

9 Mössbauer Spectroscopy

9.1 Recoil free resonance absorption

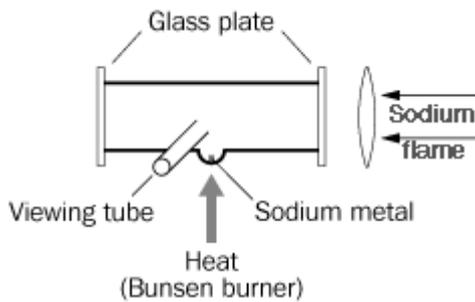
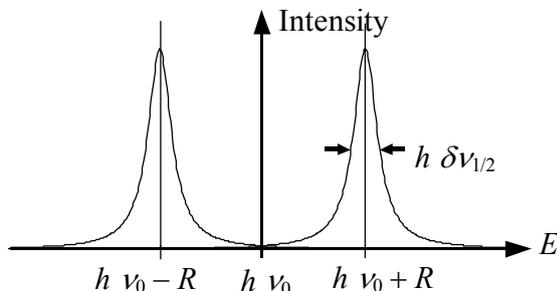


Fig. 9.1: Wood's apparatus for the resonance radiation of the sodium D lines.

Robert Wood published in 1905 an article "Resonance Radiation of Sodium Vapor" (see Literature) and reported that if a bulb containing pure sodium vapor was illuminated by light from a sodium flame, the vapor emitted a yellow light which spectroscopic analysis showed to be identical with the exciting light, in other words, the two D lines. Sodium is liquid above 98 °C, boiling point 883 °C, thus a remarkable vapor pressure exists, if sodium is heated by the Bunsen burner above 200 °C. Wood used the name "resonance radiation" for the effect of identical absorbed radiation and fluorescence radiation. Now we use the term "resonance absorption" instead.

Since 1900 γ -rays were known as a highly energetic monochromatic radiation, but the anticipated γ -ray resonance fluorescence failed to occur. Werner Kuhn succeeded in publishing such an experiment that don't work and argued in 1929: "The (third) influence, reducing the absorption, arises from the emission process of the γ -rays. The emitting atom will suffer recoil due to the projection of the γ -ray. The wavelength of the radiation is therefore shifted to the red; the emission line is displaced relative to the absorption line.... It is thus possible that by a large γ -shift, the whole emission line is brought out of the absorption region". (see Literature, Kuhn)



In the case of γ -radiation the atoms suffer recoil, which is not significant for radiation in the visible range, were the recoil energy is small compared with the linewidth of the radiation (times h), see Fig. 9.2.

Fig. 9.2 Recoil shift of the absorption line (at left) and emission line (at right).

Mössbauer used ^{191}Os as source, which decayed by the emission of β -particles and γ -rays. He passed the γ -rays through an absorber containing ^{191}Ir and constructed a cryostat in which he could maintain temperatures of liquid nitrogen. He reasoned that though the overlap would be less by the decrease of temperature (instead of increase the temperature as recommended by his PhD supervisor Professor Maier-Leibnitz), an acceptable temperature dependency might be observed. He anticipated that "... decreasing the temperature should give a reduced overlap of emission and absorption lines, resulting in an increase in transmitted line. But much contrary to his reasoning the observation yielded the opposite result", see Mössbauer 2000 in Literature. It turned out that increased resonance fluorescence was occurring. Initially he was perplexed, but he soon explained the effect by the recoil free emission and absorption of γ -ray photons.

Later he described the phenomenon picturesquely: "This situation (is)...like a person throwing a stone from a boat. The majority of the energy is submitted to the stone, but a small amount goes into the kinetic energy of the recoiling boat. During the summer time, the boat will simply pick up this recoil energy. If, however, the person throws the stone during winter time, with the boat frozen into the lake, then practically all energy is going into the stone thrown and only a negligible amount is submitted to the boat. The entire lake will, thus, take up the recoil and this procedure occurs as recoil free process." See Mössbauer 2000 in Literature.

Mössbauer published his doctoral work early in 1958 in the "Zeitschrift für Physik" (see Mössbauer 1958) and has then an afterthought "...it occurred to me that I had not performed the main experiment: it should be possible to measure the sharp resonance lines by using the linear Doppler effect. I was so excited, that I dashed across the hallway into the office of Prof. Maier-Leibnitz ... and cried 'I take the next train back to Heidelberg, because I forgot about the main experiment'". He made the second part and published the results in "Zeitschrift für Naturforschung" in the same year, see Literature.

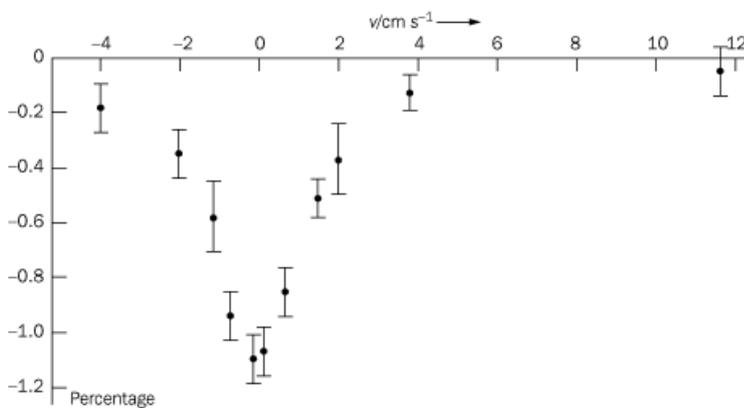


Fig. 9.3 The first Mössbauer spectrum (transmission) with ^{191}Ir as absorber, taken from Mössbauer, *Naturwissenschaften* 1968, see Literature

A particle of mass M at rest, which emits a photon of light with a wave vector \mathbf{k} having an energy $h\nu_0$ due to the spectral transition recoils backwards. The recoil pulse p is given by the relation $p = \hbar k = h\nu_0/c_0$, where ν_0 describes the frequency of the emitted photon. The backward recoil energy is given as $E_R = p^2/2M$. The emitted and the absorbed frequencies can be calculated by

$$\hbar\omega_e = \hbar\omega_0 - E_R = \hbar\omega_0 - (\hbar k)^2/2M \quad \text{and} \quad \hbar\omega_a = \hbar\omega_0 + (\hbar k)^2/2M, \quad (9.01)$$

respectively. For the second equation above we have assumed that another photon or quanta of light collides with the particles of mass M and thereby delivers an impulse to it as also excites a spectral transition with angular frequency ω_0 . With the difference between ω_a and ω_e we get

$$\Delta\omega = \omega_a - \omega_e = (\hbar k)^2/M = (\hbar\omega_0)^2/M \quad \text{or} \quad \frac{\Delta\nu}{\nu_0} = \frac{\Delta\omega}{\omega_0} = \frac{\hbar\omega_0}{Mc_0^2} = \frac{h\nu_0}{Mc_0^2}. \quad (9.02)$$

Equation (9.02) implies on the right side that the relative change in the frequency is equal to the relation of the photon energy to the rest mass energy Mc^2 of the atom.

As an example of the spectral line in visible range, we had considered in Chapter 2.6 the D₁-Fraunhofer line which occurs for the transition between the ground state of the sodium atom $3s\ ^2S_{1/2}$ and the excited state $3p\ ^2P_{1/2}$ with an averaged lifetime τ given by $\tau = 16$ ns. The wavelength of this spectral line is about $\lambda = c_0/\nu = 589,1$ nm, and the frequency ν_0 is about 5×10^{14} Hz. The natural linewidth $\delta\nu_{1/2}$ follows from the equ. (2.78) with $\delta\nu_{1/2} \approx 10^7$ Hz. The difference between the recoil energy can be obtained from the equ. (9.02) with $\Delta\nu_{\text{Recoil}} \approx 5 \times 10^4$ Hz. It is thereby evident that in the optical part of the electromagnetic spectrum the recoil frequency difference is smaller as compared to the natural linewidth of the transition.

However, the different situation illustrated in Fig. 9.2 occurs for the case of γ -ray. For the, so-called, Mössbauer-transition of the excited state of the iron nucleus, see Fig. 9.4, we have a lifetime of $T_{1/2} = 10^{-7}$ s and $\delta\nu_{1/2} \approx 1,6 \times 10^6$ Hz obtained from $\delta\omega_{1/2} = 1/T_{1/2}$, see equ. (2.87). The transition energy of 14.4 eV corresponds to an angular frequency $\omega = 2,6 \times 10^{19}$ s⁻¹. From that we obtain a value of the recoil frequency $\Delta\nu_{\text{Recoil}} \approx 10^{12}$ Hz, see equ. (9.02), which thus dominates above the natural linewidth by some six orders of magnitude.

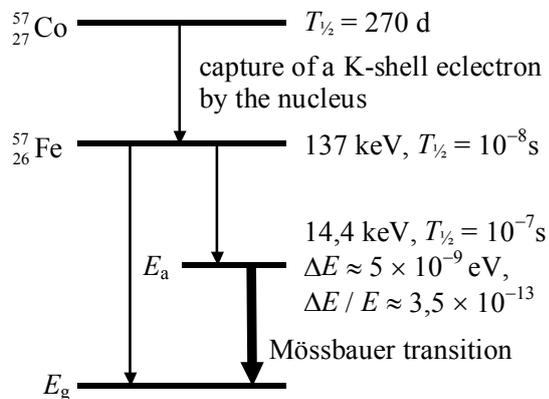


Fig. 9.4: Mössbauer transition of the iron nucleus.

Mössbauer explained the effect of the nuclear resonance (recoil free resonance absorption) with the help of theory of interaction between the neutrons and the crystal atoms that was published already in 1939 by Willis Eugene Lamb [læm]. Because of a strong bonding of the atomic nucleus to the lattice, the recoil energy of the atom is taken up and distributed in the entire lattice as lattice vibrations. These lattice vibrations are quantised and occur in discrete amounts only. With a steadily decreasing temperature the recoil free processes become more and more probable.

The Lamb-Mössbauer-factor f , also known as LMF, represents the fraction of the recoil free transitions in comparison with the total number of transitions. The LMF factor is in analogy to the Deby-Weller-factor, which gives us the value for the fraction of the thermal neutrons or X-ray photons that have been elastically scattered by the crystal relative to the total number of photons or neutrons that have been scattered, when the crystal was radiated with X-ray light or bombarded with a neutron beam, respectively. Also in the literature concerning the Mössbauer effect one more often finds the term Deby-Weller Factor (DBF) in place of the term Lamb-Mössbauer-Faktor f .

A more concrete theoretical justification for the presence of the above-mentioned LMF factor can be given by means of the Einstein model, which is the basis of the quantum mechanical theory of the thermodynamics in solid state of matter. Einstein developed the model in 1907. He made the assumption that all atoms in the solid vibrate or oscillate harmonically and in an isotropic but in uncorrelated manner way with a single frequency ω_E (Einstein-frequency) about their mean equilibrium positions. The quantum mechanically calculated value for the oscillation energy is

$$E = \hbar\omega_E (v + 1/2) \text{ and } E = \hbar\omega_E/2 \text{ for vibration quantum number } v = 0. \quad (9.03)$$

The emission of a γ -photon is accompanied by the excitation of lattice vibrations and corresponding recoil losses, if the recoil energy E_R , see equ. (9.01), is much greater than $\hbar\omega_E$. But a recoil free emission can take place in the case $E_R \ll \hbar\omega_E$.

Therefore, the mean value of the energy absorbed or taken up during the recoil of an atom can be approximately given by

$$E_R = (1 - f) \hbar\omega_E, \quad (9.04)$$

and the contribution f of the recoil free emission process can be approximated by the averaged value of the oscillator energy in the ground state. The total energy of a classical oscillator contains an equal contribution from the averaged values of kinetic energy as well potential energy terms. The first contribution can be obtained from $x = x_0 \sin \omega_E t$ and $\dot{x} = \omega_E x_0 \cos \omega_E t$ with a mean value of the amplitude as $\langle x^2 \rangle = \langle x_0^2 \sin^2 \omega_E t \rangle = \langle x_0^2 \cos^2 \omega_E t \rangle$ and the equation $E_{\text{kin}} = M \dot{x}^2 / 2$ gives $E_{\text{kin}} = M \omega_E^2 \langle x^2 \rangle / 2$. The total energy of the classical oscillator is then

$$E = M \omega_E^2 \langle x^2 \rangle = k_B T. \quad (9.05)$$

For $E = k_B T$ (k_B is the Boltzmann constant) we refer to the Chapter 2.3 of our lecture scripts in Molecular Physics. If we equate the energy value obtained above, equ. (9.05), with the quantum mechanically calculated value for $v=0$ in equ. (9.03), we have $\langle x^2 \rangle = \hbar / (2M\omega_E)$. Now we rearrange equ. (9.04), equate E_R from equ. (9.04) with E_R from equ. (9.01) and substitute $\hbar / (2M\omega_E) = \langle x^2 \rangle$. Then we obtain

$$f = 1 - \frac{E_R}{\hbar\omega_E} = 1 - \frac{\hbar^2 k^2}{2M\hbar\omega_E} = 1 - k^2 \langle x^2 \rangle, \quad (9.06)$$

where k^2 is the square of the wave vector of the emitted γ -photon as already introduced with equ.(9.01). Equation (9.06) has been derived correctly in a first-order approximation by making use of equ. (9.04). A more exact equation is given by

$$f(T) = \exp(-k^2 \langle x^2 \rangle) = \exp\left(-\frac{k^2 k_B T}{M\omega_E^2}\right), \quad (9.07)$$

which formally corresponds to Debye-Waller factor for temperatures above the Debye temperature, which describes the contribution of elastically scattered X-rays. This demonstrates the physically analogous situation. An additional factor of 3 in the denominator occurs, if the equation is derived for three dimensions.

Equation (9.07) allows us to demonstrate the conditions for the occurrence of the Mössbauer effect:

- strong attachment to the lattice (which means a large value for ω_E) and
- low temperature.

The condition $E_R \ll \hbar\omega_E$ which was described just before the equ. (9.04) causes the additional restriction:

low energy transitions with energy ≤ 150 keV.

The recoil free emitted (or absorbed) spectral lines have a natural linewidth due to the lifetimes of the states. It can be calculated by means of the uncertainty relation

$$\Delta E \Delta t \geq \frac{h}{4\pi} = \frac{\hbar}{2}. \quad (9.08)$$

ΔE If one introduces for the lifetime Δt a typical value of 10^{-7} s of the Mössbauer level 14,4 keV above the ground state of the ^{57}Fe level, one gets $\Delta E / E \approx 3,5 \times 10^{-13}$ what corresponds to an extremely narrow linewidth.

9.2 Experimental technique

From around 1300 nucleides that are known to exist, almost one hundred can be used as Mössbauer-isotopes. They belong to some 45 elements with a mass number from 40 (^{40}K , ^{57}Fe and above). About 2/3 of all Mössbauer studies concern iron, about 1/6 concern zinc and only 1/6 of all Mössbauer studies are dealing with other elements.

- ^{58}Fe : **Mössbauer effect** up to 1000 K, 2% n.a., $E_\gamma = 14,4$ keV, $T_{1/2} (^{57}_{27}\text{Co}) = 270$ d
- ^{119}Sn : **Mössbauer effect** up to 800 K, 8,7% n.a., $E_\gamma = 23,9$ keV, $T_{1/2} \approx 1$ year

The measuring set-up usually consists of a mainly electro-dynamic drive of the radioactive source. In addition to the driving coil exists a measuring coil for the electronic control of the relative velocity of the source. The absorber is fixed and contains the same nucleide as the source. The movement of the source creates the Doppler shift $\Delta E/E = v/c_0$. The velocity corresponds to a value of $0,19 \text{ mm s}^{-1}$, if we set the Doppler shift equal to the natural linewidth of ^{57}Fe . An increasing Doppler shift would cause a removal of the resonance for the case of single identical signals in source (emission) and absorber (absorption). But it gives the possibility to scan through a complicated spectrum with several signals in the absorber, if the source material emits only one narrow signal. Another γ -detection with such a high selectivity does not exist. The relative velocity of the source is the independent variable, and the associated counting rate of the γ -photons behind the absorber is the dependent variable of the Mössbauer spectrum. The number of discrete velocities between its maximum and minimum value determines the energy resolution of the spectrum. The spectral with ΔE of the absorber should be smaller than the difference between minimum and maximum velocity in the corresponding units ($\Delta v > c_0 \Delta E/E$) with the aid of the controlling drive. But the maximum velocity depends mainly on the Mössbauer isotope. It lies in the case of ^{57}Fe and ^{119}Sn in a range of 1 mm s^{-1} , and for ^{67}Zn below $1 \mu\text{m s}^{-1}$.

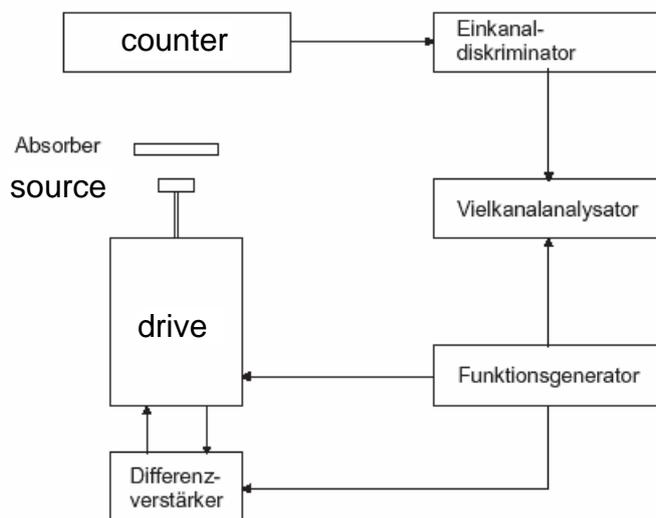


Fig. 9.5: Block diagram of a Mössbauer spectrometer used to measure the transmission. Adopted from the PhD thesis of Mr. Thorsten Pickardt, titled "Hochtemperatur-Mössbauer-Spektroskopie am metallischem Eisen und einer Eisen-Molybdän-Legierung bis 1500 °C", Hamburg University 2003.

9.3 The Mössbauer spectrum

When the source material and the absorber material are the same (for example, we use as absorber an old source which is no more radiating), then a line appears for $v = 0 \text{ mm s}^{-1}$ in the spectrum, where the γ -photon counting rate is plotted against the relative velocity. In the general case, however, we obtain a splitting of the line and a shift with respect to $v = 0$ because of the electrical and magnetic interactions between the nucleus and the electron shells surrounding it.

The isomer shift δ is caused

- firstly, due to the difference (between ground and the excited states, subscript g and e) of the electrostatic interaction between the potential of the nuclear charge and the electron charge density on the location of the nucleus;
- secondly, through the difference of the electron charge density on the location of the nucleus between the source and absorber (subscript Q and A)

We assume, for both the source and the absorber, a spherical distribution of the core electron charge density around the nucleus with an effective radius R . In the excited state the radius is changed by $\Delta R = R_e - R_g$. The isomer shift δ denotes an electrical potential energy (electrical potential times electrical charge) which corresponds to the difference potential of the nuclear charge in both states times multiplied by the difference of the core electron densities for absorber and source. Z is the atomic charge number and e the elementary charge. Then we have for the potential of the nuclear charge at the distance R from the centre of the sphere $U = eZ/4\pi\epsilon_0 R$. Upon increase of R by ΔR the volume of the sphere is increased by $4\pi R^2 \Delta R$. With $\psi(0)$ as normalized wave function of the s-electron (dimension: $\text{m}^{-3/2}$) within the nuclear sphere we get for the absolute value of the charge density of the electrons $e |\psi(0)|^2$. Subscripts Q and A denote source and absorber, respectively. The isomer shift is then

$$\delta = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{R} 4\pi R^2 \Delta R \left[|\psi_A(0)|^2 - |\psi_Q(0)|^2 \right]. \quad (9.09)$$

This simply derived equation describes the shift also for ^{57}Fe where is $\Delta R/R < 0$. Therefore with an increasing electron density at the position of the nucleus the resonance energy is shifted towards the negative Doppler velocities. The inner s-electron in ^{57}Fe are influenced by the 3d-binding electrons. Thus, the isomer shift of the core electrons reflect the chemical bonding.

A quadrupole splitting happens through the effect of the quadrupole interaction between the electrical nuclear quadrupole moment eQ (for a nucleus $I > 1/2$) and an inhomogeneous electrical field (electric field gradient, efg) at the position of nucleus. We have $I = 1/2$ in the ground state and $I = 3/2$ in the excited Mössbauer-state for ^{57}Fe .

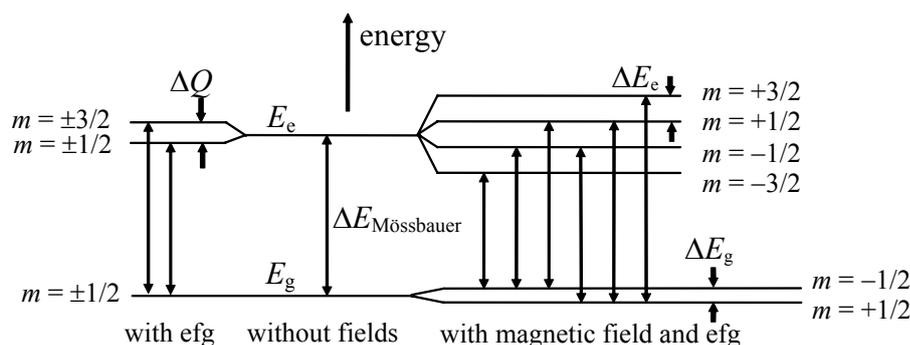


Fig. 9.6 Quadrupole splitting (at left) and Zeeman-splitting (at right) of the nuclear states for the recoil free Mössbauer transition in $^{57}_{26}\text{Fe}$ nucleus.

Therefore, one obtains a quadrupole splitting into two lines with $m = \pm 1/2$ and $m = \pm 3/2$ in the excited states and the splitting of the Mössbauer transition into two lines with

$$\Delta Q = \frac{1}{2} e^2 q Q \sqrt{1 + \frac{\eta^2}{3}}, \quad (9.10)$$

where η stands for the asymmetry parameter of the electric field. The quadrupole splitting of the source spectrum can be avoided by cubic symmetry of the electric field as it occurs, if ^{57}Co is incorporated into a copper foil.

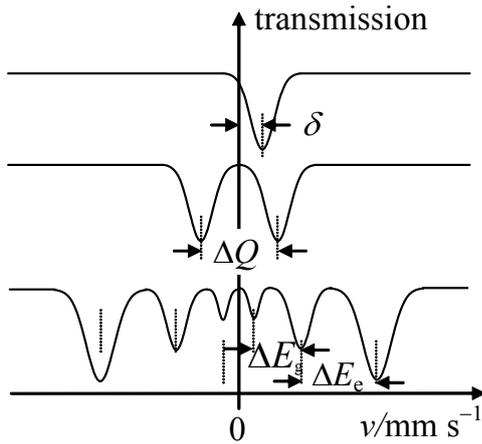


Fig. 9.7 Mössbauer spectra. On the top the isomer shift δ , middle the splitting by quadrupole interaction, and bottom the magnetic splitting for ^{57}Fe .

A magnetic splitting occurs through the interaction between the nuclear dipole moment and the magnetic field. Six lines are obtained for ^{57}Fe , see Fig. 9.6 and Fig. 9.7. The line separations are given by the expression

$$\Delta E_e = \gamma_e \hbar B_0 \quad \text{and} \quad E_g = \gamma_g \hbar B_0 \quad (9.11)$$

for each of 3 lines and each of two lines, respectively, see Fig. 9.6.

9.4 Two examples of classical applications

For many groups of substances the isomer shift has been found related to the chemical bonding. This allows applications similar to applications of analytical investigations done with the NMR shifts. One such example is shown in Fig. 9.8

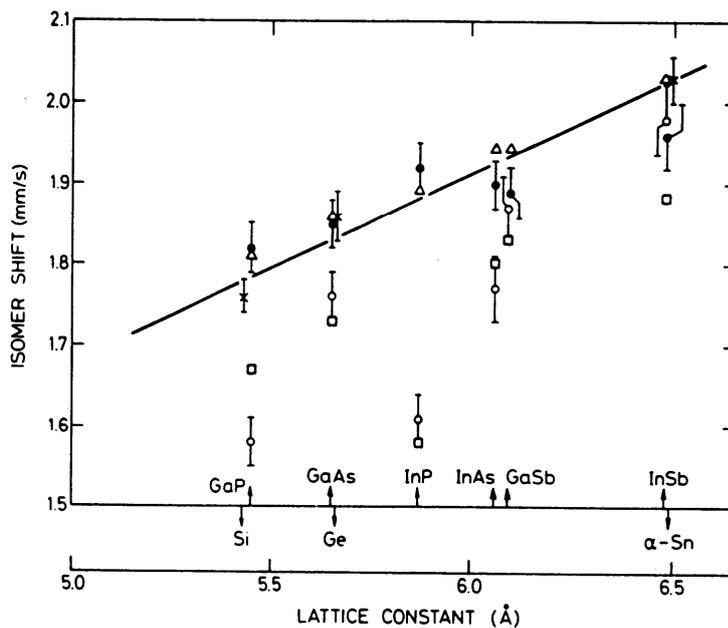
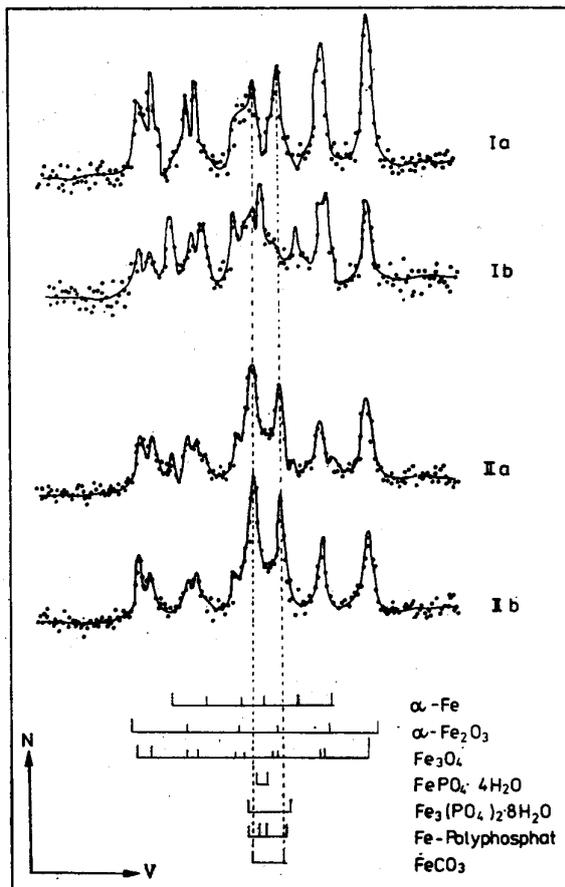


Fig. 9.8 Experimental and theoretical values of the ^{119}Sn isomer shift of Sn donors (O experiment, □ theory) and acceptors (● experiment, △ theory) in III-V compounds (Fig. 15 taken from ref. 182 in Long and Grandjean 1989, see Literature)



Iron phase analysis can be performed using the so-called fingerprint of iron-containing materials. This has been even done with a great deal of success on Mars, see Literature. The Mössbauer spectrum of all iron-phases is well known. Phase analysis can be realized by adjusting the experimentally obtained spectrum to the spectrum of the model substance. An example of such a fitting is given in the Fig. 9.9

Fig. 9.9 The scattering spectrum of a corroded hot water delivering pipe of a heating system. Taken from fig. 10.16 of publication by Barb and Meisel, see Literature. Hot water carrying pipes for warm water after 2 months (Ia, Ib), 4 months (IIa) and 8 (IIb) months of corrosion due to water flow, where the water flowing through the pipes labelled Ib, IIa, IIb was phosphated with 5 mg of P_2O_5 per liter of water.

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