Mössbauer spectra of single-domain particles with rotating magnetic moments

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Abstract

The influence of the rotation of a particle's magnetic moment in the magnetic anisotropy field on the shape of the Mössbauer spectra of hyperfine structure is analysed theoretically. It is found that, due to rotation, a renormalization of the nuclear g-factors occurs, which results in a qualitative transformation of Mössbauer absorption spectra. In particular, along with the magnetic sextet which is well known in the Mössbauer spectroscopy of the ^{57}Fe isotope, partial spectra can be formed that consist of 'magnetic' quintuplet, quartet, triplet and even doublet lines. This peculiarity in forming the spectra of magnetic hyperfine structure should be taken into account in analysing the Mössbauer spectra of materials with nano-sized magnetic particles.

1. Introduction

For more than 40 years Mössbauer spectroscopy has been known as a powerful method of investigating hyperfine interactions in solids. Until now, the mechanism that forms the hyperfine magnetic structure revealed in the absorption spectra seemed to be reliably established. The Mössbauer absorption spectra of magnetic materials are usually interpreted within a group of lines (partial spectra) that form due to the hyperfine interaction of the nuclear magnetic moment with the static hyperfine field at the nucleus. There can also arise lines originated by the quadrupolar interaction in the presence of the electric field gradient at the nucleus. For instance, as far as the ^{57}Fe isotope widely used in Mössbauer spectroscopy is concerned, the hyperfine magnetic field splits the energy level of the ground nuclear state with spin $I_g = 1/2$ into two sublevels that have different projections, m_g, of nuclear spin onto the direction of the hyperfine field, whereas the excited nuclear state with energy $E_0 = 14.4$ keV and spin $I_e = 3/2$ is split into four sublevels with different nuclear spin projections m_e, in accordance with the Hamiltonians of the Zeeman interaction between the nuclear magnetic moments and the hyperfine magnetic field H_{hf}:

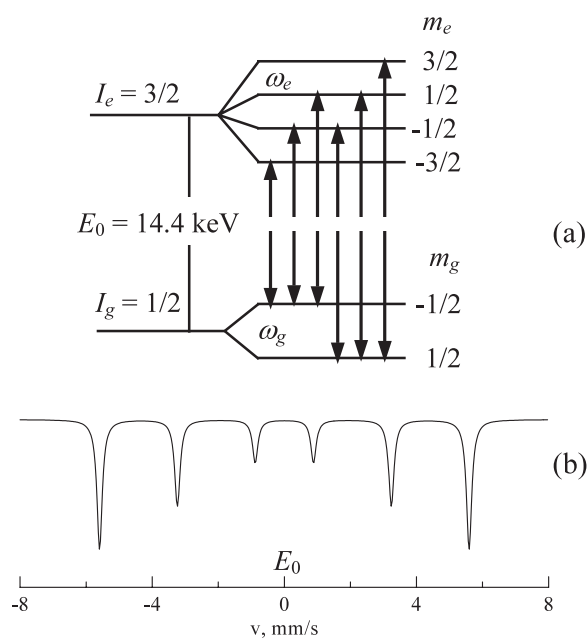$$\hat{H}^{(g,e)} = -g_{g,e}\mu_N H_{hf} \hat{I}^{(g,e)}. \tag{1}$$

Figure 1. (a) A schematic diagram of the splitting of ^{57}Fe nuclear energy levels for the excited (*e*) and ground (*g*) states in the static hyperfine field and (b) the corresponding magnetic sextet Mössbauer absorption spectrum. Here, and in the text, the spectra are calculated for non-polarized gamma radiation, randomly distributed directions of the hyperfine field, and $H_{hf} = 330$ kOe.

Here, μ_N is the nuclear magneton, $g_{g,e}$ are the nuclear *g*-factors, and $\hat{I}^{(g,e)}$ are the nuclear spin operators for the ground (*g*) and excited (*e*) states. A schematic diagram of the splitting of ^{57}Fe nuclear energy levels is shown in figure 1(a).

Transitions occur between the nuclear sublevels of the ground and excited states that are observed as just a set of lines in experimental absorption spectra. The positions and intensities of the lines are determined by the Hamiltonians (1) and multipolarity of the corresponding transition from the ground state to the excited state. For the ^{57}Fe nuclei, the M1-type magnetic dipolar radiation occurs, for which transitions with changes in nuclear spin projections of more than unity ($m_g = \pm 1/2 \rightarrow m_e = \mp 3/2$) are forbidden. Hence, the ^{57}Fe absorption spectrum consists of not eight lines but six lines (the so-called magnetic sextet) [1], corresponding to the schematic in figure 1(a). The ratios of intensities are defined by the Clebsch–Gordan coefficients and the crystal texture of the sample being studied, e.g. for iron-based polycrystalline samples or magnetic alloys, when the direction of the hyperfine field at the nucleus takes no preferential orientation and is randomly scattered, the intensities of the spectral lines obey the ratios 3:2:1:1:2:3, as shown in figure 1(b).

Most Mössbauer absorption spectra of magnetic materials are analysed on the basis of this magnetic sextet. Experimental spectra are decomposed into a superposition of sextets that correspond to different values of hyperfine field, as described by a hyperfine field distribution [2]. The spread of hyperfine fields is associated with the presence of different magnetic phases, magnetic sublattices in ferri- and antiferromagnetic materials, as well as crystal lattice defects. If this scheme of analysis within static hyperfine fields does not fit experimental spectra, then more complicated models are involved in order to describe the so-called relaxation effects [3–5] when the strength and/or direction of the hyperfine field can

change stochastically in time due to spin–lattice, spin–spin or other relaxation processes (e.g. for paramagnetic crystals [6], ferrofluids [7], single-domain particles under radio-frequency magnetic field excitation [8] or superparamagnetic relaxation [9] etc).

For small single-domain magnetic particles, the particle's magnetic moment should rotate about the easy magnetization axis, which results in rotation of the hyperfine magnetic field. This fact is known in Mössbauer spectroscopy but, in taking the effect into account, one usually assumes that the characteristic precession frequency, Ω, is much higher than the Larmor frequencies of nuclear spin precession in the hyperfine field. In this case, the magnetic sextets typical for the static hyperfine structure of ^{57}Fe nuclei remain in the absorption spectra with an effectively smaller hyperfine magnetic splitting [10]. In the general case, very different relationships between the frequency Ω and the Larmor frequencies of nuclear spin precession are realized in the samples studied. In this paper we demonstrate that, even if the relaxation effects are negligible, rotation of the hyperfine field in a small particle can also result in absorption spectra that are qualitatively different to the conventional static spectra of hyperfine magnetic structure. In particular, along with 'static' magnetic sextets for ^{57}Fe nuclei, there arise partial absorption spectra of small magnetic particles that consist of five, four, three and even two lines, i.e. 'magnetic' quintuplets, quartets, triplets and even doublets can be revealed in the partial spectra of hyperfine structure. It is obvious that these features must be taken into account in analysing experimental absorption spectra, even if the predicted anomalies are not realized in a clear form but are smeared out over the spectra due to the superposition of different magnetic components or relaxation effects.

2. Rotation of the magnetic moment of single-domain fine particles

Let us consider a magnetic particle of sufficiently small size such that it can be regarded as single domain and homogeneously magnetized. Such a particle usually exhibits magnetic anisotropy. Also, in the case of axial symmetry, the energy density of magnetic anisotropy is defined by the well known equation

$$E_{an} = -K\frac{M_z^2}{M_0^2} = -K\cos^2\theta \tag{2}$$

where K is the magnetic anisotropy constant, M_0 is the particle's magnetic moment per unit volume, M_z is the projection of the magnetic moment onto the symmetry axis, and θ is the angle between the direction of the particle's magnetic moment and the axis. Modern technology allows us to produce materials with magnetic particles of an ultra-small size of several nanometres (see, for instance, [11–16]). Due to the small volume, V, of such particles, their magnetic anisotropy energy, KV, is of the order of magnitude of several hundred kelvin so that, even at room temperature, all the energy states with arbitrary orientation of the particle's magnetic moment (with respect to the magnetic anisotropy axis) will be occupied.

The magnetic moment that is inclined by angle θ to the anisotropy axis stays in the magnetic anisotropy field

$$H_{an} = -\frac{\partial E_{an}}{\partial M_z} = 2K\frac{M_z}{M_0^2} = \frac{2K}{M_0}\cos\theta. \tag{3}$$

It is well known that, in this situation, the magnetic moment precesses about the magnetic field direction with a frequency of [17]
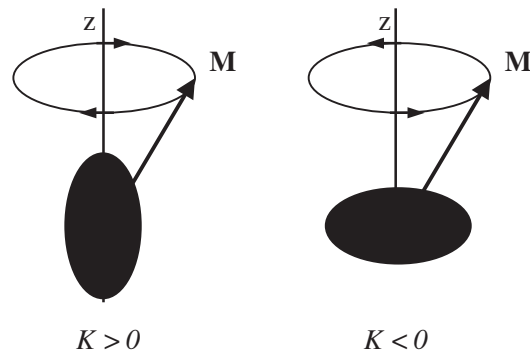
$$\Omega = -\gamma H_{an} \tag{4}$$

Figure 2. The rotation of the magnetic moment of particles with prolate ($K > 0$, $\Omega < 0$) and oblate ($K < 0$, $\Omega > 0$) spheroidal shape.

where γ is the gyromagnetic ratio. As seen from equations (3) and (4), the precession frequency can be represented in the following form:

$$\Omega = \Omega_0 \cos\theta \tag{5}$$

where

$$\Omega_0 = -2\gamma K / M_0. \tag{6}$$

One can see that the precession frequency Ω does not depend on the particle's volume and is determined by the precession angle θ.

Note that the sign of the precession of the particle's magnetic moment is defined by the sign of the anisotropy constant K. When $K > 0$, i.e. in the presence of the easy magnetization axis, counterclockwise ($\Omega < 0$) rotation of the magnetic moment occurs. In the case of magnetic anisotropy of the 'easy-plane' kind ($K < 0$), the sign of the precession of the magnetic moment becomes positive, i.e. clockwise rotation ($\Omega > 0$). These situations can be realized when the magnetic anisotropy arises from the shape of the particle, for instance in the form of prolate or oblate spheroids (see figure 2). As can be seen below, the sign of rotation of the particle's magnetic moment is very important to the specific transformation of Mössbauer absorption spectra. It is also essential that, at angles θ close to zero, the rotational frequency of the particle's magnetic moment is a maximum, $\Omega \approx \Omega_0$, and that, at $\theta = \pi/2$, the precession frequency goes to zero. Hence, there is always a range of angles θ over which the precession frequency Ω is comparable with the precession frequencies of nuclear spins in the hyperfine magnetic field at the nucleus.

3. Mössbauer spectra within rotation of the hyperfine field

The hyperfine field follows changes in the direction of the magnetic moment, i.e. it also rotates about the magnetic anisotropy axis:

$$\boldsymbol{H}_{hf}(t) = H_{hf}[\boldsymbol{n}_z \cos\theta + (\boldsymbol{n}_x \cos(\Omega t) + \boldsymbol{n}_y \sin(\Omega t)) \sin\theta] \tag{7}$$

where $\boldsymbol{n}_x$, $\boldsymbol{n}_y$ and $\boldsymbol{n}_z$ are the unit vectors along the x-, y- and z-axes, respectively. If the characteristic precession frequency, Ω, is much higher than the frequencies of nuclear spin precession that were assumed earlier in Mössbauer spectroscopy of superparamagnetic particles [10], then the time-dependent components of the hyperfine field are averaged to zero and the time-average hyperfine field is reduced to

$$\bar{\boldsymbol{H}}_{hf} = H_{hf} \cos\theta \boldsymbol{n}_z. \tag{8}$$

As simple estimates show, for small particles of the order of several nanometres in size, the parameter Ω_0 is just several times larger than the Larmor frequencies of nuclear spin precession. So, for γ-Fe$_2$O$_3$ particles with an average diameter of about 7 nm and a characteristic magnetic anisotropy energy KV of about 1000 K (see, for example, [15]), one can estimate the value of the parameter $\Omega_0/2\pi \approx 0.5$ GHz. So, for increasing angle θ, the precession frequency Ω can become comparable to, or less than, the Larmor frequencies of nuclear spin precession. As is shown below, taking the finiteness of Ω into consideration results in a cardinal transformation of the hyperfine magnetic structure of Mössbauer spectra.

In this case, the Hamiltonians of hyperfine interaction of the nuclear magnetic moments with hyperfine field $\boldsymbol{H}_{hf}(t)$ that rotate about the z-axis with frequency Ω become time dependent:

$$\hat{H}^{(g,e)}(t) = -g_{g,e}\mu_N \boldsymbol{H}_{hf}(t)\hat{\boldsymbol{I}}^{(g,e)}. \tag{9}$$

Note that, in the general case, there is also the quadrupolar interaction of a nucleus with the electric field gradient at the nucleus. However, it is usually much weaker than the hyperfine interaction and we will neglect this term in the following. To describe the Mössbauer spectra in this case, we can use a general theory of the relaxation Mössbauer absorption spectra under radio-frequency magnetic field excitation that has been developed for a hyperfine field $\boldsymbol{H}_{hf}(t)$ that depends on time in an arbitrary way [18–20]. In particular, when the hyperfine field changes in time along an arbitrary deterministic trajectory, the absorption cross section of a gamma-quantum with energy $E = \hbar\omega$ can be represented in the following way (see, for example, [19]):

$$\sigma(\omega) = \frac{2}{\Gamma_0 T_{hf}} \mathrm{Re} \int_0^{T_{hf}} dt_0 \int_{t_0}^{\infty} Sp\left\{\hat{V}^+\left[\hat{T}\exp\left\{\int_{t_0}^t i[\tilde{\omega}\hat{\boldsymbol{I}} - \hat{\boldsymbol{L}}_{\hat{H}}(t')]\,dt'\right\}\right]\hat{V}\right\} dt \tag{10}$$

where Γ_0 is the energy width for the excited nuclear state, $T_{hf} = 2\pi/\Omega$ is the period of changes in the hyperfine field, $\hat{V}$ is the operator for the interaction of the gamma-quantum with the nucleus, which determines the intensities of the nuclear transitions, $\hat{T}$ is the time-ordered operator, $\tilde{\omega} = \omega + i\Gamma_0/2$, $\hat{\boldsymbol{I}}$ is the identity operator, and $\hat{\boldsymbol{L}}_{\hat{H}}(t)$ is the Liouville operator for the hyperfine interaction, which is defined by the Hamiltonians $\hat{H}^{(g)}(t)$ and $\hat{H}^{(e)}(t)$. The super-operator $\hat{\boldsymbol{L}}_{\hat{H}}(t)$ acts in the space of $(2I^{(g)} + 1)(2I^{(e)} + 1)$ nuclear variables:

$$(\hat{\boldsymbol{L}}_{\hat{H}})_{m_e m_g m'_e m'_g} = \hat{H}^{(e)}_{m_e m'_e}\delta_{m_g m'_g} - \hat{H}^{(g)}_{m_g m'_g}\delta_{m_e m'_e} \tag{11}$$

where $m_{g,e}$ are the projections of nuclear spin onto a given axis. On the basis of equations like equation (10), calculations have been performed of absorption spectra of nanostructured ferromagnetic alloys under radio-frequency field excitation [21].

In order to transform equation (10), one can introduce the following super-operator:

$$\hat{G}(t_0, t) = \hat{T}\exp\left\{\int_{t_0}^t dt'[-i\hat{L}_{\hat{H}}(t')]\right\} = \hat{G}^{(e)}(t_0, t) \otimes \hat{G}^{(g)}(t, t_0) \tag{12}$$

which is the direct product of the evolution operators for the ground and excited nuclear states, defined by

$$\hat{G}^{(e,g)}(t_0, t) = \hat{T}\exp\left(\int_{t_0}^t dt'[-i\hat{H}^{(e,g)}(t')]\right). \tag{13}$$

In our case, equation (13) can be simplified substantially if one considers the coordinate system that rotates with frequency Ω about the z-axis. Such a transition corresponds to the unitary transformations with the elementary operators of rotation about the z-axis. This allows one to incorporate the integral over time into the evolution operators (13) and derive the following equations:
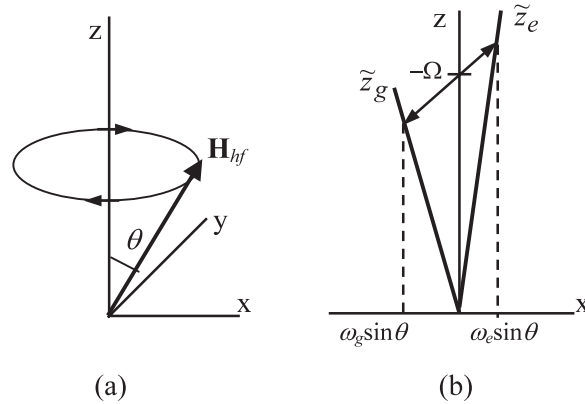
Figure 3. (a) The rotating hyperfine field in the laboratory coordinate system and (b) the quantization axes of the operators (15) for the ground and excited ^{57}Fe nuclear states ($K > 0$, $\Omega < 0$) in the rotating coordinate system.

$$\hat{G}^{(e,g)}(t_0, t) = e^{-i\Omega \hat{I}_z t_0} e^{i\Omega \hat{I}_z t_0} \hat{T} \exp\left(-i \int_{t_0}^t \hat{H}^{(g,e)}(t')\,dt'\right) e^{-i\Omega \hat{I}_z t} e^{i\Omega \hat{I}_z t}$$

$$\equiv e^{-i\Omega \hat{I}_z t_0} \exp\left(-i(t - t_0)\hat{\tilde{H}}^{(g,e)}\right) e^{i\Omega \hat{I}_z t} \tag{14}$$

where $\hat{\tilde{H}}^{(g,e)}$ are the time-independent Hamiltonians of hyperfine interaction in the ground and excited nuclear states within the rotating coordinate system, which can be written as

$$\hat{\tilde{H}}^{(g,e)} = (-\Omega + \omega_{g,e} \cos\theta)\hat{I}_z^{(g,e)} + \omega_{g,e} \sin\theta \hat{I}_x^{(g,e)}. \tag{15}$$

Here $\omega_{g,e} = -g_{g,e}\mu_N H_{hf}$ are the constants of hyperfine interaction for the ground and excited nuclear states.

Using equation (14) one can easily derive that equation (10), for the absorption cross section within the rotating hyperfine field (7), is reduced to a rather simple analytical form. Taking into account different polarizations, η, of the incident gamma-rays, the absorption cross section is given by

$$\sigma(\omega, \Omega, \theta) = -\frac{\Gamma_0}{2} \mathrm{Im} \sum_{\eta} \sum_{\substack{m_g m_e \\ \tilde{m}_g \tilde{m}_e}} V_{\tilde{m}_g \tilde{m}_e}^{(\eta)+} \frac{\langle \tilde{m}_g | m_g \rangle \langle m_e | \tilde{m}_e \rangle}{\omega - (\tilde{\lambda}_e \tilde{m}_e - \tilde{\lambda}_g \tilde{m}_g) - \Omega(m_g - m_e) + i\Gamma_0/2} V_{m_e m_g}^{(\eta)} \tag{16}$$

where $V_{m_e m_g}^{(\eta)}$ are the matrix elements for the operator of interaction of the gamma-quantum with the nucleus, $m_{g,e}$ are the projections of nuclear spins onto the z-axis, $\tilde{m}_{g,e}$ are the projections of nuclear spins onto the quantization axes for which the operators $\hat{\tilde{H}}^{(g,e)}$ are diagonal, and

$$\tilde{\lambda}_{g,e} = \sqrt{(-\Omega + \omega_{g,e} \cos\theta)^2 + \omega_{g,e}^2 \sin^2\theta}. \tag{17}$$

Note an essential circumstance that the directions of the quantization axes for the operators (15) in the ground and excited nuclear states are different, as is clearly seen in figure 3.

As follows from equation (16), in the case of the rotating hyperfine field, lines with natural line-width Γ_0 should be observed in the absorption spectrum. In the general case, the number of lines is equal to $N = (2I_g + 1)^2(2I_e + 1)^2$. For the ^{57}Fe isotope $N = 64$, however, the selection
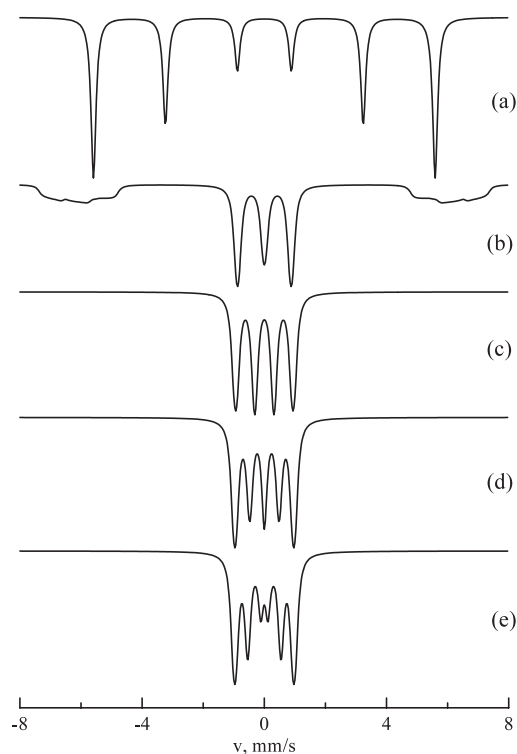
Figure 4. ^{57}Fe Mössbauer absorption spectra within the rotating hyperfine field ($\theta = 80°$) for (a)–(e) different values of the parameter $\Omega_0/2\pi = 0, -0.35, -0.8, -2.3, -50$ GHz. The spectra are averaged over the range of angles $\theta - \Delta\theta$ to $\theta + \Delta\theta$ ($\Delta\theta = 1°$).

rules for the magnetic dipolar M1 transitions reduce the number of allowed lines to 24, each being doubly degenerate because the pairs of lines with indices (m_g, m_e) and $(m_g \pm 1, m_e \pm 1)$ have the same energy of transitions.

Using equation (16), one can calculate the absorption spectrum as a function of the precession frequency Ω and the angle θ. Figures 4 and 5 show the ^{57}Fe Mössbauer absorption spectra calculated for the case of a hyperfine field rotating about an axis under $\theta = 80°$ for different values of the parameter Ω_0 (i.e. different frequencies Ω) and different signs of rotation. The spectra are actually divided into a central group of lines and side-bands. The intensity of the side-bands decreases as the rotation frequency increases and they leave the spectral range of conventional Mössbauer measurements. (Just to stay closer to reality and smear out the non-essential effects of the side-bands, we have plotted the spectra averaged over the narrow range of angles $\theta - \Delta\theta$ to $\theta + \Delta\theta$ with $\Delta\theta = 1°$.) In the limiting case of high precession frequency, independent of the sign of rotation, a 'static' magnetic sextet is observed that corresponds to the rotation-averaged hyperfine field (8). Within an intermediate range of precession frequencies, a non-trivial transformation of the spectra is observed. It is seen clearly that, instead of the classic sextet of the static hyperfine structure (top spectra in figures 4 and 5), there can appear unusual spectra consisting of a triplet, quartet and quintuplet of lines for negative values of the precession frequency Ω ($K > 0$) and a doublet of lines for a positive sign of rotation ($K < 0$). That is, rotation of the hyperfine field can drastically change the Mössbauer line-shape of the hyperfine magnetic structure.
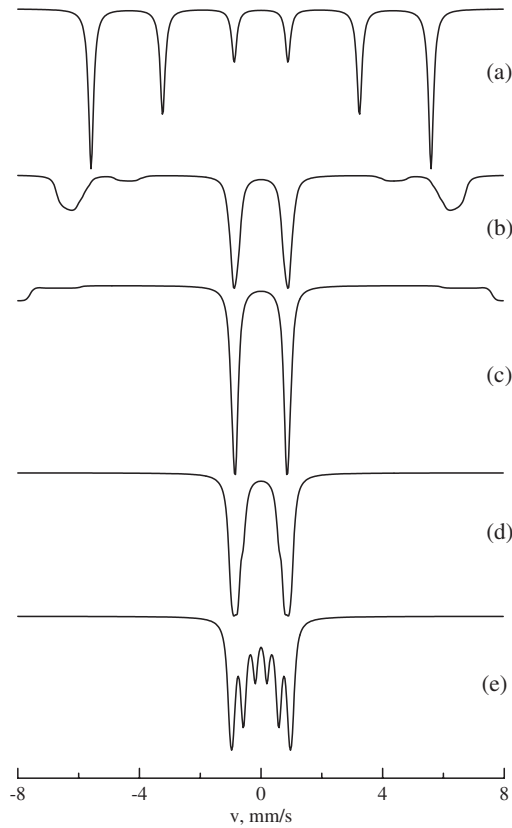
Figure 5. ^{57}Fe Mössbauer absorption spectra within the rotating hyperfine field ($\theta = 80°$) for (a)–(e) different values of the parameter $\Omega_0/2\pi = 0, 0.35, 0.5, 0.7, 50$ GHz. The spectra are averaged over the range of angles $\theta - \Delta\theta$ to $\theta + \Delta\theta$ ($\Delta\theta = 1°$).

4. High-precession-frequency limit

To clarify the physical nature of this qualitative transformation of Mössbauer spectra in the rotating hyperfine field, let us analyse the case of high precession frequency when

$$|\Omega| \gg |\omega_{g,e}|. \tag{18}$$

In this case, the absorption spectrum consists of the central group of six double-degenerate lines and side-bands. If condition (18) holds, then the side-bands leave the ordinary spectral range and become of minor intensity, so that one can neglect them to a first approximation.

The major contribution to the absorption spectrum is given by the central lines with indices $\tilde{m}_g = m_g$ and $\tilde{m}_e = m_e$, so that equation (16) for the absorption cross section is reduced to the following approximate expression:

$$\sigma(\omega, \Omega, \theta) = -\frac{\Gamma_0}{2} \operatorname{Im} \sum_{\eta} \sum_{m_g m_e} |V_{m_e m_g}^{(\eta)}|^2 \frac{1}{\omega - (\tilde{\omega}_e m_e - \tilde{\omega}_g m_g) + i\Gamma_0/2} \tag{19}$$

where $\tilde{\omega}_g$ and $\tilde{\omega}_e$ are the effective constants of hyperfine interaction for the ground and excited nuclear states, which are found from equations (17). By providing the precession frequency to meet the condition (18), these are determined by

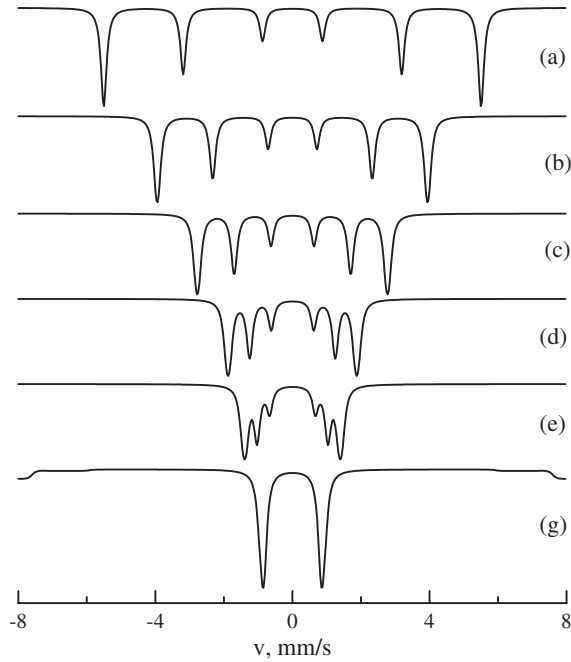$$\tilde{\omega}_{g,e} = -\tilde{g}_{g,e}\mu_N H_{hf} \cos\theta \tag{20}$$

Figure 6. ^{57}Fe Mössbauer absorption spectra within the rotating hyperfine field for different values of the angle $\theta = 10°, 45°, 60°, 70°, 75°, 80°$ (a)–(g) and the parameter $\Omega_0/2\pi = 0.5$ GHz. The spectra are averaged over the range of angles $\theta - \Delta\theta$ to $\theta + \Delta\theta$ ($\Delta\theta = 1°$).

where the renormalized nuclear g-factors for the ground and excited nuclear states are introduced as follows:

$$\tilde{g}_{g,e} = g_{g,e}\left(1 - \frac{\omega_{g,e}}{2\Omega}\sin\theta\tan\theta\right). \tag{21}$$

As seen from equation (20), apart from the effective decrease in the value of hyperfine field proportionally to $\cos\theta$ in accordance with equation (8), the rotation transforms qualitatively the Mössbauer spectra of hyperfine structure through the renormalization of the nuclear g-factors, according to equation (21). With that, changes in the effective $\tilde{g}$-factors for the ground and excited nuclear states appear to be different, since the initial g_g- and g_e-factors are different. Note that, for the ^{57}Fe isotope g-factors for the ground and excited nuclear state are different not only by value but also by sign ($g_g = 0.18$ and $g_e = -0.10$).

As follows from equation (21), for the counterclockwise rotation ($\Omega < 0$, $K > 0$) the $\tilde{g}$-factor for the ground nuclear state decreases in its absolute value, whereas that for the excited nuclear state increases compared to the real g-factors. It is clear that, for angles θ close to $\pi/2$, the effective factor $\tilde{g}_g$ for the ground nuclear state can even change to the opposite sign. Precisely this circumstance is the reason for the qualitative transformation of Mössbauer spectra, in particular for the appearance of the triplet, quartet and quintuplet of lines shown in figure 4. For instance, if the angle θ satisfies the following condition

$$\cos\theta = \sqrt{\frac{\omega_g}{2\Omega_0}}, \tag{22}$$

then the effective factor $\tilde{g}_g$ for the ground nuclear state is equal to zero, so that a 'magnetic' quartet of lines is to be observed in the absorption spectrum. The schematic diagram in figure 7
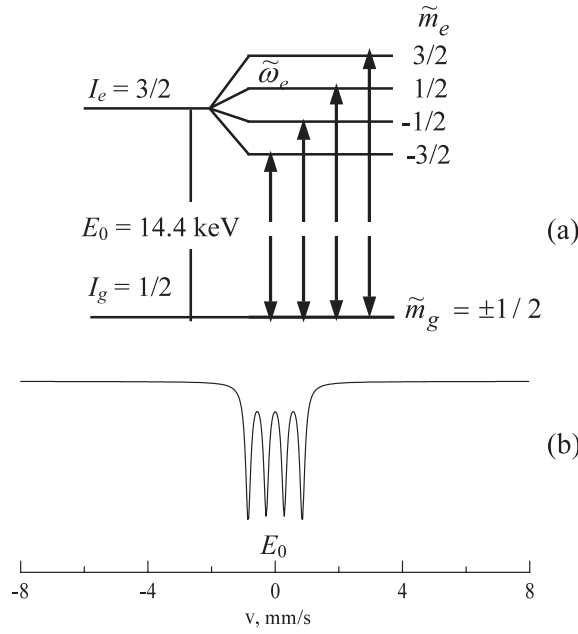
Figure 7. (a) A schematic showing the ^{57}Fe nuclear energy-level splitting for the excited and ground states in the rotating hyperfine field with $\Omega_0/2\pi = -1$ GHz, $\theta = 81°$, $\tilde{\omega}_g = 0$ and (b) the corresponding magnetic 'quartet' Mössbauer absorption spectrum.

shows the splitting of the energy levels in the hyperfine field for this case and the corresponding Mössbauer absorption spectrum.

In turn, for the clockwise rotation ($\Omega > 0$, $K < 0$) the $\tilde{g}$-factor for the excited nuclear state decreases in absolute value, whereas that for the ground nuclear state increases compared to the real g-factors. In this case, for angles θ close to $\pi/2$, the effective factor $\tilde{g}_e$ for the excited nuclear state can change its sign. And, if the angle θ meets the following condition

$$\cos\theta = \sqrt{\frac{\omega_e}{2\Omega_0}}, \qquad (23)$$

then the effective factor $\tilde{g}_e$ for the excited nuclear state is equal to zero and the absorption spectrum looks like a 'magnetic' doublet of lines. The corresponding schematic of the energy-level splitting in the hyperfine field and Mössbauer absorption spectrum are shown in figure 8.

5. Resulting Mössbauer spectrum of a single-domain particle within rotation of the hyperfine field

It is obvious that the resulting Mössbauer spectrum of a single-domain fine particle is a superposition of partial spectra corresponding to energy states with different orientations of the particle's magnetic moment with respect to the magnetic anisotropy axis. Figures 6 shows the ^{57}Fe Mössbauer absorption spectra calculated for the case of the hyperfine field rotating about an axis under different angles θ for the parameter $\Omega_0/2\pi = 0.5$ GHz, corresponding to γ-Fe$_2$O$_3$ particles with an average diameter of about 7 nm [15]. One can see that the hyperfine magnetic structure with the renormalized $\tilde{g}$-factors is observed distinctly in the absorption spectra for angles $\theta > 70°$. For decreasing angle θ, the qualitative effect of rotation on the
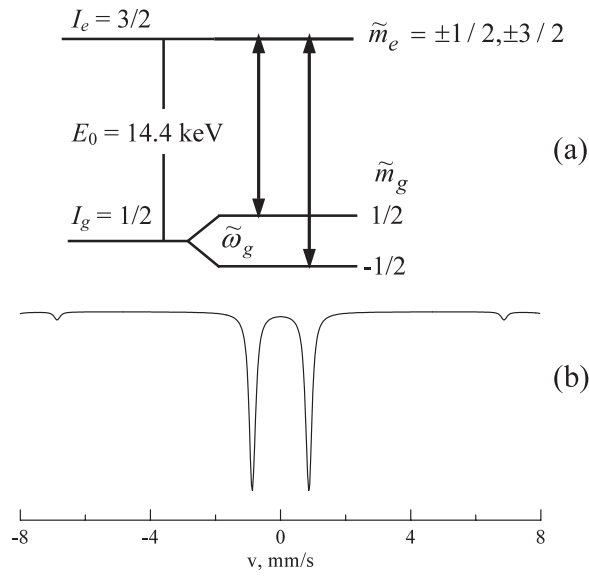
Figure 8. (a) A schematic showing the ^{57}Fe nuclear energy-level splitting for the excited and ground states in the rotating hyperfine field with $\Omega_0/2\pi = 0.5$ GHz, $\theta = 80°$, $\tilde{\omega}_e = 0$ and (b) the corresponding magnetic 'doublet' Mössbauer absorption spectrum.

shape of the Mössbauer spectra becomes weaker and the hyperfine structure with just the rotation-averaged hyperfine field (8) remains in the spectra. However, one should bear in mind that an appreciable rotation effect can be registered not only if the spectra take the non-conventional shape shown in figures 4 and 5 but also when the corresponding line-shifts are comparable to the natural line-width Γ_0. For example, for the parameter $\Omega_0/2\pi = 0.5$ GHz, one can estimate the rotation effect to be detectable for angles $\theta > 30°$.

In the absence of relaxation effects, the resulting absorption spectrum of a single particle with axial magnetic anisotropy (2) is defined by the weighted sum of partial spectra (16) with different angles θ as follows:

$$\bar{\sigma}(\omega) = \int \sigma(\omega, \Omega_0 \cos\theta, \theta) P(\theta) \sin\theta \, d\theta \tag{24}$$

where $P(\theta)$ represents populations of different energy states with different orientations of the particle's magnetic moment at a given temperature T,

$$P(\theta) = C \exp\left(\frac{KV \cos^2\theta}{k_B T}\right) \tag{25}$$

(k_B is the Boltzmann constant and C is the normalization factor).

As follows from equation (24), for small particles of nanometre size, if all the states with different orientations of the particle's magnetic moment are populated, then the non-conventional features observed in the partial spectra of figures 4 and 5 would be considerably smeared out in their superposition in the resulting spectrum. However, as can clearly be seen—even from visual comparison of the two series of spectra shown in figures 4 and 5—the degree of smearing should be substantially different for different signs of rotation of the hyperfine field. A wide spread of line positions can be observed in partial spectra for the negative precession frequency Ω ($K > 0$), so that it is scarcely possible to observe any distinct hyperfine structure in the resulting spectrum. At the same time, for positive Ω ($K < 0$), a topological spectral
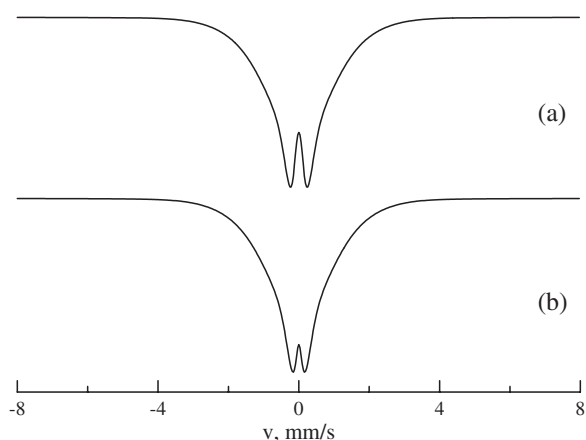
Figure 9. ^{57}Fe Mössbauer absorption spectra of a single-domain particle with the magnetic anisotropy constant $K < 0$ for the parameter $\Omega_0/2\pi = 0.5$ GHz (a) and 1 GHz (b).

shape like a magnetic 'doublet' remains over a wide range of Ω (or a wide range of angles θ at a given value of the parameter Ω_0). In this case, one can hope to find such a rotational 'doublet' in the resulting spectrum of the hyperfine structure of small magnetic particles. As an example, figure 9 shows the ^{57}Fe Mössbauer absorption spectra calculated within equation (24) for the parameters $KV/k_BT = -5$ and $\Omega_0/2\pi = 0.5$ GHz. As can clearly be seen from the figure, the magnetic 'doublet' can remain in the resulting spectra of small magnetic particles.

6. Conclusions

In conclusion, we would like to stress that, even if the predicted features of the hyperfine structure formation were not revealed clearly because of the superposition of different partial spectra and the relaxation effects in real situations, the specific transformation of Mössbauer absorption spectra under a rotation of the hyperfine magnetic field should be taken into consideration in analysing the experimental spectra of small magnetic particles. Moreover, the example of the effective magnetic 'doublet', revealed in the resulting spectra shown in figure 9, is of particular interest. Indeed, many Mössbauer studies of different magnetic materials result in absorption spectra with distinct hyperfine magnetic splitting and negligible quadrupolar splitting at low temperature, while the higher-temperature spectra manifest the presence of doublets of lines with remarkable quadrupolar splitting. The only conventional explanation for this fact is the assumption that the hyperfine field is perpendicular to the principal axis of the electric field gradient at the nucleus. An alternative reason for such behaviour could be just the appearance of the effective magnetic 'doublets' due to the re-distribution of populations of the different energy states with increasing temperature.

To observe the qualitative effects discussed above in a distinct form, one needs to realize a situation where the hyperfine field is forced by an external perturbation to rotate at a given frequency and angle. For instance, this can be done by collecting the Mössbauer absorption spectra of fine magnetic particles under excitation within an external rotating radio-frequency magnetic field that is strong enough to make the particles' magnetic moments follow the changes in the external field (i.e. rotate about the corresponding axis at the given angle). By providing the appropriate characteristics of the external rotating magnetic field, one can realize the conditions necessary for observing the specific shapes of Mössbauer absorption spectra shown in figures 4 and 5.

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