Preface

Rudolph Mössbauer discovered the phenomenon of recoil-free nuclear resonance fluorescence in 1957–58 and the first indications of hyperfine interactions in a chemical compound were obtained by Kistner and Sunyar in 1960. From these beginnings the technique of Mössbauer spectroscopy rapidly emerged and the astonishing versatility of this new technique soon led to its extensive application to a wide variety of chemical and solid-state problems. This book reviews the results obtained by Mössbauer spectroscopy during the past ten years in the belief that this will provide a firm basis for the continued development and application of the technique to new problems in the future.

It has been our aim to write a unified and consistent treatment which firstly presents the basic principles underlying the phenomena involved, then outlines the experimental techniques used, and finally summarises the wealth of experimental and theoretical results which have been obtained. We have tried to give some feeling for the physical basis of the Mössbauer effect without extensive use of mathematical formalism, and some appreciation of the experimental methods employed without embarking on a detailed discussion of electronics and instrumentation. However, full references to the original literature are provided and particular points can readily be pursued in more detail if required.

The vast amount of work which has been published using the ^{57}Fe resonance is summarised in nine chapters and again full references to the relevant literature are given. The aim here has been to give a critical treatment which provides perspective without loss of detail. The text has been updated to the beginning of 1970 and numerous references to important results after that time have also been included.

A similar approach has been adopted for tin-119 and for each of the forty other elements for which Mössbauer resonances have been observed. Though the results here are much less extensive than for iron, many new points of theory emerge and numerous ingenious applications have been devised. Indeed, one of the great attractions of Mössbauer spectroscopy is its applicability to a wide range of very diverse problems. At all times we have tried to

emphasise the chemical implications of the results and have indicated both the inherent advantages and the occasional limitations of the technique.

Our own interest in Mössbauer spectroscopy dates from 1962 and, from the outset, we were helped immeasurably by that small international band of enthusiasts who in the early days so generously shared their theoretical insight and instrumental expertise with us. As more chemists became aware of the technique, various international conferences were arranged and, in this country, the Mössbauer Discussion Group was formed. The wide range of topics discussed at these meetings testifies to the metamorphosis of Mössbauer spectroscopy from its initial 'technique oriented phase' to its present, more mature 'problem oriented phase'. Accordingly, Mössbauer spectroscopy is now widely employed as one of a variety of experimental techniques appropriate to the particular problem being studied. With this maturity comes the realisation that in future it will no longer be feasible, or indeed desirable, to review each individual application of Mössbauer spectroscopy or to delineate its distinctive contribution to the solution of a particular problem. However, the present book, in reviewing the first decade of Mössbauer spectroscopy, enables an overall view of the scope of the method to be appreciated. We hope that it will serve both as an introductory text for those wishing to become familiar with the technique, and as a detailed source-book of references and ideas for those actively working in this field.

The book was written whilst we were in the Department of Inorganic Chemistry at the University of Newcastle upon Tyne, and it is a pleasure to record our appreciation of the friendly and stimulating discussions we have had over the years with the other members of staff, graduate students, and visiting research fellows in the Mössbauer Group which grew up there. We are indebted to Mrs Mary Dalgliesh for her good-humoured persistence and technical skill in preparing the extensive and often complex typescript, and would also like to thank Mrs Linda Cook, Mrs Millie Fenwick, and Miss Anne Greenwood for their help in checking proofs and preparing the indexes.

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1 | The Mössbauer Effect

The phenomenon of the emission or absorption of a γ-ray photon without loss of energy due to recoil of the nucleus and without thermal broadening is known as the Mössbauer effect. It was discovered by Rudolph Mössbauer in 1957 [1] and has had an important influence in many branches of physics and chemistry, particularly during the last five years. Its unique feature is in the production of monochromatic electromagnetic radiation with a very narrowly defined energy spectrum, so that it can be used to resolve minute energy differences. The direct application of the Mössbauer effect to chemistry arises from its ability to detect the slight variations in the energy of interaction between the nucleus and the extra-nuclear electrons, variations which had previously been considered negligible.

The Mössbauer effect has been detected in a total of 88 γ-ray transitions in 72 isotopes of 42 different elements. Although in theory it is present for all excited-state–ground-state γ-ray transitions, its magnitude can be so low as to preclude detection with current techniques. As will be seen presently, there are several criteria which define a useful Mössbauer isotope for chemical applications, and such applications have so far been restricted to about a dozen elements, notably iron, tin, antimony, tellurium, iodine, xenon, europium, gold, and neptunium, and to a lesser extent nickel, ruthenium, tungsten, and iridium. The situation thus parallels experience in nuclear magnetic resonance spectroscopy where virtually all elements have at least one naturally occurring isotope with a nuclear magnetic moment, though less than a dozen can be run on a routine basis (e.g. hydrogen, boron, carbon-13, fluorine, phosphorus, etc.). However, advances in technique will undoubtedly allow the development of other nuclei for chemical Mössbauer spectroscopy.

To gain an insight into the physical basis of the Mössbauer effect and the importance of recoilless emission of γ-rays, we must consider the interplay of a variety of factors. These are best treated under five separate headings:

1.1 Energetics of free-atom recoil and thermal broadening.
1.2 Heisenberg natural linewidth.
1.3 Energy and momentum transfer to the lattice.

1.1 Energetics of Free-atom Recoil and Thermal Broadening

Let us consider an isolated atom in the gas phase and define the energy difference between the ground state of the nucleus (E_g) and its excited state (E_e) as

$$E = E_e - E_g$$

The following treatment refers for simplicity to one dimension only, that in which a γ-ray photon is emitted and in which the atom recoils. This simplification causes no loss of generality as the components of motion in the other two dimensions remain unchanged. If the photon is emitted from a nucleus of mass M moving with an initial velocity V_x in the chosen direction x at the moment of emission (see Fig. 1.1), then its total energy above the ground

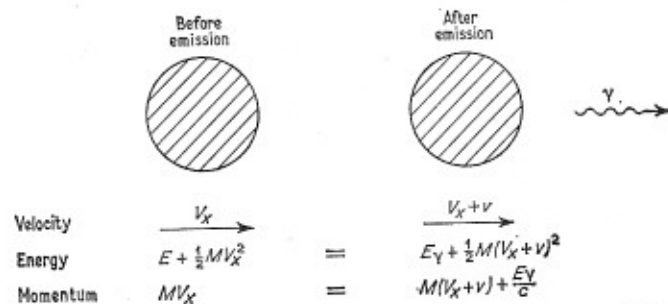|	Before emission		After emission
Velocity	$\xrightarrow{V_x}$		$\xrightarrow{V_x+v}$
Energy	$E + \frac{1}{2}MV_x^2$	$=$	$E_\gamma + \frac{1}{2}M(V_x+v)^2$
Momentum	MV_x	$=$	$M(V_x+v)+\dfrac{E_\gamma}{c}$

Fig. 1.1 The energy and momentum are conserved in the gamma emission process.

state nucleus *at rest* is ($E + \frac{1}{2}MV_x^2$). After emission the γ-ray will have an energy E_γ and the nucleus a new velocity ($V_x + v$) due to recoil (note that v is a vector so that its direction can be opposite to V_x). The total energy of the system is $E_\gamma + \frac{1}{2}M(V_x + v)^2$. By conservation of energy

$$E + \tfrac{1}{2}MV_x^2 = E_\gamma + \tfrac{1}{2}M(V_x + v)^2$$

The difference between the energy of the nuclear transition (E) and the energy of the emitted γ-ray photon (E_γ) is

$$\delta E = E - E_\gamma = \tfrac{1}{2}Mv^2 + MvV_x$$
$$\delta E = E_R + E_D \qquad \qquad 1.1$$

The γ-ray energy is thus seen to differ from the nuclear energy level separation by an amount which depends firstly on the recoil kinetic energy ($E_R = \frac{1}{2}Mv^2$) which is independent of the velocity V_x, and secondly on the term $E_D = MvV_x$ which is proportional to the atom velocity V_x and is a

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Doppler-effect energy. Since V_x and v are both much smaller than the speed of light it is permissible to use non-relativistic mechanics.

The mean kinetic energy per translational degree of freedom of a free atom in a gas with random thermal motion is given by

$$\overline{E_K} = \tfrac{1}{2}M\overline{V_x^2} \simeq \tfrac{1}{2}kT$$

where $\overline{V_x^2}$ is the mean square velocity of the atoms, k is the Boltzmann constant and T the absolute temperature.

Hence $(\overline{V_x^2})^{\frac{1}{2}} = \sqrt{(2\overline{E_K}/M)}$ and the mean broadening

$$\overline{E_D} = Mv(\overline{V_x^2})^{\frac{1}{2}} = \sqrt{(2\overline{E_K}Mv^2)} = 2\sqrt{(\overline{E_K}E_R)} \qquad 1.2$$

Thus referring to equation 1.1, the γ-ray distribution is displaced by E_R and broadened by twice the geometric mean of the recoil energy and the average thermal energy. The distribution itself is Gaussian and is shown diagrammatically in Fig. 1.2. For E and E_γ having values of about 10^4 eV E_R and $\overline{E_D}$ are
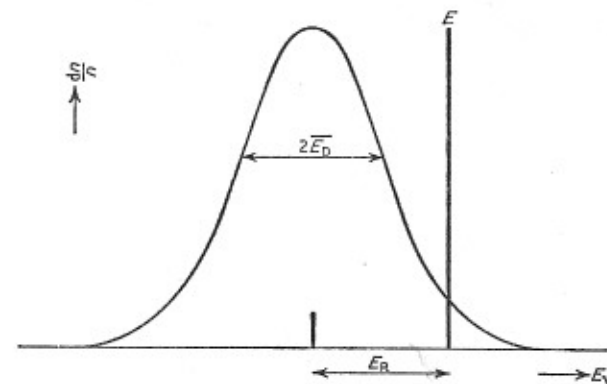

Fig. 1.2 The statistical energy distribution of the emitted γ-ray showing the inter-relationship of E, E_R, and $\overline{E_D}$.

about 10^{-2} eV. (The 14·4-keV ^{57}Fe transition at 300 K has $E_R = 1·95 \times 10^{-3}$ eV and $\overline{E_D} \sim 1·0 \times 10^{-2}$ eV).

The values of E_R and $\overline{E_D}$ can be more conveniently expressed in terms of the γ-ray energy E_γ. Thus

$$E_R = \tfrac{1}{2}Mv^2 = \frac{(Mv)^2}{2M} = \frac{p^2}{2M}$$

where p is the recoil momentum of the atom. Since momentum must be conserved, this will be equal and opposite to the momentum of the γ-ray photon, p_γ,

$$p = -p_\gamma = -\frac{E_\gamma}{c}$$

hence

$$E_R = \frac{E_\gamma{}^2}{2Mc^2} \qquad 1.3$$

Expressing E_γ in eV, M in a.m.u., and with $c = 2{\cdot}998 \times 10^{11}$ mm s^{-1} gives

$$E_R \text{ (eV)} = 5{\cdot}369 \times 10^{-10} \frac{E_\gamma{}^2}{M} \qquad 1.4$$

Likewise from equations 1.2 and 1.3

$$\overline{E_D} = 2\sqrt{(\overline{E_K}E_R)} = E_\gamma \sqrt{\frac{2\overline{E_K}}{(Mc^2)}} \qquad 1.5$$

The relevance of E_R and $\overline{E_D}$ to gamma resonance emission and absorption can now be discussed. Fundamental radiation theory tells us that the proportion of absorption is determined by the overlap between the exciting and excited energy distributions. In this case the γ-ray has lost energy E_R due to recoil of the emitting nucleus. It can easily be seen that for the reverse process where a γ-ray is reabsorbed by a nucleus a further increment of energy E_R is required since the γ-ray must provide both the nuclear excitation energy and the recoil energy of the absorbing atom $(E + E_R)$. For example, for $E_\gamma = 10^4$ eV and a mass of $M = 100$ a.m.u., it is found that $E_R = 5{\cdot}4 \times 10^{-4}$ eV and $\overline{E_D} \sim 5 \times 10^{-3}$ eV at 300 K. The amount of resonance overlap is illustrated (not to scale) as the shaded area in Fig. 1.3 and is extremely small.
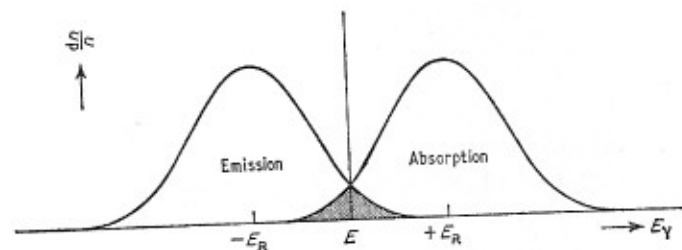

Fig. 1.3 The resonance overlap for free-atom nuclear gamma resonance is small and is shown shaded in black.

It is interesting to note that the principles outlined above are also relevant to the resonance absorption of ultraviolet radiation by atoms. However, for the typical values of $E = 6{\cdot}2$ eV (50,000 cm^{-1}) and $M = 100$ a.m.u. E_R is only $2{\cdot}1 \times 10^{-10}$ eV and E_D is $\sim 3 \times 10^{-6}$ eV. In this case strong resonance absorption is expected because the emission and absorption profiles overlap strongly. The problems associated with recoil phenomena are thus only important for very energetic transitions.

The earliest attempts to compensate for the energy disparity $2E_R$ involved the provision of a large closing Doppler velocity of about $2v$.

$$2v = \frac{2p}{M} = \frac{2p_\gamma}{M} = \frac{2E_\gamma}{Mc}$$

This was first successfully achieved by Moon [2] in 1950 using an ultracentrifuge. A mercury absorber was used, together with a ^{198}Au β-active source to generate an excited state of ^{198}Hg. The required velocity was about 7×10^5 mm s^{-1} (1600 mph). Since that time recoil has been compensated by a variety of techniques including prior radioactive decay, nuclear reactions, and the use of high temperatures to increase the Doppler broadening of the emission and absorption lines and so improve the resonant overlap. It is important to note that in all these techniques the recoil energy is being compensated for, whereas in the Mössbauer effect the recoil energy is eliminated and no compensation for recoil is required.

1.2 Heisenberg Natural Linewidth

One of the most important influences on a γ-ray energy distribution is the mean lifetime of the excited state. The uncertainties in energy and time are related to Planck's constant $h\,(= 2\pi\hbar)$ by the Heisenberg uncertainty principle

$$\Delta E\, \Delta t \geqslant \hbar$$

The ground-state nuclear level has an infinite lifetime and hence a zero uncertainty in energy. However, the excited state of the source has a mean life τ of a microsecond or less, so that there will be a spread of γ-ray energies of width Γ_s at half height where

$$\Gamma_s \tau = \hbar$$

Whence, substituting numerical values and remembering that the mean life τ is related to the half-life $t_{\frac{1}{2}}$ by the relation $\tau = \ln 2 \times t_{\frac{1}{2}}$:

$$\Gamma_s \text{ (eV)} = \frac{4{\cdot}562 \times 10^{-16}}{t_{\frac{1}{2}} \text{ (s)}} \qquad 1.6$$

For a typical case (^{57}Fe), $t_{\frac{1}{2}}$ is $97{\cdot}7$ ns and Γ_s is $4{\cdot}67 \times 10^{-9}$ eV. This is some 10^6–10^7 times less than the values of E_R and $\overline{E_D}$ for a free atom and so can be neglected in that case; this was done implicitly in the preceding section where the γ-transition energy E was represented as a single value rather than as an energy profile. However, it can be seen that if the recoil and thermal broadening could be eliminated, radiation with a monochromaticity approaching 1 part in 10^{12} could be obtained.

1.3 Energy and Momentum Transfer to the Lattice

Chemical binding and lattice energies in solids are of the order of 1–10 eV, and are considerably greater than the free-atom recoil energies E_R. If the emitting atom is unable to recoil freely because of chemical binding, the recoiling mass can be considered to be the mass of the whole crystal rather than the mass of the single emitting atom. Equation 1.3 will still apply, but the mass M is now that of the whole crystallite which even in a fine powder contains at least 10^{15} atoms. This diminution of E_R by a factor of 10^{15} makes it completely negligible. From equation 1.5, $\overline{E_D}$ will also be negligible in these circumstances.

However, the foregoing treatment is somewhat of an over-simplification. The nucleus is not bound rigidly in the crystal as assumed above, but is free to vibrate. In these circumstances it is still true that the recoil momentum is transferred to the crystal as a whole, since the mean displacement of the vibrating atom about its lattice position averages essentially to zero during the time of the nuclear decay, and the only random translational motion involves the whole crystal, and is negligible. However, the recoil energy of a single nucleus can be taken up either by the whole crystal as envisaged above or it can be transferred to the lattice by increasing the vibrational energy of the crystal, particularly as the two energies are of the same order of magnitude. The vibrational energy levels of the crystal are quantised: only certain energy increments are allowed and unless the recoil energy corresponds closely with one of the allowed increments it cannot be transferred to the lattice, thus ensuring that the whole crystal recoils, leading to negligible recoil energy. It can be seen that the necessary condition for the Mössbauer effect to occur is that the nucleus emitting the γ-photon should be in an atom which has established vibrational integrity with the solid matrix. In practice this criterion can be relaxed slightly (see p. 346) and the effect can sometimes be observed in viscous liquids.

The vibrational energy of the lattice as a whole can only change by discrete amounts 0, $\pm\hbar\omega$, $\pm 2\hbar\omega$, etc. If $E_R < \hbar\omega$ then either zero or $\hbar\omega$ units of vibrational energy but nothing intermediate can be transferred. If a fraction, f, of γ-photons are emitted without transfer of recoil energy to the vibrational states of the lattice (zero-phonon transitions), then a fraction $(1-f)$ will transfer one phonon $\hbar\omega$, neglecting all higher multiples of $\hbar\omega$ to a first approximation. Lipkin [3] has shown that if many emission processes are considered, the average energy transferred per event is exactly the free-atom recoil energy: or on our simple model

$$E_R = (1-f)\hbar\omega \qquad 1.7$$

$$f = 1 - \frac{E_R}{\hbar\omega}$$

Since the preceding discussion is fundamental to an understanding of the Mössbauer effect, it is worthwhile restating the main lines of argument to emphasise their significance. The relevant orders of magnitude of the energy terms are given in Table 1.1. The Heisenberg widths of the Mössbauer γ-rays

Table 1.1 Some typical energies
(1 eV = 23·06 kcal mole^{-1} = 96·48 kJ mole^{-1})

Mössbauer γ-ray energies (E_γ)	10^4–10^5 eV
Chemical binding and lattice energies	1–10 eV
Free-atom recoil energies (E_R)	10^{-4}–10^{-1} eV
Lattice vibration phonon energies	10^{-3}–10^{-1} eV
Heisenberg natural linewidths (Γ_s)	10^{-9}–10^{-6} eV

permit an intrinsic resolving power of 10^{-10} to 10^{-14} of the γ-ray energies. When compared with other spectroscopic methods (e.g. u.v.–visible $\sim 10^{-1}$, gas-phase infrared $\sim 10^{-3}$, atomic line spectra $\sim 10^{-8}$), this emphasises the enormous potential for measuring minute proportionate energy differences. However, in the presence of free-atom recoil and thermal broadening effects the resolution drops to 10^{-6} to 10^{-9}.

It is important to emphasise that γ-ray energies cannot be measured with this accuracy on an absolute scale; indeed these energies are seldom known to better than 1 part in 10^4. In order to use the precision of the Heisenberg width, it is customary to use as a reference a radioactive source in which all the emitting atoms have an identical chemical environment. This is then compared to an absorbing chemical matrix of the same element and only the minute *difference* between the two transition energies is measured. The means whereby this is accomplished will be discussed shortly.

To summarise: in the Mössbauer experiment the emitting and absorbing nuclei are embedded in a solid lattice or matrix; this results in the recoil momentum being taken up by the crystal as a whole since the free-atom recoil energy ($\leqslant 10^{-1}$ eV) is insufficient to eject the atom from the lattice site (binding energy 1–10 eV) thus precluding momentum transfer to linear translational motion of the nucleus, and the lattice vibrations cannot take up the momentum because a time-average of zero is established within the decay time. Similarly, the total energy of the γ-transition E must be conserved and can only be shared between

(a) the energy of the γ-photon, E_γ;
(b) the lattice vibrations;
(c) the translational kinetic energy of the individual atom;
(d) the translational kinetic energy of the solid as a whole.

The third of these possibilities is eliminated by the high chemical binding energy and the fourth has been shown to be minute because of the large mass

involved. The γ-transition energy is thus shared between the γ-photons and the lattice vibration phonons. Because of quantisation conditions, a fraction of events, f, occur with no change in the lattice vibrations and the entire transition energy E is manifest in the γ-photon energy ($E = E_\gamma$).

It must be emphasised that the preceding discussion represents a considerable simplification of the actual situation. For example, a single lattice vibration frequency corresponds to an Einstein solid. A Debye model is more realistic, and includes frequencies ranging from zero to a maximum value ω_D. Fortunately, the very low frequencies are difficult to excite, otherwise the Mössbauer effect would not exist. Although it is not intended to discuss more advanced treatments here, several texts are readily available [4–5]. Since our main interest is in the events without recoil, the fact that γ-rays with an energy different to E are produced is often forgotten. A theoretical γ-photon energy spectrum calculated by Visscher [4] for iridium is shown in Fig. 1.4. The recoil-free line with zero energy shift should be contrasted with the very broad distribution of events with phonon excitations.
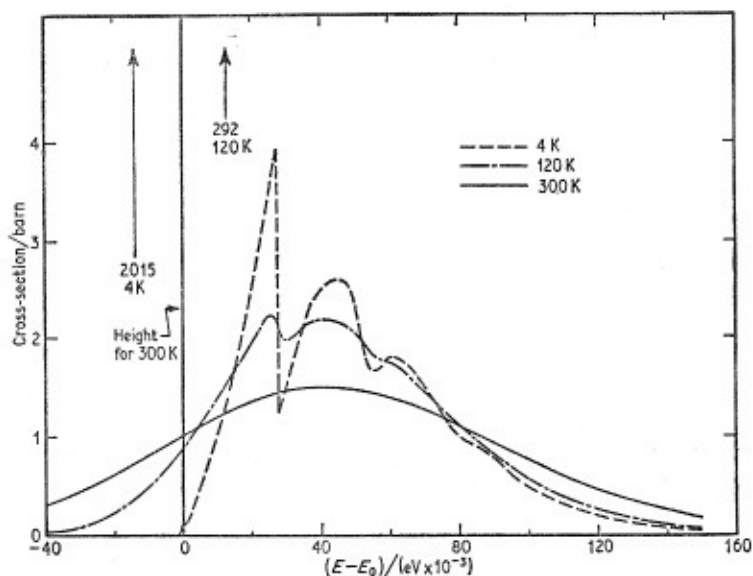

Fig. 1.4 The absorption cross-section for a nucleus in iridium metal calculated assuming a Debye model for the lattice vibrations at three different temperatures.

Looking back, physicists have been tempted to wonder why the recoilless emission of γ-rays was not discovered earlier. The full theory had been worked out by Lamb in 1939 for the analogous case of absorption of neutrons [6]. Similarly the diffraction of X-rays depends on the same effect. namely the elastic scattering which leaves the wavelength (energy) of the X-ray beam unchanged. Indeed, the fact that in X-ray diffraction thermal motion of the

atoms weakens the diffraction maxima but does not broaden them is precisely the Mössbauer effect: the probability of zero-phonon events diminishes but those observed are still unbroadened by Doppler or recoil effects.

We have now reached the stage of realising that, for a γ-emitter in a solid, there is a finite probability that the γ-ray can be emitted essentially without recoil or thermal broadening and that the width of the line derives from the Heisenberg uncertainty principle. We next seek to calculate what this probability will be.

1.4 Recoil-free Fraction and Debye–Waller Factor

We have already seen qualitatively that the recoil-free fraction or probability of zero-phonon events will depend on three things:

(a) the free-atom recoil energy, which is itself proportional to E_γ^2;
(b) the properties of the solid lattice;
(c) the ambient temperature.

Thus f will be greater the smaller the probability of exciting lattice vibrations, i.e. the smaller the γ-ray energy, the firmer the binding of the atom in the lattice and the lower the temperature.

From a quantitative viewpoint, the probability W of zero-phonon γ-emission from a nucleus embedded in a solid which simultaneously changes its vibration state can be calculated by dispersion theory [3, 5]; it is proportional to the square of the matrix element connecting the initial $|\,i\rangle$ and final $\langle f\,|$ states.

$$W = \text{const} \times |\langle f\,|\,\mathscr{H}\,|\,i\rangle|^2$$

where $\mathscr{H}$ is the interaction Hamiltonian operator and depends upon the positional coordinates of the atom (nucleus) and the momenta and spins of the particles within the nucleus. The forces acting within the nucleus are extremely short range whereas those holding the lattice together are of much longer range [6]. Hence the nuclear decay is independent of the vibrational state and *vice versa*, thus enabling the matrix element to be split into two parts of which the nuclear part will be a constant depending only on the properties of the particular nucleus. The matrix element can now be reduced to the one term for the transition from the initial vibrational state L_i to the final state L_f. The form of the operator is such that

$$W = \text{const} \times |\langle L_f\,|\,e^{ik.x}\,|\,L_i\rangle|^2$$

where $k\,(= p/\hbar)$ is the wave vector for the emitted γ-photon, i.e. the number of units of momentum it carries, and x is the coordinate vector of the centre of mass of the decaying nucleus. For zero-phonon emission the lattice modes are unchanged and hence the probability for recoilless emission is

$$f = \text{const} \times |\langle L_i\,|\,e^{ik.x}\,|\,L_i\rangle|^2 \qquad 1.8$$

and since L_i is normalised

$$f = e^{-k^2 \cdot x^2} \qquad 1.9$$

Further, since x is a random vibration vector, x^2 can be replaced by $\langle x^2 \rangle$, the component of the mean square vibrational amplitude of the emitting atom in the direction of the γ-ray. Since $k^2 = 4\pi^2/\lambda^2 = E_\gamma^2/(\hbar c)^2$, where λ is the wavelength of the γ-ray, we obtain

$$f = \exp\left(\frac{-4\pi^2 \langle x^2 \rangle}{\lambda^2}\right) = \exp\left(\frac{-E_\gamma^2 \langle x^2 \rangle}{(\hbar c)^2}\right) \qquad 1.10$$

Equation (1.10) indicates that the probability of zero-phonon emission decreases exponentially with the square of the γ-ray energy. This places an upper limit on the usable values of E_γ, and the highest transition energy for which a measurable Mössbauer effect has been reported is 155 keV for ^{188}Os. Equation 1.10 also shows that f increases exponentially with decrease in $\langle x^2 \rangle$ which in turn depends on the firmness of binding and on the temperature. The displacement of the nucleus must be small compared to the wavelength λ of the γ-ray. This is why the Mössbauer effect is not detectable in gases and non-viscous liquids. Clearly, however, a study of the temperature dependence of the recoil-free fraction affords a valuable means of studying the lattice dynamics of crystals.

To proceed further it is necessary to assume some model for the vibrational modes of the crystal. The mathematics become more severe and the results are somewhat unrewarding, since very few of the solids which chemists may be interested in approximate even remotely to the assumptions made in setting up the models. However, the form of the expressions is instructive.

The simplest model is due to Einstein (1907) and assumes the solid to be composed of a large number of independent linear harmonic oscillators each vibrating at a frequency ω_E. The appropriate integration of equation 1.8 gives

$$f = \exp\left(\frac{-E_R}{\hbar \omega_E}\right) = \exp\left(\frac{-E_R}{k\theta_E}\right) \qquad 1.11$$

where θ_E is a characteristic temperature of the lattice given by $k\theta_E = \hbar\omega_E$. If $E_R \ll k\theta_E$ then $f \simeq 1 - E_R/k\theta_E$ as intuitively derived in equation 1.7.

The Debye model (1912) abandons the idea of a single vibration frequency and embodies a continuum of oscillator frequencies ranging from zero up to a maximum ω_D and following the distribution formula $N(\omega) = \text{const} \times \omega^2$. A characteristic temperature called the Debye temperature θ_D is defined as $\hbar\omega_D = k\theta_D$, and the average frequency is

$$\hbar\bar{\omega} = \tfrac{3}{4}\hbar\omega_D$$

The Debye temperature θ_D for metals varies from 88 K for lead to 1000 K for beryllium. Values of θ_D are often also assigned to chemical compounds,

but since the Debye model is grossly inadequate even for many of the pure metals, the values used for compounds are merely an indication of the approximate lattice properties and should not be considered too seriously.

The Debye model leads to

$$k^2 \cdot x^2 = \frac{\hbar}{2M} \int_0^{\omega_D} \frac{N(\omega)}{\omega} \coth\left(\frac{\hbar\omega}{2kT}\right) d\omega$$

which integrates to the more familiar equation

$$f = \exp\left[\frac{-6E_R}{k\theta_D}\left\{\frac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} \frac{x\,dx}{e^x - 1}\right\}\right] \qquad 1.12$$

This is often written as $f = e^{-2W}$. The factor W is sometimes loosely called the Debye–Waller factor though it might be better in this context to call it the Lamb–Mössbauer factor.

The Debye–Waller factor was originally derived during the development of Bragg X-ray scattering theory. The difference between the two effects is that X-ray scattering is fast when compared with the characteristic time for lattice vibrations whereas the mean lifetime of a Mössbauer nucleus is long when compared with the lattice time.

At low temperatures where $T \ll \theta_D$ we can reduce equation 1.12 to the approximation

$$f = \exp\left[\frac{-E_R}{k\theta_D}\left\{\frac{3}{2} + \frac{\pi^2 T^2}{\theta_D^2}\right\}\right] \qquad T \ll \theta_D \qquad 1.13$$

and at absolute zero

$$f = \exp\left[\frac{-3E_R}{2k\theta_D}\right] \qquad 1.14$$

In the high temperature limit

$$f = \exp\left[\frac{-6E_R T}{k\theta_D^2}\right] \qquad T \gg \tfrac{1}{2}\theta_D \qquad 1.15$$

From equation 1.15 W is proportional to T at high temperatures. Experience shows that experimentally this is usually not the case because of anharmonicity of the lattice vibrations. The effects of anharmonicity have been discussed at length by Boyle and Hall [7] and will be met again in connection with the intensities of individual lines in hyperfine interactions.

1.5 Cross-section for Resonant Reabsorption

We have described the mechanism by which a γ-ray can be emitted without recoil and the same arguments apply to resonant reabsorption. Since Mössbauer experiments usually utilise the recoilless emission of γ-rays by a

radioactive source followed by their subsequent resonant recoilless reabsorption by a non-active absorber, we must now consider this process in detail.

The probability of recoilless emission from the source is f_s. This recoilless radiation has a Heisenberg width at half height of Γ_s and the distribution of energies about the energy E_γ is given by the Breit–Wigner formula [8]. This leads to a Lorentzian distribution, i.e. the number of transitions $N(E)$ with energy between $(E_\gamma - E)$ and $(E_\gamma - E + \mathrm{d}E)$ is given by

$$N(E)\,\mathrm{d}E = \frac{f_s\Gamma_s}{2\pi}\,\frac{\mathrm{d}E}{(E - E_\gamma)^2 + (\Gamma_s/2)^2} \qquad 1.16$$

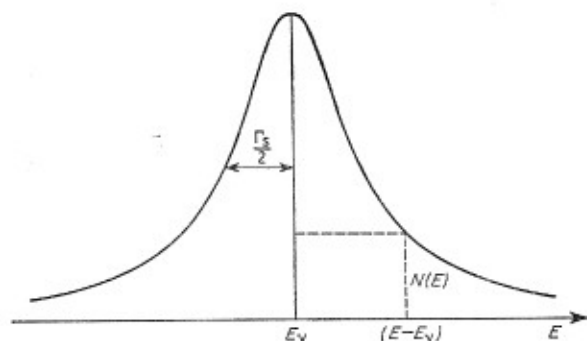This distribution is illustrated in Fig. 1.5.

Fig. 1.5 The Lorentzian energy distribution of the source recoilless radiation.

The resonant absorption cross-section $\sigma(E)$ can be similarly expressed as

$$\sigma(E) = \sigma_0\frac{(\Gamma_a/2)^2}{(E - E_\gamma)^2 + (\Gamma_a/2)^2} \qquad 1.17$$

where Γ_a is the Heisenberg width at half-height of the absorption profile and σ_0 is the effective cross-section given by

$$\sigma_0 = 2\pi\lambda^2\frac{2I_e + 1}{2I_g + 1}\frac{1}{1 + \alpha} \qquad 1.18$$

where I_e and I_g are the nuclear spin quantum numbers of the excited and ground states and α is the internal conversion coefficient of the γ-ray of wavelength λ. (Not all nuclear γ transitions produce a physically detectable γ-ray; a proportion eject electrons from the atomic orbitals, giving X-rays and these internal conversion electrons instead. The internal conversion coefficient of a γ-transition is defined as the ratio of the number of conversion electrons to

the number of γ-ray photons emitted.) Using the relation between λ and E_γ in equation 1.10 we obtain the expression

$$\sigma_0(\mathrm{cm}^2) = \frac{2\cdot446 \times 10^{-15}}{(E_\gamma\,\mathrm{keV})^2}\frac{2I_e + 1}{2I_g + 1}\frac{1}{1 + \alpha} \qquad 1.19$$

σ_0 values are sometimes expressed in units of barns ($= 10^{-24}\,\mathrm{cm}^2$). Equation 1.19 shows that the desirability of a high absorption cross-section requires that both E_γ and α have low values. The resonant absorption process will also be in competition with other absorption processes such as photoelectric absorption, and it is important that the cross-section for nuclear resonance absorption should be higher than that for any other method of γ-ray attenuation. A full tabulation of physical parameters for Mössbauer resonances is to be found in Appendix 1 on p. 607.

The preceding equations already indicate the numerous parameters which will influence the intensity of an emission-absorption resonance:

(a) nuclear properties: the cross-section of γ-ray absorption and hence E_γ, I_e, I_g, and α
(b) source properties: the recoil-free fraction f_s and the Heisenberg width Γ_s
(c) absorber properties: the recoil-free fraction for absorption f_a and the Heisenberg width Γ_a.

A completely general evaluation of the problem is impossible, but useful results are obtained if we assume that both source and absorber have the same linewidth ($\Gamma = \Gamma_s = \Gamma_a$). Margulies and Ehrman [9] showed that the γ-transmission through a uniform resonant absorber can be represented by

$$T(\varepsilon) = e^{-\mu_a t_a}\left\{(1 - f_s)\int_0^\infty \rho(x)\,e^{-\mu_s x}\,\mathrm{d}x\right.$$

$$+ \frac{f_s\Gamma}{2\pi}\int_{-\infty}^\infty \exp\left[-f_a n_a a_a \sigma_0 t_a\frac{(\Gamma/2)^2}{(E - E_\gamma)^2 + (\Gamma/2)^2}\right]$$

$$\times \int_0^\infty \frac{\rho(x)}{(E - E_\gamma + \varepsilon)^2 + (\Gamma/2)^2}$$

$$\left.\times \exp\left[-\left(f_s n_s a_s \sigma_0\frac{(\Gamma/2)^2}{(E - E_\gamma + \varepsilon)^2 + (\Gamma/2)^2} + \mu_s\right)x\right]\mathrm{d}x\,\mathrm{d}E\right\} \qquad 1.20$$

where ε is an energy displacement between the source and absorber distribution maxima,
n_s, n_a = number of atoms of the element concerned per cm^3 in the source and the absorber respectively,
a_s, a_a = fractional abundance of the resonant isotope,

μ_s, μ_a = mass absorption coefficients (cm^{-1}) for the source and absorber evaluated at energy E_γ,

t_a = thickness of the absorber in cm,

x = depth of the emitting atom normal to the surface of the source as shown in Fig. 1.6.

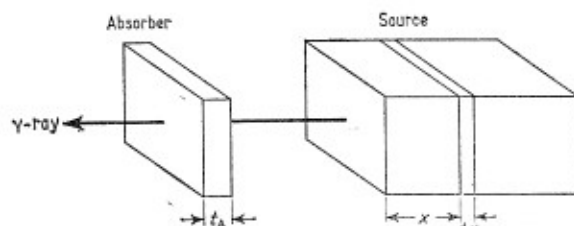$\rho(x)$ = distribution of emitting atoms along the x direction in the source.

Fig. 1.6 Schematic representation of parameters used in calculating resonant transmission for source and absorber of finite thickness.

The first term in equation 1.20 is the transmission of the non-resonant radiation and is independent of ε. The first part of the second term is the resonant absorption in the absorber and the second part is the resonant absorption in the source. The factor $\varepsilon^{-\mu_a t_a}$ accounts for non-resonant scattering in the absorber.

Margulies and Ehrman solved this equation for certain interesting simplified cases. If the source and absorber have a thickness tending to zero (i.e. are ideally thin), the decrease in transmission with respect to ε is given by

$$I(\varepsilon) = \frac{\Gamma_r}{2\pi} \times \frac{1}{(\varepsilon - E_\gamma)^2 + (\Gamma_r/2)^2} \qquad 1.21$$

This is normalised so that $\int_0^\infty I(\varepsilon)\, d\varepsilon = 1$.

Γ_r is the sum of the emission and absorption half-widths, i.e. $\Gamma_r = 2\Gamma$ and the distribution is still Lorentzian. If the absorber has an effective thickness $T = f_a n_a a_a \sigma_o t_a$ the shape is still basically Lorentzian but will be broadened[5] so that

$$\frac{\Gamma_r}{\Gamma} = 2{\cdot}00 + 0{\cdot}27T \qquad 0 < T \leqslant 5 \qquad 1.22$$

$$\frac{\Gamma_r}{\Gamma} = 2{\cdot}02 + 0{\cdot}29T - 0{\cdot}005T^2 \qquad 4 \leqslant T \leqslant 10$$

If we can measure Γ_r for a series of thicknesses, T, it is possible to obtain the true value of $\Gamma = \frac{1}{2}\Gamma_r (T \to 0)$.

The numerical significance of the equations will be discussed more fully in connection with absorber preparation in Chapter 2.

1.6 A Mössbauer Spectrum

The preceding five sections have provided the basic concepts necessary for an understanding of the Mössbauer effect and we now describe the experimental observation of a Mössbauer spectrum. If γ-rays from a source which has a substantial recoil-free fraction are passed through an absorber of the same material the transmission of the γ-rays in the direction of the beam will be less than expected because of their resonant reabsorption and subsequent re-emission over a 4π solid angle. Paradoxically, this resonance can only be shown to be present by its destruction, e.g. by warming the absorber so that the fraction of recoil-free events will decrease and the transmission increase. The principal technique of Mössbauer spectroscopy is, however, rather more subtle. It was shown in the previous section in equation 1.21 that the decrease in transmission (i.e. decrease in the extent of resonant overlap) is affected by the difference in the relative values of E_γ for the source and the absorber. The *effective* E_γ value can be altered by moving the source and absorber relative to each other with a velocity v, i.e. by using an externally applied Doppler effect [$\varepsilon = (v/c)E_\gamma$]. If the effective E_γ values are exactly matched at a certain Doppler velocity, resonance will be at a maximum and the count-rate a minimum. At any higher or lower applied velocity, the resonance will
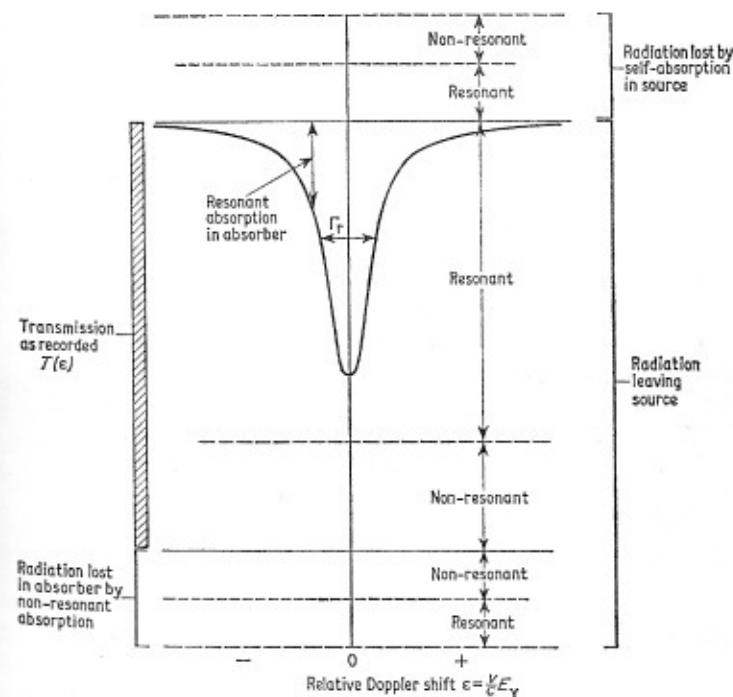

Fig. 1.7 A Mössbauer transmission spectrum produced by Doppler scanning, and the factors influencing it.

decrease until it is effectively zero at velocities well away from that defining the maximum resonance.

This is the basic form of a Mössbauer spectrum; a plot of transmission versus a series of Doppler velocities between source and absorber (i.e. versus the effective γ-ray energy), the absorption line being Lorentzian in shape with a width at half-height corresponding to 2Γ. The various factors influencing the transmission spectrum are illustrated schematically in Fig. 1.7, which is self-explanatory.

It should not be forgotten that the excited absorber nuclei re-emit the γ-ray within $\sim 10^{-7}$ s. However, if the internal conversion coefficient is high, correspondingly fewer γ-rays will be emitted. More important, however, the re-emission is not directional but takes place over the full 4π solid angle. Consequently the number of secondary events recorded at the detector in a collimated transmission experiment are few and are usually neglected.

We shall return to the theoretical discussion again in Chapter 3 to see how the spectrum can be influenced in detail by various properties of the resonant nucleus and by the extra-nuclear electrons. Before then, however, it will be convenient to outline the experimental techniques of Mössbauer spectroscopy and this forms the subject of the next chapter.

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2 | Experimental Techniques

In this chapter we shall consider the various techniques which have been used for observation of the Mössbauer effect, together with methods of source and absorber preparation and computer techniques for data analysis. Some of the advantages and limitations of Mössbauer spectroscopy will become apparent during the discussion of these problems. References to more recent development will be found in the review by J. R. De Voe and J. J. Spijkerman in *Analytical Chemistry*, 1970, **42**, 366R, and in 'Spectroscopic Properties of Inorganic and Organometallic Compounds' published annually by the Chemical Society (London).

A few of the very earliest observations of the Mössbauer effect involved a static experiment in which a source and absorber of identical chemical form were maintained in a stationary transmission arrangement. Under these conditions one would expect some nuclear resonance absorption but this can only be verified by demonstrating its diminution or increase; thus an increase in the temperature of the system will increase the counting rate because of the decreasing fraction of resonant absorption, whereas a lowering of the temperature increases the recoil-free fraction and lowers the counting rate of transmitted γ-photons. This technique was the basis of Mössbauer's original observations [1]. It does not however provide much significant information and may fail completely if the source and absorber are not chemically identical.

The method of velocity modulation of the γ-ray energy by means of the Doppler effect was described by Mössbauer in 1958 [2] and provides the basis for all modern spectrometers.

2.1 Velocity Modulation of Gamma-rays

The recoil-free γ-ray energy of a typical Mössbauer transition is so precisely defined that its Heisenberg width corresponds to the energy change produced by an applied Doppler velocity of the order of 1 mm s^{-1}. It is therefore possible to imagine a particular relative velocity between source and absorber at which the γ-ray energy from the source will precisely match the nuclear