom in a host lattice has been treated by many authors and most recently by Mannheim and Simopolous (1968), who have detected the presence of localized vibration modes for iron in a Vanadium lattice. They have calculated and verified experimentally that an increase in the force constant at the impurity site gives rise to an increase in f.

The above discussion is valid only for crystals with cubic symmetry. For lower symmetries one has to consider £x^2§ along the various crystal axes as has been shown for the case of potassium ferrocyanide (Duerdoth 1964) where f exhibits an angular dependence.

In general, to obtain a high recoilless fraction, a host lattice with a high Debye temperature has to be selected, one in which impurity atoms are strongly bound in a localized position.

4. <u>Transmission Line Width</u>.

Ideally it should be possible to obtain an emission and absorption line of natural line width Γ with a resulting transmission line width of 2Γ. In practice, however, one

needs a finite absorber thickness to obtain a sizeable resonance effect, which will appreciably broaden the transmission line. Also the various hyperfine interactions can produce a shifting or splitting of the line which, when unresolved, can cause additional broadening. These effects are generally well understood and are described below.

5. Isomeric Shift.

The isomeric shift was first observed by Kistner and Sunyar (1960) and results from the difference in the chemical environments at the source and absorber nuclei. The nucleus having a finite radius R will interact electrostatically with the electron charge density at the nucleus e $|\psi(0)|^2$. This Coulomb interaction relative to that experienced by a point nucleus is $\frac{2\pi}{5} Ze_e^2 |\psi(0)|^2 R^2$. If the charge radii R_{ex}, R_{gr} of the excited and the ground state of the nucleus are different, a change in the gamma ray transition energy will result, which is

$$\delta E = \frac{2\pi}{5} Ze_e^2 |\psi(0)|^2 \left(R^2{}_{ex} - R^2{}_{gr}\right)$$

A relative shift between the emission and the absorption line will then occur if the chemical environments in the source and the absorber are different; i.e., if the respective electron charge densities at the nucleus $e|\psi_s(0)|^2$ and $e|\psi_a(0)|^2$ are different. This shift is

$$\Delta E_{IS} = \delta E_a - \delta E_s = \frac{2\pi}{5} Ze_e^2 \left(|\psi_a(0)|^2 - |\psi_s(0)|^2\right)\left(R^2{}_{ex} - R^2{}_{gr}\right)$$

and is analogous to the isotope shift observed in atomic transitions (Breit, 1958).

Table 2.1

Source Lattice	Crystal Structure	f_s [1)]	θ_D [2)]	ΔE_{1S} (mm/sec) [3)]
Rhodium	f.c.c.	.70	350	-.114
Copper	"	.61	340	-.226
Palladium	"	.55	275	-.185
Platinum	"	.53	230	-.347
Gold	"	.37	165	-.632
Molybdenum	b.c.c.	.64	425	-0.60
Chromium	"	.60	400	+.152
Tungsten	"	.52	380	
Tantalum	"	.52	230	-.033

1) Values obtained by Quaim (1965). For the case of Rh, Pd the values are quoted for the sources used.

2) Obtained from specific heat measurements (Kittel, 1957).

3) Shift quoted relative to natural iron (Mössbauer Data Index, 1966).

Only this relative shift is directly measurable and has been studied in detail for ^{57}Fe, ^{119}Sn, and ^{197}Au. For the 14.4 kev level in ^{57}Fe, it was found (Walker, et al., 1961) that a decrease in the electron charge density produced an increase in the gamma ray transition energy from which it can be concluded that R_{gr} is larger than R_{ex}. Table 1

shows the shifts that have been generally observed for iron in the various host lattices. A positive shift corresponds to a decrease (increase) in the source (absorber) transition energy.

No full explanation, which accounts quantitatively for the observed shifts, has as yet been given. Some attempts have, however, been made for the transition metals by correlating the shifts with the filling of the d-shells (Qaim, 1967) taking into consideration the effect of the shielding of the 3s by the 3d electrons (Walker, et al., 1961; Ingalls, 1967).

6. Electric Quadrupole Splitting.

In the previous section the nucleus was assumed to be spherical and the charge distribution uniform. More generally, nuclei that have a spin $I \neq 0, \frac{1}{2}$ will exhibit an electric quadrupole moment eQ, which in the presence of a local electric field gradient will split the line. If this gradient is axially symmetrical about the crystal z-axis, the energy splitting will be given by (Abragam, 1961).

$$E_Q = \frac{e^2 qQ}{4I(2I-1)} \left(3m_I^2 - I(I+1)\right) \qquad \text{... 6.1.}$$

where $eq = \partial^2 V / \partial z^2$ and I,m are the spin quantum numbers of the particular nuclear level. The substates $\pm m_I$ will be degenerate and in fact will remain so even in the presence of an axially non-symmetrical field gradient if I is half integral. In the latter case Equation 2.6.1 will be modified by an asymmetry parameter.

For ^{57}Fe with $I_{gr} = \frac{1}{2}$ and $I_{ex} = \frac{3}{2}$, the ground state is spherical, and any quadrupole splitting will only be due to the excited state. Because of the double degeneracy of the four substates $\pm\frac{1}{2}, \pm\frac{3}{2}$ a doublet will result.

The electric field gradient will vanish in a lattice of cubic symmetry like that of natural iron and many of the other transition metals. In other substances like FeF_2 (Wertheim, 1961) a splitting is observed that can be readily resolved. In the ferro cyanides the quadrupole splitting cannot be resolved and is only deduced from the broadened transmission line. As the intensity of the two components in the doublet varies, depending on the angle θ between the crystal z-axis and the direction of emission (absorption) of the gamma ray, the unresolved splitting will appear as an angle dependent shift of the transmission line (Evans, 1968). The angular dependence of the intensity of the two components is characterized by the classical radiation pattern for $\Delta m = 0,1$ and is given by (Wertheim, 1964) (see next section)

$$\begin{aligned} &\frac{3}{2}\left(1+\cos^2\theta\right) \quad \text{for } \Delta m = \pm 1 \\ &1+\frac{3}{2}\sin^2\theta \quad \text{for } \Delta m = 0 \end{aligned} \qquad \text{... 6.2.}$$

The ratio of the two intensities varies from 3 for θ = 0° to 3/5 for θ = 90°. For a polycrystal the intensities will be equal unless the recoilless fraction should also be angle dependent as is the case for potassium ferrocyanide.

7. <u>Magnetic Hyperfine Splitting</u>.

The interaction between the nuclear magnetic dipole moment μ and the magnetic field at the nucleus H will produce a splitting of each nuclear level into 2I + 1

components. Each substate m_I, where m_I takes on the values I, I-1, ... -I, will be shifted by an amount

$$\Delta E_M = g\mu_n H m_I$$

where g is the nuclear gyromagnetic ratio, and μ_n the nuclear magneton $e\hbar / 2m_p c$ equal to 3.15 x 10^{-12} eV/gauss. As the various components are equally spaced and for ferromagnetic substances like iron easily resolved, it becomes easy to measure the relative transition probabilities between given substates, as calculated by squaring the corresponding Clebsch Gordon coefficients, and the radiation pattern relative to the direction of the magnetic field. For a pure multipole transition the angular dependence of the individual components is given by $\left|\mathrm{X}_{L,m}(\theta,\psi)\right|^2$, where L is the angular momentum carried off by the gamma ray and θ is the angle between the direction of the magnetic field and that of the emission (absorption) of the gamma rays. $\left|\mathrm{X}_{L,m}(\theta,\psi)\right|^2$ is the vector spherical harmonic (Jackson, 1963).

For the MI transition of ^{57}Fe (14.4 kev) the angular dependent intensity of the various transitions is given by

$$\frac{3}{2}\left(1+\cos^2\theta\right) \quad \text{for} \pm\frac{3}{2} \rightarrow \pm\frac{1}{2}\left(\Delta m = \mp 1\right)$$

$$2\sin^2\theta \qquad \text{for } \pm\frac{1}{2} \rightarrow \pm\frac{1}{2}\left(\Delta m = 0\right)$$

$$\frac{1}{2}\left(1+\cos^2\theta\right) \qquad \text{for } \pm\frac{1}{2} \rightarrow \mp\frac{1}{2}\left(\Delta m = \mp 1\right)$$

For an unmagnetized ferromagnetic material, the intensity of the three components will be in the ratio 3:2:1. Often one finds, however, that thin foils are preferentially magnetized in the plane of the foil, which tends to increase the intensity of

the $\pm\frac{1}{2} \rightarrow \pm\frac{1}{2}$ transition, while saturation effects, arising from the thickness of the absorber, tend to reduce the outer components.

Given the knowledge of the nuclear magnetic moment of the ground state of, for instance, ^{57}Fe (0.0902 nm) one can readily deduce the magnetic moment of the excited state (0.155 nm) and the effective field H_{eff} at the nucleus. The magnetic hyperfine structure has been used extensively for that purpose and also to determine the sign of H_{eff}. For iron at room temperature H_{eff} is –330kG, and the resulting energy splitting can be used as a convenient standard (Preston, et al., 1962).

Experiments conducted with Co-Pd and Fe-Pd alloys of varying concentrations have indicated (Clogston, et al., 1962) that the palladium atoms take part in the magnetic coupling so that quite small concentrations of a ferromagnetic metal, like 0.5% of iron, can produce ferromagnetism in the alloy. No such effect has been observed for rhodium alloys.

8. <u>Thermal Shift</u>.

Pound and Rebka (1960) and Josephson (1960) have pointed out that gamma rays emitted without recoil are still affected by the mean square velocity £v_s^2§, £v_a^2§ of the nuclei in the source and absorber, respectively, which gives rise to an energy shift

$$\frac{\Delta E_{th}}{E} = \frac{1}{2c^2}\left(\left\langle v_s^{\,2}\right\rangle - \left\langle v_a^{\,2}\right\rangle\right)$$

This shift can be explained in terms of the relativistic second order Doppler shift or as being due to the resulting change in mass of the nucleus during the emission or absorption of a gamma quantum. Both views appear to be equivalent.

When the source and the absorber are both at the same temperature, the corresponding shifts occurring during the emission and absorption processes will compensate each other. Expressing this shift as a function of the net temperature difference between that of the absorber and the source, one obtains

$$\frac{1}{E}\frac{\partial E}{\partial T} = -\frac{1}{2c^2}\frac{\partial}{\partial T}\left\langle \mathrm{v}^2 \right\rangle$$

which for a monatomic solid with harmonic lattice forces becomes

$$\frac{1}{E}\frac{\partial E}{\partial T} = -\frac{1}{2Mc^2}\frac{\partial U}{\partial T} = \frac{C_p}{2c^2}$$

where U is the lattice energy per atom (of mass M) and C_p is the specific heat of the lattice.

For iron at room temperature the total temperature shift observed was (-2.09 ± 0.05) x 10^{-15} per °K (Pound, et al., 1961). It consists of the contribution of the second order Doppler shift (-2.24 x 10^{-15} per °K) and a correction factor due to the temperature dependent contribution of the isomer shift arising from the thermal expansion of the lattice.

The second order Doppler shift has also recently been used to establish the presence of localized vibrational modes for dilute iron impurities in a vanadium lattice and to detect changes in the force constant between the iron and neighbouring atoms (Mannheim and Simopolous, 1968).

9. Pressure Effects.

An increase in the ambient pressure at the source and the absorber not only increases the recoilless fraction of both, but it also affects the isomeric and the thermal shifts. Pound, et al., (1961) have given the relative contribution of each as

$$\frac{1}{E}\left(\frac{\partial E}{\partial P}\right)_T = \frac{1}{E}\left(\frac{\partial E_{IS}}{\partial \ln \mathrm{V}}\right)\left(\frac{\partial \ln \mathrm{V}}{\partial P}\right) - \frac{1}{E}\left(\frac{\partial E_{th}}{\partial \ln \mathrm{V}}\right)\left(\frac{\partial \ln \mathrm{V}}{\partial P}\right)$$
$$= -aK\left(\frac{\partial |\psi(0)|^2}{\partial \ln \mathrm{V}}\right)_T - \frac{3}{20}\ \frac{k_\beta \theta_D{}^2 \gamma K}{Mc^2 T}$$

where a is the proportionality constant relating the isomeric shift with $|\psi(0)|^2$. The first contribution is the predominant one (~ 95%) and has been attributed by the above authors as being due to a change of the 4s electron density $|\psi_{4s}(0)|^2$. This effect has been examined in more detail for the transition metals (Ingalls, et al., 1967). It was found that the above conclusion by Pound, et al., is not necessarily accurate for some of the metals like Fe, Ti, and Cu, where, most likely, the 3s electron density $|\psi_{3s}(0)|^2$ is affected by the shielding of the outer d electrons giving rise to a small additional volume dependence. The observed pressure induced shifts vary from 1.5 x 10^{-4} mm/sec per kbar pressure for platinum to 6.4 x 10^{-4} mm/sec per kbar for iron and vanadium, with 3.1 x 10^{-4} mm/sec per kbar for palladium. This indicates that the pressures reached with the ultracentrifuge (~ 10 kbar) can be neglected.

10. Relaxation Effects.

So far only time independent hyperfine interactions have been discussed. Generally one would also expect time dependent ones to exist. They may arise from effects associated with the excitation of the Mössbauer level or from others involving electronic relaxations.

Transients, as occur when the nucleus is perturbed by a previous nuclear transition or reaction, can leave the atom in different charge states. If the time needed for the atom to return to its equilibrium charge state is comparable with the nuclear life time, the emission spectrum will exhibit the shifts and/or splittings representative of the various

charge states present. This has been observed for ^{57}Co (E.C.$\rightarrow^{57}Fe$) in $Co(NH_4SO_4).6H_2O$ where the emission spectrum could be decomposed into two shifted and quadrupole split lines due to Fe^{++} and Fe^{+++} (Ingalls and De Pasquali, 1965). It would also be reasonable to expect that the perturbations occurring during the creation of the Mössbauer level could decrease the effective f_S. No effect, however, using Pd and Cu lattices has been found (Craig, et al., 1964).

Recently paramagnetic hyperfine interactions have been investigated for a number of substances (Wickman, et al., 1966; Lang and Marshall, 1966) where relaxation effects arise because of spin-spin or spin-lattice interactions. Usually these effects are only substantial at low temperatures when the relaxation times are larger than the Larmor precession period of the nucleus, though for a few special cases, like the Fe-Pd alloys, they might still have to be considered at room temperature.