

THE PROBLEM OF TEXTURE IN MÖSSBAUER SPECTROSCOPY

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In Mössbauer spectroscopy it is desirable to work with single crystals or with polycrystalline material of random orientation. The actual, most occurring, case of preferred orientation (texture) and its influence on the relative line intensities of hyperfine split Mössbauer spectra is analysed. Texture information which can be obtained from such an analysis is demonstrated with variously prepared barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$) samples.

INTRODUCTION

Concerning the relative line intensities the interpretation of hyperfine split Mössbauer spectra on polycrystalline samples is complicated because of the existence of three different effects influencing the intensity ratios: effective thickness of the absorber, lattice vibrational anisotropy (Goldanskii–Karyagin effect) and preferred orientation of the crystallites (texture). While the effective thickness of the absorber in most cases can be kept small it is very difficult to produce a random orientation distribution in powder samples. Thus, an interpretation of the line intensities, in general, has to take into account the lattice vibrational anisotropy and the effect of preferentially oriented crystallites. In a recent study¹ the two competing effects have been analysed; and it was pointed out that the effect of the lattice vibrational anisotropy is often overestimated. A computer program, which calculates Mössbauer spectra for simultaneous magnetic dipole and electric quadrupole interaction of a polycrystalline sample with any distribution of the crystallites, allows one to estimate the non-random orientation effect. Thus the relative magnitude of the two contributions (Goldanskii–Karyagin effect vs. texture) influencing the relative line intensities in Mössbauer spectroscopy can be determined. In the meantime, one will also obtain useful information about the orientation distribution function of the electric field gradient and the internal magnetic field.

We have recently determined the spin orientation in Fe_3C by correlating X-ray textures with relative Mössbauer line intensities². Now we have reversed

the problem. That is, from the relative Mössbauer line intensities and the known orientation relation of spin and quadrupole parameters in regard to the crystal axes we wish to obtain information about the texture of the specimens.

DEFINITION OF CORRELATIONS

The line positions of a Mössbauer spectrum are given by the transition energies between the excited and the ground states of the Mössbauer nucleus, and the line intensities are proportional to the transition probabilities P which depend on the orientations of the magnetic field at the nucleus $\vec{H}(0)$ and of the axes of the electric field gradient (EFG) tensor $((V_{ik})_i, k = x, y, z)$ with respect to the propagation direction \vec{k}_γ of the γ -rays. Figure 1 defines the angles θ, ϕ, ϑ and φ , which specify the orientation of $\vec{H}(0)$ and the γ -beam with respect to the EFG axes V_{xx}, V_{yy} and V_{zz} .

The probability of a transition between the excited state $|i\rangle$ and the ground state $|j\rangle$ may be given by $P(\theta, \phi, \vartheta, \varphi, i, j)$. So the intensity I of the transition in a polycrystalline sample with an orientation distribution of the crystallites described by a distribution function $F(\vartheta, \vartheta_0, \varphi, \varphi_0)$ will be given by the expression

$$I(\theta, \phi, \vartheta_0, \varphi_0, i, j) \propto \int_0^\pi d\vartheta \int_0^{2\pi} d\varphi P(\theta, \phi, \vartheta, \varphi, i, j) F(\vartheta, \vartheta_0, \varphi, \varphi_0) \sin\vartheta \quad (1)$$

The angles ϑ_0 and φ_0 define the preferred orientation of the EFG axes with respect to the propaga-

tion direction of the γ -rays (see Figure 2). The distribution function $F(\vartheta, \vartheta_0, \varphi, \varphi_0) d\Omega$ represents the probability to find a crystallite with V_{zz} -axis within the solid angle element $d\Omega$. The probability

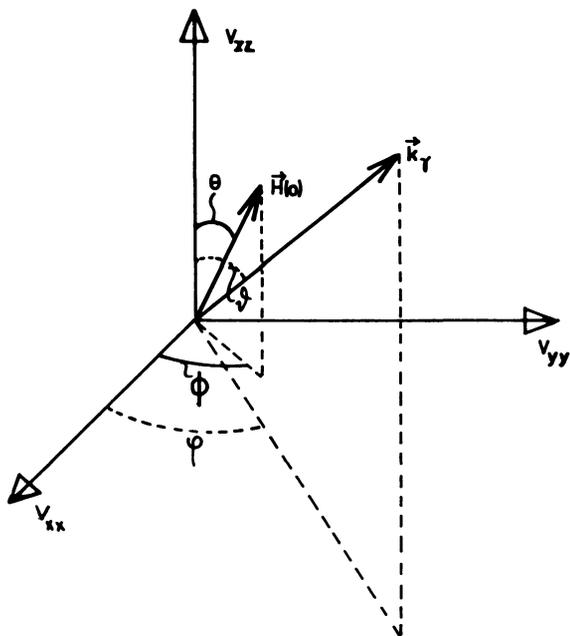


FIGURE 1 The angles θ , ϕ and ϑ , φ defining the orientations of the internal field $\vec{H}(0)$ and the propagation direction \vec{k}_γ of the γ -beam, respectively.

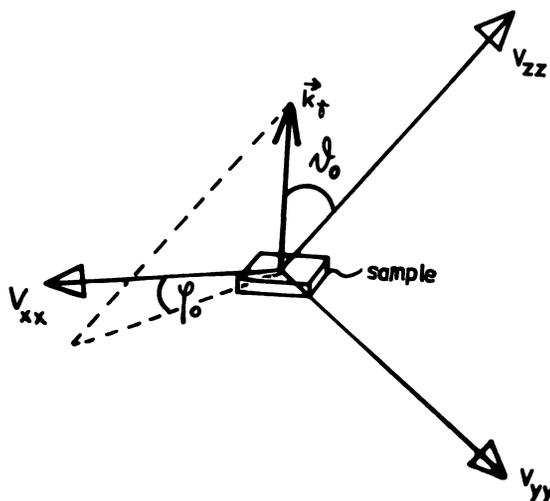


FIGURE 2 The angles ϑ_0 , φ_0 defining the center of the orientation distribution of the V_{zz} -axis.

to find a crystallite with any orientation of the V_{zz} -axis must be unity. So the distribution function has to be normalized by the condition:

$$\int_0^\pi d\vartheta \int_0^{2\pi} d\varphi F(\vartheta, \vartheta_0, \varphi, \varphi_0) = 1. \quad (2)$$

THE PROGRAM

The program is an extension of the work by W. Kündig³, which generates theoretically Mössbauer spectra for powder and single crystal samples containing the Fe^{57} Mössbauer nucleus. In order to gain the line intensities for a preferentially oriented sample the single crystal solution (i.e. transition probabilities $P(\theta, \phi, \vartheta, \varphi, i, j)$) is multiplied by the distribution function F and the double integral with respect to the angles ϑ and φ (according to Eq. (1)) is carried out numerically.

The program uses as input parameters the angles θ and ϕ , the asymmetry parameter of the EFG tensor $\eta = (V_{xx} - V_{yy})/V_{zz}$, the half line width (in percent of the total splitting), the interaction ratio R of the electric quadrupole and magnetic dipole interaction and some specifications determining the distribution function (per example: center and line width of a Lorentzian or Gaussian function). The interaction ratio R is defined by

$$R = \frac{e Q V_{zz}}{2g \mu H(0)}; \quad (3)$$

e is the charge of the proton, Q , the electric quadrupole moment of the nucleus, g , the nuclear g -factor of the excited state and μ , the nuclear magneton.

The various distribution functions F are calculated in a subprogram; thus the number of distribution functions can easily be completed. In general, it will be difficult to perform the physically correct normalization condition (2). The area of the functions used in this work (Lorentzian and Gaussian functions) is proportional to the width and the depth of the lines, so we normalized our distribution functions dividing by the width of the distribution.

The numerical integration with respect to the angles ϑ and φ is carried out in steps of ten degrees. In order to check the program we calculated a Mössbauer spectrum for a randomly oriented powder sample (distribution function equal to unity). We obtained the normalized intensity values 0.2475, 0.1699, 0.0825, 0.0825, 0.1699 and 0.2475

whereas a calculation with Kündig's original powder program³ leads to the intensities 0.2500, 0.1667, 0.0833, 0.0833, 0.1667 and 0.2500. Using steps of five degrees for the numerical integration (requiring fourfold computer time) we obtained the values: 0.24937, 0.16751, 0.08312, 0.08312, 0.16750 and 0.24936.

APPLICATIONS

In the interpretation of the relative line intensities of an experimentally obtained Mössbauer spectrum the influence of the absorber thickness can be estimated^{4,5}. However, it is difficult to differentiate between the two contributions: preferred orientation of the crystallites and lattice vibrational anisotropy.

The influence of preferred orientation on the intensity ratios for the special cases of pure electric quadrupole interaction (assuming axial symmetry of the EFG tensor ($\eta = 0$)) and of pure magnetic dipole interaction has been calculated¹. This program generates Mössbauer spectra resulting from transitions between Fe^{57} nuclear levels for a general combination of magnetic dipole and electric quadrupole interaction and for any orientation distribution of the EFG axes. Assuming different functions for the orientation distribution of the EFG axes used for the calculation of Mössbauer spectra, the program is useful (i) to estimate the effect of preferred orientation, (ii) to obtain information about the distribution function of the EFG axes, and (iii) to evaluate the distribution of the internal magnetic field directions (by knowing the angles θ and ϕ used as input parameters).

Furthermore, this program might have some significant technological applications in regard to the orientation distribution of the internal magnetic fields. For example, the important permanent magnets consisting of Me-ferrite, $\text{MeFe}_{12}\text{O}_{19}$, (Me = Ba, Sr, Pb) are made by orienting very fine powder in a magnetic field under pressure (we used a similar procedure preparing sample 2, see below). The width of the $H(0)$ orientation distribution may be used as a parameter, which contains information about the magnetic properties of the product.

Samples Preparation

Measurements with three different barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$) absorbers have been carried out. In order to evaluate the three spectra this program

has been applied. The samples have been prepared as follows:

Sample 1 9 mg of very fine barium ferrite powder have been embedded in Araldit; the density of the absorber was $0.15 \text{ mg Fe}^{57}/\text{cm}^2$ yielding for the effective thickness $T_A = n f \sigma_0 = 2.4$, where n is the number of Fe^{57} atoms per unit area, f is the absolute Debye-Waller factor, and σ_0 represents the resonance cross section.

Sample 2 In order to prepare a preferentially oriented powder sample we mixed 9 mg of very fine barium ferrite powder with Araldit (density $0.15 \text{ mg Fe}^{57}/\text{cm}^2$) and put the mixture in a magnetic field of about 1 kOe. The direction of the field was parallel to the plane of the sample. Due to the high uniaxial crystal energy of the hexagonal crystal lattice the c -axes of the particles are forced to align themselves preferentially in the direction of the external magnetic field.

Sample 3 An industrial permanent magnet (DE 1, Siemens) was ground to a thickness of about 0.01 cm (density of about $0.2 \text{ mg Fe}^{57}/\text{cm}^2$). The preferred orientation was perpendicular to the plane of the sample.

Measurements on the three samples were made at room temperature with a single line source (Co^{57} in a Cu matrix) moved with constant acceleration. A proportional counter detected the transmitted γ -rays which were stored in 512 channels of a multichannel analyzer.

Results and Discussion

The barium ferrite spectrum consists of a superposition of five different subspectra corresponding to the five different iron sublattices⁶⁻¹¹. We have been able to fit the obtained Mössbauer spectra by resolving four spectra. In the case when the propagation direction of the γ -rays was parallel to the preferred orientation (sample 3) we could only separate three spectra; the spectrum corresponding to the bipyramidal lattice site (2b) could not be observed in this experimental arrangement, because of the strong anisotropy of the recoil-free fraction of the 2b site¹². No vibrational anisotropy was found for the other sublattices. The measured Mössbauer spectra and their computer analysis are shown in Figure 3. For clarity only the spectrum corresponding to the most occurring lattice site (12 k) is shown by a dashed line.

The method described by W. Kündig³ yields the values $\theta = 0^\circ$, $\phi = 0^\circ$ and $\eta = 0$. As the direction of the internal magnetic field $H(0)$ coincides with

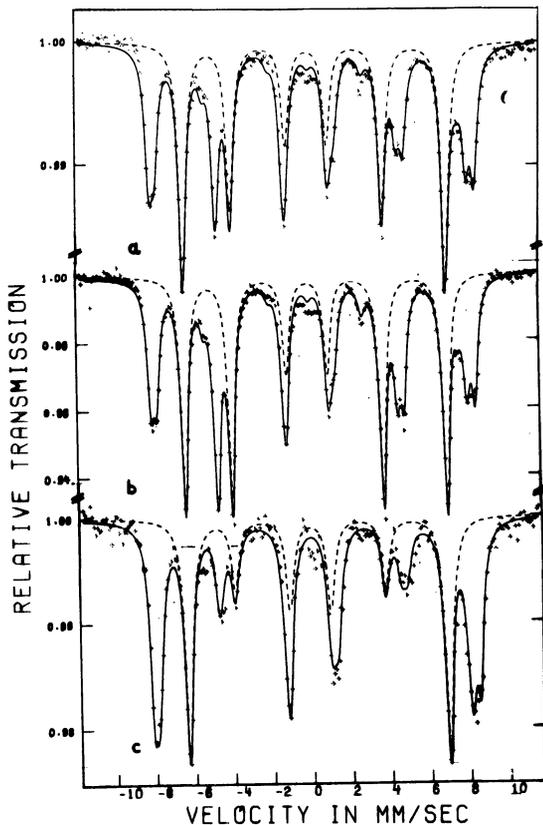


FIGURE 3 Experimental Mössbauer spectra and the calculated fit-curves of (a) sample 1, (b) sample 2 and (c) sample 3 (see text). The considered subspectrum corresponding to the sublattice 12 k is indicated by dashed lines.

the z -axis of the electric field gradient tensor, V_{zz} , the orientation distribution found for the EFG axes is the distribution of the internal magnetic field directions.

For the computer fits we used different intensity ratios of the inner lines 3 or 4 ($\Delta m = \pm 1$ transitions) to the lines 2 or 5 ($\Delta m = 0$ transitions). The best fitted Mössbauer spectra were obtained using the intensity ratios summarized in the left column of Table I.

In order to synthesize the measured Mössbauer spectra, we assumed, in the thin absorber approximation, Lorentzian and Gaussian shapes of the orientation distribution functions. We used as input parameters the known values $\theta = 0^\circ$, $\phi = 0^\circ$, $\eta = 0$ and the interaction ratio $R = 0.14$ (quadrupole splitting $\Delta E_Q = 0.41$ mm/sec and internal field $H(0) = 415$ kOe for the considered spectrum 12 k. Sample 1 and sample 3 can be expected to be randomly oriented with respect to the

azimuthal angle ϕ . In this case the distribution function depends only on the angle ϑ . Sample 2, however, does not have an orientation with rotational symmetry relative to the γ -beam. So we have to use a distribution function depending on both ϑ and ϕ . It was realized by the multiplication of a ϑ dependent Lorentzian (Gaussian) function with a ϕ dependent Lorentzian (Gaussian) function.

TABLE I

Experimentally obtained intensity ratios and the specifications of orientation distribution functions used for the calculation of theoretical Mössbauer spectra

	Experimentally obtained intensity ratios	Distribution functions used for the calculation of Mössbauer spectra			
		Lorentzian shape		Gaussian shape	
		Center	Width	Center	Width
Sample 1	0.59	$\vartheta: 0^\circ$	100°	$\vartheta: 0^\circ$	106°
Sample 2	0.44	$\vartheta: 90^\circ$	166°	$\vartheta: 90^\circ$	134°
		$\phi: 90^\circ$	166°	$\phi: 90^\circ$	134°
Sample 3	1.33	$\vartheta: 0^\circ$	11°	$\vartheta: 0^\circ$	54°

Using the known values for θ , ϕ , η and R , and the distribution functions determined by the parameters shown in Table I, we calculated Mössbauer spectra showing the experimentally obtained intensity ratios. For the three selected cases, the theoretically generated Mössbauer spectra of the 12 k sublattice are shown in Figure 4. The Lorentzian distribution functions are plotted in Figure 5.

The intensity ratio of a randomly oriented powder sample has the value of 0.5 (1 : 2). The experimentally found value of 0.59 for sample 1 indicates a small deviation from randomness. The c -axes of the crystallites, and also the internal fields, are slightly preferentially oriented parallel to the γ -ray propagation direction. Quantitatively the data can be explained by assuming an orientation distribution described by a Lorentzian (Gaussian) function with the center at $\vartheta_0 = 0^\circ$ and a width of 100° (106°).

Concerning sample 2 we used distribution functions which are the product of a ϑ -dependent and a ϕ -dependent Lorentzian (Gaussian) function. The ϑ and ϕ distributions were assumed to have equal widths. The intensity ratio has been obtained using a Lorentzian (Gaussian) distribution with $\vartheta_0 = \phi_0 = 90^\circ$, and widths of 166° (134°). Thus the

magnetic field of about 1 kOe used for the preparation of sample 2 was too weak in order to generate a strong texture with c -axes preferentially oriented parallel to the plane of the absorber. This can be

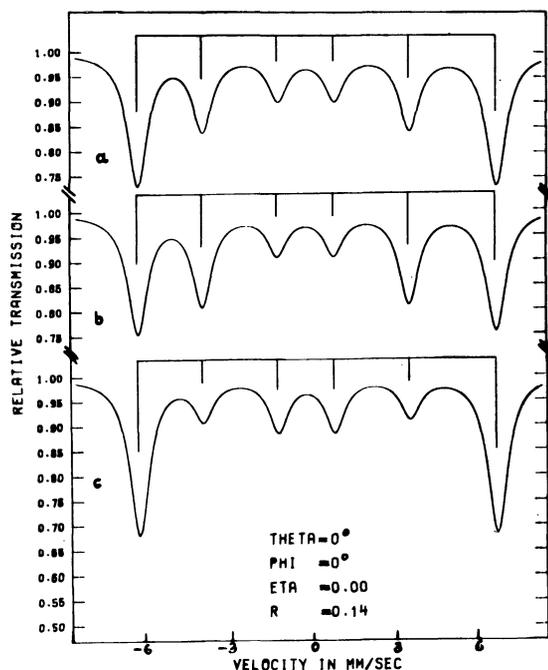


FIGURE 4 The synthesized Mössbauer spectra for the 12 k-sub-spectrum of (a) sample 1, (b) sample 2 and (c) sample 3 (see text).

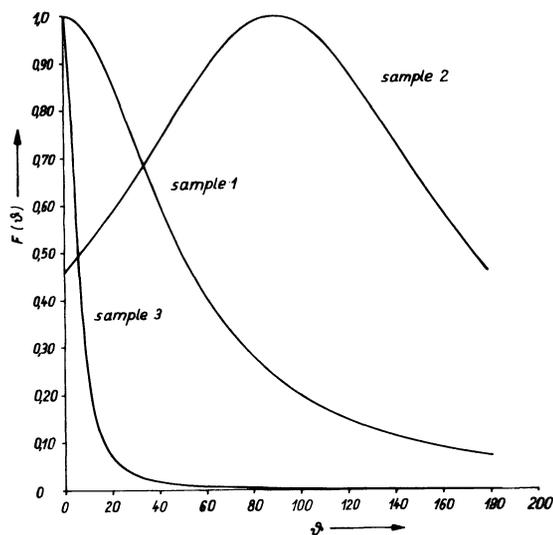


FIGURE 5 Lorentzian distribution functions used for the calculation of theoretical Mössbauer spectra (Figure 4). Concerning sample 2 only the β -dependent part of the distribution function is plotted.

understood by the fact, that the original crystallites had the form of platelets with c -axes ($H(0)$ orientation) perpendicular to the plane¹³. This special shape of the $\text{BaFe}_{12}\text{O}_{19}$ crystallites may also be the reason for the observed deviation from randomness of sample 1.

For the spectrum of sample 3 we obtain a Lorentzian (Gaussian) distribution with the center at $\vartheta_0 = 0^\circ$ and width of 11° (54°). The industrial permanent magnet (sample 3) shows a very strong texture, a feature which is important for the technological application of barium ferrite.

In this work we used two special distribution functions, and we made comparisons with experimental intensity ratios for each of the two functions. Other functions could be used likewise. However, for many practical cases the Lorentzian or Gaussian functions are reasonable approximations to the physical reality. It is clear that the described method cannot determine the distribution function in a definite manner, but it yields some information regarding direction and the magnitude of the texture. Also, there might be some biological application of this method, where, instead of the orientation distribution of the crystallites, the distribution of the principal axes of the EFG is of interest. A Fortran listing of the computer program is available on request.

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