A new method of general use to obtain random powder spectra in ^{57}Fe Mössbauer spectroscopy: the rotating-sample recording

Jean-Marc Greneche, F. Varret

► To cite this version:

Jean-Marc Greneche, F. Varret. A new method of general use to obtain random powder spectra in ^{57}Fe Mössbauer spectroscopy: the rotating-sample recording. *Journal de Physique Lettres*, 1982, 43 (7), pp.233-237. 10.1051/jphyslet:01982004307023300 . jpa-00232037

HAL Id: jpa-00232037

<https://hal.science/jpa-00232037>

Submitted on 1 Jan 1982

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification
Physics Abstracts
76.80 — 33.40

A new method of general use to obtain random powder spectra in ^{57}Fe Mössbauer spectroscopy : the rotating-sample recording

J. M. Greneche and F. Varret

E.R.A. C.N.R.S. n° 682, Faculté des Sciences, 72017 Le Mans Cedex, France.

(Reçu le 14 décembre 1981, accepté le 8 février 1982)

Résumé. — Nous démontrons, dans le cas de la spectrométrie non polarisée de ^{57}Fe , que l'on peut obtenir avec un échantillon quelconque, présentant une interaction hyperfine quelconque, un spectre Mössbauer de poudre isotrope : pendant l'accumulation du spectre, il suffit de faire tourner pas à pas l'échantillon dans un plan faisant avec la direction de propagation du rayonnement un angle de $35,3^\circ$; on peut aussi superposer quatre spectres de ce plan.

Abstract. — In the case of unpolarized ^{57}Fe Mössbauer spectrometry, a method is described which provides the equivalent random powder spectrum for any sample, with any hyperfine interaction. The spectrum is recorded while the sample is rotated stepwise within a plane lying at 35.3° from the radiation direction. An alternative method consists in superimposing spectra for 4 orientations of the sample in the same plane.

1. Introduction. — The preparation of Mössbauer polycrystalline samples, or of amorphous samples, often leads to preferred orientation of the EFG axes, or of the spin direction. This is called the « texture » effect [1], and it can result in sizeable changes in the relative values of the line intensities.

The texture effect should therefore be avoided in many cases, for instance when the Goldanskii-Karyagin effect is involved, or merely to obtain a reasonable fit of the spectrum ; also, texture-free spectra can be used as « standard spectra » to determine line intensities in the case of overlapping lines [2, 3].

At present, the problem of texture-free spectra in the case of ^{57}Fe unpolarized spectrometry has been partly solved :

(i) in the case of a polycrystalline quadrupole absorber having axial texture, Ericsson and Wappling [4] proposed tilting the sample at the « magic angle » ($\theta = 54.7^\circ$ between the radiation direction and the normal to the sample plane) ;

(ii) we recently found that the same method could be extended to the case of a general spin texture, provided that the hyperfine interaction is axial. The method consists in superimposing several spectra (up to 4 according to the texture symmetry), recorded at the « magic angle » [3].

In the present letter we show how the « magic angle » method applies to the most general case : any texture and any combination of hyperfine interactions.

2. Theory. — We first consider a single-crystal absorber (the generalization to any textured sample is obvious).

$$\begin{aligned}
& -g_1^2 e_1 e_{-1}^* e^{i\alpha} \frac{\sin \beta \cos \beta}{3} + g_1^* g_{-1} e_1^2 e^{-i\alpha} \frac{\sin \beta \cos \beta}{3} \\
& + g_1^* g_{-1} e_1 e_{-1}^* \frac{2 \sin^2 \beta}{3} \\
& - g_1^* g_{-1} e_1 e_{-3}^* \frac{\sin \beta \cos \beta}{\sqrt{3}} e^{i\alpha} - g_1^2 e_{-1} e_1^* e^{-i\alpha} \frac{\sin \beta \cos \beta}{3} \\
& + g_1^* g_{-1} e_1^* e_{-1} e^{-2i\alpha} \frac{1 - \cos^2 \beta}{6} - g_1^* g_{-1} e_{-1}^2 \frac{\sin \beta \cos \beta}{3} e^{-i\alpha} \\
& + g_1^* g_{-1} e_{-1} e_{-3}^* \frac{1 + \cos^2 \beta}{2\sqrt{3}} \\
& + e^{i\alpha} g_{-1}^2 e_1 e_{-1}^* \frac{\sin \beta \cos \beta}{3} + g_{-1}^2 e_1 e_{-3}^* e^{2i\alpha} \frac{1 - \cos^2 \beta}{2\sqrt{3}} \\
& - g_{-1}^2 e_{-1} e_{-3}^* e^{i\alpha} \frac{\sin \beta \cos \beta}{\sqrt{3}} \Big] + [\text{conj. complex}]. \quad (2)
\end{aligned}$$

The Euler angles β, α are the polar angles of the propagation direction $\mathbf{u}$ in the absorber axes. Let us calculate now :

$$\begin{aligned}
\int_0^{2\pi} I_{ge}(\alpha, 54.7^\circ) d\alpha = & \\
= \frac{2}{3} \Big[& g_1^2 e_3^2 + \frac{2}{3} g_1^2 e_1^2 + \frac{1}{3} g_1^2 e_{-1}^2 + \frac{1}{3} g_{-1}^2 e_1^2 + \frac{2}{3} g_{-1}^2 e_{-1}^2 \\
& + g_{-1}^2 e_{-3}^2 + g_1^* g_{-1} e_1 e_{-1}^* + g_{-1}^* g_1 e_{-1} e_1^* \Big] \\
& + \frac{2}{3\sqrt{3}} \Big[g_1^* g_{-1} e_3 e_1^* + g_1^* g_{-1} e_{-1} e_{-3}^* + g_{-1}^* g_1 e_1 e_3^* + g_{-1}^* g_1 e_{-3} e_{-1}^* \Big]. \quad (3)
\end{aligned}$$

The same result is obtained by performing the integration over the whole solid angle (random powder sample) :

$$\frac{1}{4\pi} \int_0^{2\pi} d\alpha \int_0^\pi I_{ge}(\alpha, \beta) \sin \beta d\beta$$

or by developing the following expressions (given by Gabriel [5]) :

$$\begin{aligned}
& \frac{2}{3} [|\langle g | \mathcal{M}^{(+)} | e \rangle|^2 + |\langle g | \mathcal{M}^{(0)} | e \rangle|^2 + |\langle g | \mathcal{M}^{(-)} | e \rangle|^2] \\
& \frac{2}{3} [|\langle g | M^{(+)} | e \rangle|^2 + |\langle g | M^{(0)} | e \rangle|^2 + |\langle g | M^{(-)} | e \rangle|^2].
\end{aligned}$$

We have thus demonstrated that the random-powder spectrum can be also obtained by integrating over α for $\beta = \text{constant} = 54.7^\circ$. A convenient experimental device consists in rotating stepwise the sample within a fixed plane, whose normal lies at 54.7° to the propagation

direction. The stepwise motion has to be preferred to the constant velocity rotation because the latter introduces a Doppler broadening of the Mössbauer lines.

An alternative method consists in superimposing four spectra, as in [3]. It turns out that :

$$I_{ge}(\text{tot}) = I_{ge}(\alpha, 54.7^\circ) + I_{ge}(\alpha + 90^\circ, 54.7^\circ) + I_{ge}(\alpha + 180^\circ, 54.7^\circ) + I_{ge}(\alpha + 270^\circ, 54.7^\circ) \\ = \frac{8}{3} [|\langle g | M^{(+)} | e \rangle|^2 + |\langle g | M^{(0)} | e \rangle|^2 + |\langle g | M^{(-)} | e \rangle|^2],$$

again equal to the line intensity of a random powder spectrum.

We emphasize that the present results apply to any case of texture since each nucleus in the polycrystalline (or amorphous) sample will give the random-powder line intensities.

3. An experimental example. — The usefulness of this method is well illustrated by considering a single crystal sample, as this is equivalent to the extreme case of texture. Large single crystal platelets of RbFeCl_3 [7], containing the main EFG axis in their plane, can be obtained for Mössbauer studies [8]. We show on figure 2 some quadrupole spectra obtained at room temperature; the main EFG axis was along the Ox sample axis ($\alpha = 0$; $\beta = 90^\circ$). Two crystals with thickness

Fig. 2. — Mössbauer spectra of RbFeCl_3 : single-crystal (2) for various radiation directions; spectrum c has been obtained with the stepwise rotating device.

Table I. — *Mössbauer experiments on a RbFeCl₃ single-crystal, as a function of the propagation direction.*

Crystal	β	α	Γ_1	Γ_2	I_1	I_2
	deg.	deg.	mm.s ⁻¹ (± 0.01)	mm.s ⁻¹ (± 0.01)	% (± 1)	% (± 1)
1	0		0.30	0.29	42	58
1	54.7°	0	0.31	0.29	56	44
1	54.7°	90	0.34	0.31	47	53
1	54.7°	180	0.31	0.29	57	43
1	54.7°	270	0.32	0.30	45	55
1 (average)	54.7	0 + 90 + 180 + 270	0.32	0.30	51	49
1 (average)	54.7	45 + 135 + 225 + 315	0.32	0.30	52	48
2	54.7	0	0.26	0.26	60	40
	54.7	90	0.27	0.27	42	58
2	54.7	rotation	0.26	0.26	50	50

β, α = polar angles of the propagation direction in the absorber axes.

Γ = linewidth (Lorentzian).

I = relative area of the line.

0.3 mm and 0.1 mm (labelled 1 and 2) were studied. Only crystal 2 had a circular shape, so that it could be directly examined by the rotating method without having to introduce corrections due to variations of the solid angle.

The rotation of the sample was performed by steps (16 positions) [9].

All fitted line intensities are listed in table I.

The line intensities obtained by the present methods, from the single crystals, compare well with the expected ratio 50 : 50. The small departures from this ratio, observed in crystal 1, might be due to a small amount of Fe³⁺ also responsible for the extra-broadening of line 1.

4. Conclusion. — The rotating-sample method has been shown to provide random powder unpolarized ⁵⁷Fe Mössbauer spectra for any case. Experiments with mixed quadrupole-Zeeman interactions are in progress. The influence of sample thickness will be investigated.

References

- [1] GONSER, U., PFANNES, H. D., *J. Physique Colloq.* **35** (1974) C6-113.
- [2] GRENECHE, J. M., Thèse 3^e cycle, Le Mans (1981).
- [3] GRENECHE, J. M., HENRY, M., VARRET, F., *Int. Conf. Mössbauer Spectroscopy*, Jaipur (Déc. 1981).
- [4] ERICSONN, T., WAPPLING, R., *J. Physique Colloq.* **37** (1976) C6-719.
- [5] GABRIEL, J., *Mössbauer Effect Methodology*, ed. I. J. Gruverman, Vol. **1** (1965) p. 121.
- [6] HENRY, M., TEILLET, J., VARRET, F., *Revue Phys. Appl.* **15** (1980) 1095.
- [7] Crystals grown by HENRY, M. (Le Mans).
- [8] MONTANO, P. A., COHEN, E., SHECHTER, H., MAKOVSKY, J., *Phys. Rev.* **B 7** (1973) 1180.
- [9] Device designed and realized by D. JOLY.