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On the validity of a ^{57}Fe hyperfine magnetic field distribution measured by a monochromatic, circularly polarized Mössbauer source

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Abstract. It is demonstrated that when in a standard Mössbauer spectroscopy experiment two different hyperfine magnetic field distributions describe experimental data equally well, measurements by means of a monochromatic circularly polarized source lead to the correct choice of the solution. The problem of the asymmetry of the spectrum in the case of a polarized source and pure magnetic interaction is discussed and constraints for the line intensities are given.

1. Introduction

One of the most important problems in Mössbauer spectroscopy is determination of the hyperfine magnetic field distribution (h.m.f.d.). Model independent algorithms are reviewed by Le Caër *et al* (1984) and Campbell and Aubertin (1989). A validity diagram was constructed which shows a conditions under which h.m.f.d. can be determined uniquely. In the case of pure magnetic interactions standard procedures work properly when peaks Nos 1 and 2 (and 5 and 6) in the Zeeman sextet do not overlap which is equivalent to the approximate condition $\sigma_B/B < 0.13$, where B and σ_B are the mean value and the width of the h.m.f.d., respectively (Le Caër *et al* 1984).

To illustrate a problem, which still remains to be solved, let us imagine that a true distribution consists of a single peak while directions of magnetic moments are distributed at random. The spectrum then consists of six overlapping peaks with relative intensities 3:2:1:1:2:3. However, one may try to evaluate the spectrum by a Zeeman component in which peaks Nos 2 and 5 have intensities smaller than 2. In this case one has to add an extra sextet in which positions of the outer peaks are located approximately at the position of peaks Nos 2 and 5 of the original sextet. In such a way an artificial extra peak in the h.m.f.d. can be created. A few methods have been reported for avoiding the discussed artefact: tilting the sample having magnetic texture with axial symmetry at the 'magic angle' (Ericsonn and Wappling 1976), decomposition of a spectrum measured with different orientations of the absorber (Vincze 1978), the rotating-sample recording method (Greneche and Varret 1982) or a simultaneous fit for spectra recorded with and without an external magnetic field (Satuła *et al* 1995).

A recently developed measurement technique by the monochromatic circularly polarized Mössbauer source (MCPMS) (Szymański *et al* 1996) offers additional experimental information which is useful in the h.m.f.d. determination. Nuclear transitions in the ^{57}Fe for which $\Delta m = 0$ are not sensitive to the helicity of the resonant radiation. When the

hyperfine magnetic field is parallel to the radiation direction, transitions with $\Delta m = +1$ are active for one helicity while those with $\Delta m = -1$ are active for the opposite helicity. Thus performing absorption measurements with two helicities of radiation but the same external conditions (sample orientation, direction of applied field, magnetic texture) one obtains two different spectra, the sum of which is equivalent to the spectrum measured by the standard technique. Analysis of the dependence of resonant absorption on the helicity can give, in principle, information about location (on the velocity scale) of transitions with $\Delta m = +1, 0$ and -1.

To demonstrate advantages of the MCPMS in the determination of the h.m.f.d., we present an example of polycrystalline, ordered $Fe_{2.5}Cr_{0.5}Al$ alloy, belonging to the class of DO_3 type alloys investigated earlier. The spectrum consists of enough wide and overlapping absorption lines resulting in ambiguities when standard analysis is applied. From the methodological point of view, the spatial spin structure should not be complex. This is the case since the alloy is a soft magnetic material and saturates easily during the measurements in external magnetic field.

The paper presents experimental details concerning sample preparation and the apparatus. Next, we discuss the problem of the symmetry of the spectra measured with MCPMS. Further on we present measurements and compare results of the standard analysis with analysis of the spectra measured by MCPMS.

2. Sample preparation and the apparatus

An $Fe_{2.5}Cr_{0.5}Al$ polycrystalline alloy was prepared using an argon arc melting technique. The alloy was crushed into powder and annealed in Ar atmosphere: after reaching the temperature $800\,^{\circ}C$ the sample was cooled in a controlled way at the rate of $56\,^{\circ}C\,h^{-1}$. The x-ray diffraction analysis showed that the sample has the DO_3-type structure with the lattice parameter of $5.7748(2)$ Å, in agreement with Satuła *et al* (1997).

Mössbauer absorbers in the form of pellets containing 9.7 mg of $Fe_{2.5}Cr_{0.5}Al$ per square cm were prepared by mixing the powdered alloy with Li_2CO_3 filler (transparent for 14.4 keV radiation and epoxy glue. The standard Mössbauer measurements were performed in constant acceleration mode. Commercial ^{57}CO in Cr matrix was used as a source.

The polarized source was obtained by introducing a resonant filter between the source and the absorber (Szymański *et al* 1996). The filter was driven together with the source by a standard Mössbauer transducer. Atomic Fe moments of the filter were oriented using an applied longitudinal magnetic field. The filter resonantly absorbs photons with only one helicity. Remaining photons, passing through the filter, were used for Mössbauer measurements of the absorber oriented by an external longitudinal field. The average width of the lines in the calibration spectrum of an α-Fe measured with a polarized source was equal to $0.30(1)$ mm s^{-1}. Other details are given in (Szymański 1995) and (Szymański *et al* 1996).

3. Spectrum asymmetry in the MCPMS measurements

The magnetic texture problem as observed by the means of MCPMS has been discussed already (Szymański 1998), and expressions for the line intensities have been given in the cited paper for any magnetic texture (by the line intensity the area under the absorption line is understood). A characteristic feature of the MCPMS measurements is the asymmetry of the line intensities Nos 1 and 6 and 3 and 4. Let us define spectrum asymmetry A as a measure of the difference

between line intensities:

$$A = \frac{|I_1 - I_6|}{I_1 + I_6} = \frac{|I_3 - I_4|}{I_3 + I_4}. \tag{1}$$

In the ideal case of a fully polarized source and perfectly aligned magnetic moments in the absorber, the spectrum may consist of only two lines: Nos 1 and 4 or Nos 3 and 6, depending on the helicity of radiation. In that case the spectrum asymmetry has maximum value equal to 1. If the directions of the magnetic moments are randomly distributed, the spectrum asymmetry is equal to zero. In the real experiment the spectrum asymmetry depends on the magnetic texture and the beam polarization.

Let us consider now the following problem. Assume that the normalized intensities of the lines Nos 2 and 5 were determined in a standard experiment and they are equal to I_{25} (normalization of the intensities means setting the sum of the six line intensities to one). What value of A can be expected to appear in the MCPMS experiment? To answer this question we insert the expression for the line intensity given in (Szymański 1998) into equation (1) and we obtain

$$A = \frac{2\langle \vec{m}\vec{\gamma} \rangle}{1 + \langle (\vec{m}\vec{\gamma})^2 \rangle} \tag{2}$$

where $\vec{m}$ is a unit vector along the direction of the nuclear moment of ^{57}Fe, $\vec{\gamma}$ is the unit vector parallel to the wave vector of the radiation and $\langle (\cdot) \rangle$ denotes weighted averaging of $(\cdot)$ within a sphere with the weights determined by the texture function. $\langle (\vec{m}\vec{\gamma})^2 \rangle$ is the average cosine square of the angle between the observation direction and the direction of the magnetic moment which is equal to $1 - 4I_{25}$. Using the Buniakovski–Schwartz inequality we can write

$$\langle \vec{m}\vec{\gamma} \rangle \leqslant \sqrt{\langle (\vec{m}\vec{\gamma})^2 \rangle}. \tag{3}$$

Thus

$$A \leqslant \frac{2\sqrt{\langle (\vec{m}\vec{\gamma})^2 \rangle}}{1 + \langle (\vec{m}\vec{\gamma})^2 \rangle} = \frac{\sqrt{1 - 4I_{25}}}{1 - 2I_{25}}. \tag{4}$$

Inequality (4) gives the upper limit of the spectrum asymmetry for a given value of the normalized intensity of line Nos 2 and 5. In the standard Mössbauer spectroscopy line intensities are usually expressed in the form $3:z:1:1:z:3$. In that case inequality (4) takes the form:

$$A \leqslant \tfrac{1}{4}\sqrt{16 - z^2}. \tag{5}$$

4. Results and discussion

The spectrum measured in applied field at room temperature is shown in figure 1. Because the investigated sample is an ordered, crystalline alloy, one can expect the existence of only a few components reflecting the well defined composition of the nearest neighbouring iron atoms. However, a variety of more distant coordination shells disturb the hyperfine fields resulting in the appearance of a hyperfine field distribution. In this situation we fit the spectrum by a set of Zeeman components each one having Gaussian h.m.f.d. For each component the isomer shift was a free parameter. The quadrupole splitting was assumed to be zero. The same value of z was used for all components. The fitted line is shown in figure 1(*a*); the resulting h.m.f.d. is shown in figure 2 by a dotted line. The parameters obtained from the fit with $z = 0.1$ are listed in table 1. One should note that the ratio of B_3/B_1 is equal to 0.56(2) which is equal to the ratio of the separation between the lines in the Zeeman sextet: $(v_5 - v_2)/(v_6 - v_1) = 0.578\,95$
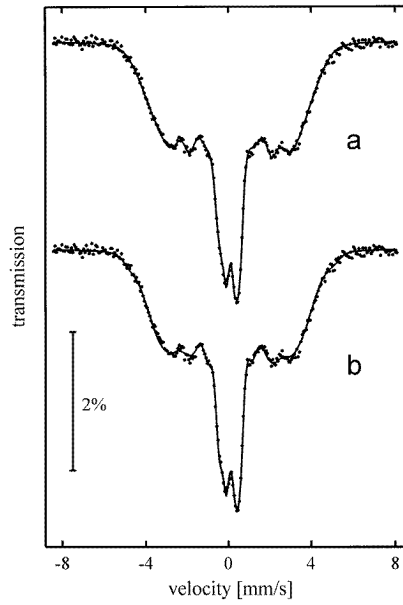
Figure 1. Mössbauer spectrum of $Fe_{2.5}Cr_{0.5}Al$ measured at room temperature and fitted under assumptions that (*a*) spins are nearly perfectly aligned and (*b*) spins are disordered.
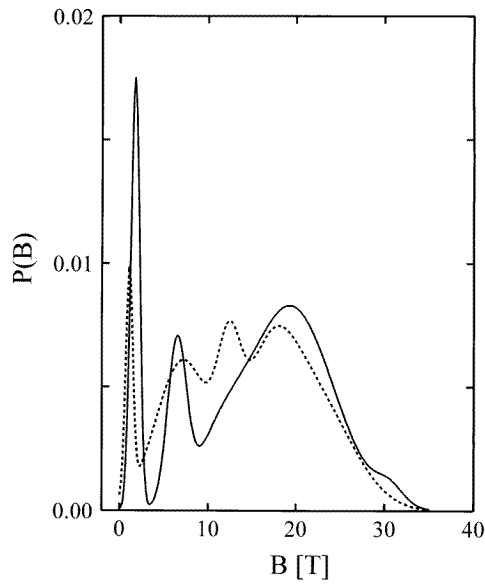

Figure 2. Shape of the h.m.f.d. for nearly aligned spins (dotted line) and disordered spins (solid line).

(Robinson 1981). It means that lines Nos 1 and 6 of the third sextet are located in the vicinity of peaks Nos 2 and 5 of the first sextet. This is just the situation discussed in the introduction. One may suspect that the assumed value of the relative line intensity of lines Nos 2 and 5 which corresponds to $z = 0.1$ is incorrect. Assuming that spins are not perfectly aligned, taking

Table 1. The parameters obtained from the fit under the assumption that spins are aligned ($z = 0.1$). The letters A, IS, B and σB abbreviate area, isomer shift with respect to α-Fe, mean value of the Gaussian distribution and a standard deviation of the Gaussian distribution, respectively. The symbol * means that the value was not a free parameter. Numbers in parenthesis are statistical errors.

i	A_i	IS_i [mm s^{-1}]	B_i [T]	σB_i [T]
1	31(6)	0.047(6)	22.1(8)	4.3(3)
2	25(7)	0.099(9)	16.8(3)	3.1(4)
3	9(2)	0.119(6)	12.3(1)	1.3(2)
4	30(1)	0.113(5)	7.1(1)	3.0(2)
5	5.8(3)	0.102(5)	1.08(3)	0.4*

Table 2. Same as in table 1 for $z = 0.95$.

i	A_i	IS_i [mm s^{-1}]	B_i [T]	σB_i [T]
1	1.7(3)	0.15(2)	30.6(3)	1.5(4)
2	65(1)	0.067(3)	19.34(7)	4.93(7)
3	8(1)	0.28(1)	11.2(3)	2.7(3)
4	10.9(5)	0.087(6)	6.48(5)	1.06(6)
5	13.9(1)	0.102(3)	1.74(2)	0.50(7)

$z = 0.95$, and using exactly the same number of Zeeman components, we obtain another fit shown in figure 1(*b*), for which parameters are listed in table 2. The h.m.f.d. is drawn by a solid line in figure 2. One see that nearly the same quality of the fit (figures 1(*a*) and 1(*b*)) corresponds to quite different h.m.f.ds.

A few words concerning the choice of the numerical values of z: the z value may have a value between 0 (all spins parallel) and 4 (all spins perpendicular to the beam direction). We have found that there are at least two local minima of the sum of the squares of the fitted function. One minimum corresponds to $z = 0.0$ (perfect alignment) which is an apparent artefact: there is non-zero angular divergence of the beam and the applied magnetic field direction is not fully controlled. We thus choose a more reasonable value of $z = 0.1$. The second value of $z = 0.95$ describes well the spectra and corresponds to the second local minimum in the fit.

The same sample geometry and the same permanent magnet was used for the MCPMS experiment. The spectra measured with two opposite helicities are shown in figures 3(*a*) and 3(*c*), respectively. In order to describe these spectra we used the values listed in table 1 and fitted the spectra with parameter A (corresponding to the asymmetry, see equation (1)) as the only free parameter. The fitted lines are shown in figures 3(*a*) and 3(*c*). We similarly proceeded with the second h.m.f.d. for which parameters are given in table 2. Again only one free parameter was describing the asymmetry. The resulting fits are shown in figures 3(*b*) and 3(*d*). It is evident that the assumption about nearly perfect spin alignment is consistent with MCPMS experiment while assumption about partial spin disorder does not agree with the MCPMS measurements. In fact, such a result should be expected for $Fe_{2.5}Cr_{0.5}Al$ which is known to be a soft magnetic material at room temperature (Satuła 1998), and should easily saturate in the field of 1 T.

In both considered cases the spectrum asymmetry fulfils inequality (5). For another system, however, it could be not fulfilled. This would indicate the incorrectness of the h.m.f.d. considered. In fact, the inequality (5) can be used as an indicator of the maximum value of the parameter z, consistent with observed asymmetry of the spectra.
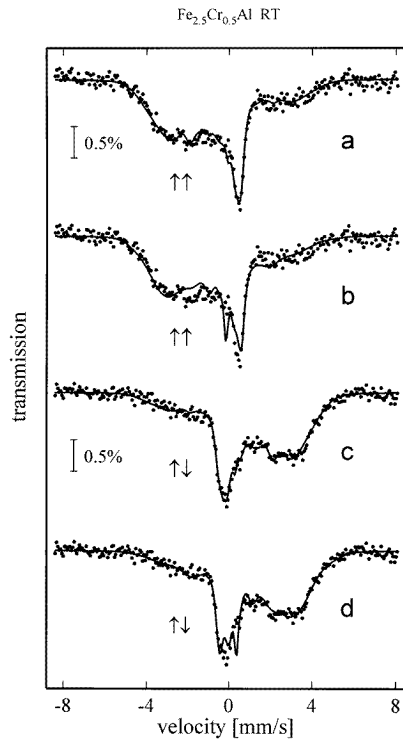
Figure 3. Mössbauer spectra of $Fe_{2.5}Cr_{0.5}Al$ measured with a polarized source and fitted under the assumption that spins are nearly perfectly aligned ((a) and (c)) and that spins are disordered ((b) and (d)). The arrows ↑↑ and ↑↓ denote two opposite helicities of the radiation.

One may suspect that there is a paramagnetic contribution to the spectra seen as a doublet located close to zero velocity. We have thus performed fits in which a doublet was used instead of the low field Zeeman component. The shape of the h.m.f.d. formed by four remaining Zeeman components is not disturbed by this operation and the main conclusion remains unchanged. The problem of a paramagnetic contribution in the MCPMS technique will be considered in a separate paper.

The hyperfine fields arising from the MCPMS measurements are fully consistent with the ones obtained earlier (Satuła *et al* 1995). The components listed in table 1 correspond to the different local environments of iron in highly ordered alloy. The indices $i = 5$, 4 and 3 from table 1 correspond to the three peaks in the h.m.f.d. (see the dotted line in figure 2) and the local environments of the Fe atom, having as its nearest neighbours one, two or three iron atoms, respectively. Poorly resolved peaks in figure 2 for indices $i = 1$ and 2 correspond to the iron atoms having more than three Fe in its first coordination shell. There is a clear maximum of the IS against index i, see table 1. The explanation of this behaviour is the following. It is known from the literature that the Al atom increases the local contribution to the IS (Athanasiadis *et al* 1977) while Cr acts in the opposite direction (Dubiel and Zukrowski 1981). In the spectrum of ordered $Fe_{2.5}Cr_{0.5}Al$ there is contribution of the subspectrum resulting from iron atoms having four Al and four Fe in the first coordination shell. This subspectrum has the largest isomer shift and moderate values of the hyperfine magnetic field. Chromium atoms enter preferentially into one of the iron sites and cause lowering of the isomer shift as well as the hyperfine magnetic

field. This results in the presence of paramagnetic and low field components with small isomer shift. For more detailed discussion see Satuła *et al* (1995).

5. Conclusions

We have demonstrated that analysis of standard Mössbauer measurement of ordered polycrystalline $Fe_{2.5}Cr_{0.5}Al$ alloy leads to ambiguity of the h.m.f.d. MCPMS measurements with two different polarizations allow one to choose the correct solution. The asymmetry of any spectrum with pure magnetic interactions in the MCPMS experiment is constrained by the relative height of lines Nos 2 and 5 by the simple relation (5).

Acknowledgments

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