Mössbauer spectroscopy and its applications

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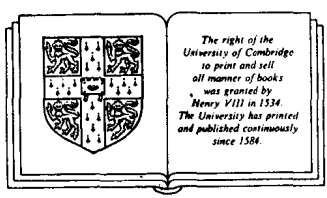

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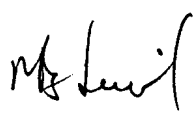
FOREWORD

It is more than 25 years since R.L. Mössbauer carried out the pioneering experiments on Resonance Spectroscopy of Gamma-rays which developed into the now well established powerful and versatile tool, known as Mössbauer Spectroscopy, for the study of solid state properties. The intrinsically high energy sensitivity of the technique and the relatively simple instrumentation needed, have led to the general availability of the technique and to a wide range of applications in many different fields.

The present volume aims at providing an introduction to the fundamental phenomena of the Mössbauer effect, to the experimental methods, and to the applications of Mössbauer Spectroscopy in many fields, including Solid State Physics and Chemistry, Metallurgy, Magnetism, Radiation Damage, Surface Science, Biochemistry, and Archaeology. The book should serve as an introductory text to final year undergraduates and to graduate students, and should provide the specialist with information outside his immediate field of interest.



P.B. Hirsch

Oxford 1985

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CHAPTER I

THE MÖSSBAUER EFFECT

Resonance Absorption of Radiation by Free Atoms

The resonance absorption of radiation is a phenomenon well known in many branches of physics. The excitation of a tuning fork by sound at its resonance frequency, the scattering of sodium light by sodium vapour and the excitation of a dipole by radiofrequency radiation are some familiar examples. It might be thought that the same phenomenon should occur for the γ-radiation emitted when nuclei in excited states lose their energy by radiation. However, the effect of the recoil momentum, which can be neglected for sound and light, becomes dominant for γ-radiation, because of its much higher energy. This may be illustrated by comparing typical cases of γ-emission and optical emission.

Consider the emission of radiation from free atoms. Let the energy of the excited state be E_1 above that of the ground state, and the energy of the photon be E_γ. Then the momentum of the photon is $p = E_\gamma/c$. By the conservation of momentum this is the momentum p_R of the recoiling atom, so the recoil energy E_R of the atom is

$$E_R = \frac{p_R^2}{2M} = \frac{E_\gamma^2}{2Mc^2} \approx \frac{E_1^2}{2Mc^2} \qquad (1.1)$$

where M is the mass of the atom. Thus

$$E_\gamma = E_1 - E_R \approx E_1 - \frac{E_1^2}{2Mc^2} \qquad (1.2)$$

In absorption, the recoil momentum is in the opposite direction, so that the absorbed energy is less than E_1 by twice the recoil energy i.e. E_1^2/Mc^2.

In all this it has been assumed that the emitting atom is at rest. In a gas the motion of the atoms will broaden the energy of the γ-rays. Let us suppose that an atom has velocity v making an angle θ with the direction of emission. Then the energy of the photon is changed by the Doppler effect to E'_γ so that

$$E'_\gamma = E_\gamma + E_\gamma \frac{v}{c} \cos\theta \qquad (1.3)$$

The expressions become simpler if we write $\epsilon = \frac{1}{2}Mv^2$ for the kinetic energy of the atom. Then

$$\Delta E_\gamma = E'_\gamma - E_\gamma = E_\gamma \frac{v}{c} \cos\theta = 2\sqrt{\epsilon E_R} \cos\theta \qquad (1.4)$$

Then if we allow θ to take all possible values, the spectrum is broadened by an amount

$$\Delta = 2\sqrt{\bar{\epsilon} E_R} \qquad (1.5)$$

Where $\bar{\epsilon}$ is the mean value of ε. Table I shows the values of E_I E_R and Δ for typical cases of optical emission (E = 2eV, equivalent to a wavelength of 6000Å) and γ-ray emission (E = 100 keV), assuming as mass M = 100 and $\bar{\epsilon} \simeq 0.025$ eV corresponding to room temperature.

TABLE I

	optical	γ-ray
	eV	eV
E_I	2	10^5
E_R	2×10^{-11}	10^{-1}
Δ	10^{-6}	10^{-1}

We see that in the optical case, the recoil energy is negligible compared with the Doppler broadening, whereas in the case of

γ-emission, the two are comparable. The comparison is more striking when we note that the "natural width" of the lines may be closely the same.

The "natural width" can be envisaged in the following way. A decaying nucleus produces an electric field at a point x given by

$$\xi_o(x,t) = \xi_o \exp \{i(\omega_o t - \kappa x) - \Gamma t/2\} \qquad (1.6)$$

where ω_o and κ are the angular frequency and wave vector of the radiation. Then the probability P(t) of detection of the decay is given by $|\xi(t)|^2$ which decreases with a lifetime $\tau = 1/\Gamma$. Quantum mechanically the natural width Γ of the state obeys a relation similar to the Heisenberg Uncertainty relation,

$$\Gamma \tau \geq \hbar \qquad (1.7)$$

where τ is the lifetime for decay of the excited state. In both optical and γ-ray cases, we might have a lifetime of 10^{-7} s corresponding to $\Gamma \sim 10^{-8}$ eV. Then for the optical case the recoil energy is negligible. The Doppler broadening is somewhat greater than the line width, and may be observed in suitably designed experiments. For the γ-ray case, on the contrary, both the Doppler broadening Δ and the recoil energy E_R are much larger than the line width Γ and resonance absorption may not be observable.

Before the discovery of the Mössbauer effect, some successful experiments on nuclear resonance absorption had been carried out. These experiments made use of two ideas: (i) the energy difference $2E_R$ may be directly supplied by utilising the Doppler effect as shown in Figs. 1. 1a and 1b. The velocities required are high ($\sim 10^2 - 10^3$ m s^{-1}), and were obtained by two methods: The emitting nuclei may be mounted on a high speed rotor, or the nuclei may be given their velocity by recoiling from a prior nuclear disintegration. (ii) the thermal broadening may be increased by heating the source and absorber, so that some overlap of the lines occurs, as shown in Fig. 1.2. In 1957, R.L. Mössbauer (1958) carrying out experiments of this kind on the nucleus ^{191}Ir found that lowering the temperature increases the absorption rather than decreasing it. This was due to a previously unsuspected effect which Mössbauer was able

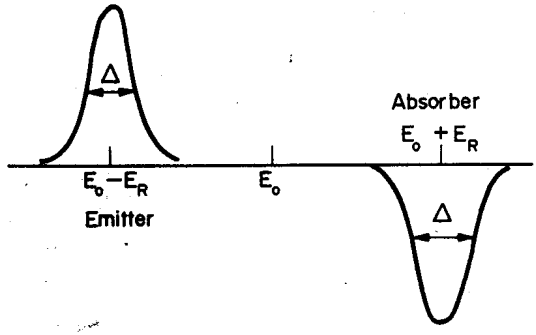

Fig. 1.1a Recoil energy prevents the observation of NRA (Nuclear resonance absorption)

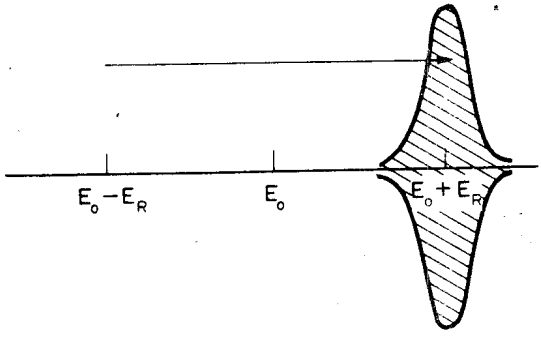

Fig. 1.1b NRA may be observed if the γ-ray energy is Doppler shifted by $2E_R$

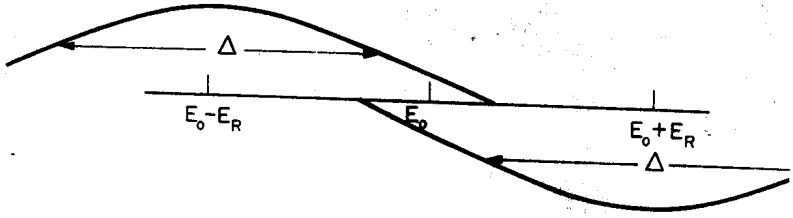

Fig. 1.2 NRA may be observed if the source and absorber are heated

to explain, and which is now known as the Mössbauer Effect.

Resonance Absorption of Radiation by Atoms Bound in a Solid

(i) Classical description

The Mössbauer effect arises when we consider emitting atoms which are bound in a crystal and we take into account the fact that they are no longer able to recoil individually. A full account of the energy distribution of the radiation requires a quantum mechanical treatment, but we first give a classical account which brings out several of the essential points.

A classical radiator does not experience the recoil effect, but the distribution in frequency is entirely governed by the Doppler effect. Thus we return to (1.6) and neglecting the effect of decay

$$\xi = \xi_o \exp \{i(\omega_o t - \kappa x)\} \qquad (1.8)$$

gives the disturbance due to an emitter at x. If $x = vt$, we have

$$\xi = \xi_o \exp \{i(\omega_o - \kappa v)t\} \qquad (1.9)$$

which is the expression for the Doppler effect. Now suppose $v = a \cos \omega t$, representing a source oscillating harmonically about the origin with velocity amplitude a and frequency ω. Then

$$\xi = \xi_o \exp (i \omega_o t) \exp (-i\kappa a \cos \omega t)t$$

$$= \xi_o \exp \{i(\omega_o - a\kappa \cos \omega t)t\} \qquad (1.10)$$

This is the expression for a frequency modulated wave with the "modulation index" $m_\omega = \frac{a\kappa}{\omega}$, which can be Fourier analysed into a component with frequency ω_o and "sidebands" at frequencies $\omega_o \pm n\omega$ where $n = 1, 2 \ldots\ldots$ If m_ω is small, the standard theory shows that the intensity of radiation with frequency ω_o is $J_o^2 (m_\omega)$, or f, the fraction of the radiated energy with

frequency ω_o, is given by

$$f = J_o^2 (\kappa x_o) \tag{1.11}$$

where x_o is the peak displacement of the atom from its equilibrium position and J_o is the Bessel function of order one. This is the answer for an Einstein crystal, where atoms are represented by harmonic oscillators of frequency ω_E.

In a more realistic model, there will be a large number of frequencies, and the expression for the intensity in the undisturbed line becomes

$$f = \prod_m J_o^2 (\kappa x_m) \tag{1.12}$$

where x_m is the peak amplitude for the m^{th} mode. Since x_m is small for each value of m, we can make use of the expansion

$$J_o(y) = 1 - \tfrac{1}{4} y^2 \tag{1.13}$$

and then

$$\ln f = 2 \sum_m \ln J_o \sim 2 \sum_m \ln \{1 - \tfrac{1}{4} (\kappa x_m)^2\}$$

$$\sim = 2 \sum_m \tfrac{1}{4} \kappa^2 x_m^2 \tag{1.14}$$

For harmonic oscillation, the mean square deviation is given by $\langle x^2 \rangle = \frac{1}{2} \sum_m x_m^2$ so that

$$f = \exp (-\kappa^2 \langle x^2 \rangle) \tag{1.15}$$

(ii) Quantum description

In a quantum mechanical description, the physical origin of the Mössbauer Effect, i.e. of the possibility of momentum transfer without energy transfer, lies in the quantum nature of lattice

vibrations. On the Einstein model of a solid the lattice can only have an energy 0, $h\omega_E$, $2h\omega_E$, ... and so can only change its energy in units of $h\omega_E$. So if E_R is less than $h\omega$ the lattice cannot absorb the recoil energy, and the γ-ray is emitted with energy E_1. On the Debye model there is a spectrum of frequencies ω up to a maximum cut-off frequency ω_D. The conclusion when E_R is less than $h\omega_D$ is the same as for the Einstein frequency, but we now have to consider the possibility of the excitation of the lattice (phonons) at a lower frequency, say ω_D/N. It turns out that this involves the excitation of N atoms together, so that the recoil energy to be absorbed is now smaller and is E_R/N, which is again too small to excite the lattice.

The detailed quantum mechanical calculation shows that the probability of recoilless emission on absorption is

$$f = \exp\ (-\kappa^2 \langle x^2 \rangle)$$

the same result as previously obtained by a classical treatment.

The recoilless fraction f

The probability of emission (or absorption) of γ-rays is given by (1.15). Before proceeding to a calculation of $\langle x^2 \rangle$ for crystals, it will be instructive to consider the implications of (1.15) in some more unusual cases. The value of $\langle x^2 \rangle$ with which we are concerned is the average over a time of the order of the lifetime of the nuclear state, e.g. $\sim 10^{-7}$ s for ^{57}Fe. For a typical low energy γ-ray $\kappa \sim 5 \times 10^{10}\ m^{-1}$. The case for an optical level with $\kappa \sim 10^7\ m^{-1}$ was discussed by Dicke (1952) long before the discovery of the Mössbauer effect. He showed that in a gas the restriction of $\langle x^2 \rangle$ by collisions with other atoms can result in a strong narrowing of the line, and as a simple model, Dicke considered an atom moving in a box. This situation is approximately realized for γ-rays by the radiation emitted from krypton in a clathrate compound, where the Kr atom is trapped inside a large molecule, and only weak van der Waals type forces exist between it and its surrounding. $\langle x^2 \rangle$ is thus fixed by the structure of the molecule. It is found that over a considerable temperature region, f is independent of temperature. (Hazony et al. 1962, Steyert and Craig, 1962). We see that it is the mean square displacement of the atom which determines f, rather than its velocity or energy. As the

temperature is lowered, and the thermal energy becomes small compared with the binding energy, then the value of f starts to increase because the atom, so to speak, "sticks to the wall". A similar effect is found with Fe dissolved in In.

To estimate the value of $\langle x^2 \rangle$, we need a model of the crystal lattice, and various levels of approximation are discussed in Chapter IV on lattice dynamics. For the Einstein model $\langle x^2 \rangle = \kappa T/m\omega^2$ at high temperatures so that

$$f = \exp\left(-\kappa^2 \frac{kT}{M\omega^2}\right)$$

where ω is the characteristic frequency. For the Debye model at high temperatures

$$f = \exp\left(-6 \frac{E_R T}{k\theta_D^2}\right)$$

where $\theta_D = h\omega_D/k$ is the characteristic Debye temperature.

With zero point motion included, the Debye model gives the probability f at any temperature T that a nucleus will emit (or absorb) a γ-ray without losing (or gaining) energy from the lattice as

$$f = \exp\left\{ -\frac{3}{2} \frac{E_R}{k\theta_D} \left[1 + 4 \left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} \frac{x\, dx}{e^x - 1} \right] \right\} \quad (1.16)$$

As the temperature T increases, the fraction f decreases. We can now see the explanation of Mössbauer's result on Ir^{191}. The energy distribution for the emitted and absorbed γ-rays in a solid are as shown in Fig. 1.3. There is a zero-phonon peak whose intensity decreases with increasing temperature. Resonant absorption therefore takes place without any Doppler shift, but the effect decreases as the source and absorber are heated in contrast to the free atom case Fig. 1.2. Conversely as the temperature decreases f increases, but not indefinitely owing to zero-point energy which limits it to a maximum of $\exp\left(-\frac{3}{2} \frac{E_R}{k\theta_D}\right)$.

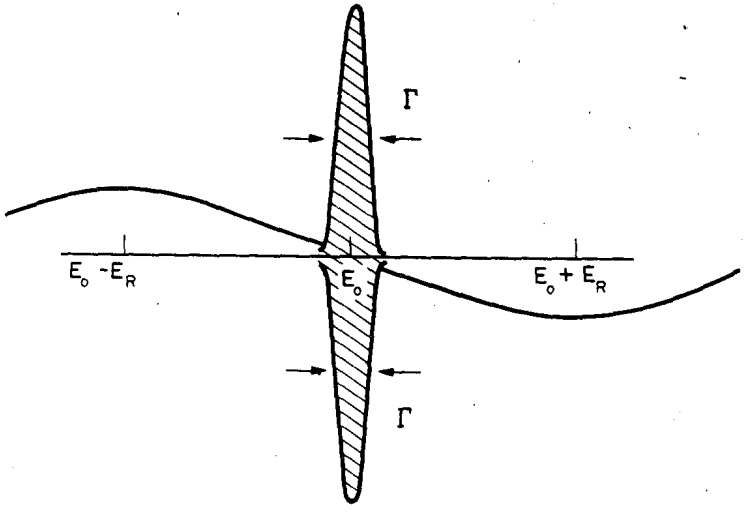

Fig. 1.3 For a bound nucleus when $E_R << k\theta_D$ there is a zero-phonon peak

The fundamental condition necessary for the Mössbauer Effect to occur is that the root mean square displacement of the nuclei (or atoms) in a solid should be less than the wavelength of the γ-radiation (see (1.15)).

The essential practical condition necessary to observe the Mössbauer Effect is $E_R < k\theta_D$ and we see thst we need γ-rays of low energy and solids with a high Debye temperature, i.e. large binding energy. Since Debye temperatures are of the order of a few hundred degrees the γ-ray energy must be of the order of 10 - 100 keV. The Mössbauer Effect has now been observed in about 100 nuclei of which the best known are ^{57}Fe (E_γ = 14.4 keV) and ^{119}Sn (E_γ = 26 keV).

Cross-section

The ease with which the Mössbauer Effect may be observed stems

from the large value of the nuclear absorption cross-section σ_o at resonance. This is given by

$$\sigma_o = \frac{1}{1+\alpha} \frac{2I_e+1}{2I_g+1} \frac{2\pi}{\kappa^2} \qquad (1.16)$$

So that when κ^2 is small (as is required to make f large) σ_o will be large. Indeed σ_o for the 14.4 KeV γ-ray of ^{57}Fe is enormous ($\sim 10^6$ barns) and is much larger than the cross-section for any other absorption process e.g. by the photo-electric effect or the Compton effect. The statistical factor $(2I_e+1)/(2I_g+1)$ is just the ratio of the degeneracy of the excited state to that of the ground state, when I_e and I_g respectively are the spins of the states, α is the internal conversion coefficient i.e. $1/(1+\alpha)$ is the fraction of transitions which occur by photons.

In terms of the resonant cross-section the shape of the absorption line is given by the Breit-Wigner formula for the cross-section σ as a function of energy E

$$\sigma = \sigma_o \frac{\Gamma^2/4}{(E-E_\gamma)^2+\Gamma^2/4} \qquad (1.17)$$

Since the emission line has an identical shape, the observed line will be the convolution of the source and absorber lines which is a Lorentzian of width (full width at half maximum) 2Γ.

Apparatus for Mössbauer Spectroscopy

The Mössbauer Effect (recoilless nuclear transition) thus enables the resonant absorption of γ-rays of "natural width" to be observed. Nuclei in solids have their energy levels split or shifted by internal (hyperfine) interactions but these have previously been undetectable by γ spectroscopy because of the thermal broadening of the line. The discovery of the Mössbauer Effect makes possible the observation of these splittings, so that we now have a useful and valuable experimental tool for probing the electronic environment of the nuclei.

The conventional type of x-ray spectrometer uses a crystal lattice set at the Bragg angle to the x-ray beam to achieve