The method of invariants in $^{57}$Fe Mössbauer spectroscopy on selected examples

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Abstract. The method of invariants is an effective tool for decomposition of Mössbauer spectra into components resulting from electric quadrupole and magnetic dipole interactions. The invariants can be next analysed to obtain all possible values of hyperfine interaction parameters. In some cases it is possible to determine the parameters with satisfactory precision. The method was applied to not fully ordered UFe$_4$Al$_8$. Obtained results indicate that the dominant component of the electric field gradient is negative and is oriented almost perpendicularly to the direction of the hyperfine magnetic field. Another example shows that the method of invariants results in substantial reduction of the number of calculated components in modeling of hyperfine interactions in $\gamma$-FeMn.

1. Introduction
Mixed hyperfine interactions, e.g. magnetic dipole and electric quadrupole ones, in case of 1/2-3/2 spin transition cause difficulties in the interpretation of Mössbauer spectra because of the ambiguity problem [1]. Derivation of complete set of hyperfine parameters corresponding to specified values of invariants was considered in [2]. The proposed treatment was, however, not widely used. Explicit formulas for the intensity tensor [3] allow one to use the invariants (instead of hyperfine fields) for description of the absorption line positions and intensities as well. The method of Mössbauer spectra analysis making use of the invariants for proper description of the spectra components was recently proposed in [4]. Although the method described in [4] does not allow determination of the complete set of hyperfine interactions parameters, of invariants, and the analysis proposed in [2], may lead to satisfactory characterisation of the system. In particular the method is sensitive to the changes of local direction of hyperfine magnetic field ($\text{HMF}$) with respect to the electric field gradient ($\text{EFG}$) diagonal directions, see [4] for details.
UFe₄Al₈ intermetallic compound attracted considerable interest and the magnetic structure was recently determined [5,6]. Although the unit cell of UFe₄Al₈ is tetragonal, local symmetry of Fe is low [5], see Fig. 1a. The orientation of the EFG axes can not be simply deduced from the structure. Also experiments with ¹⁸¹Ta local probe in UFe₄Al₈ [7] were not conclusive and to our best knowledge EFG at Fe(8f) in UFe₄Al₈ is not known. This motivated us to analyze the Mössbauer data of UFe₄Al₈ by the method of invariants. Unfortunately, probably because of the sample quality, the spectra collected close to the transition temperature could not be characterized by single site static behaviour. We thus restrict the analysis to the spectra measured at low temperatures only. The spectrum measured in paramagnetic phase will be analysed as well.

Another selected example was disordered γ-FeMn antiferromagnetic alloy, interesting for spintronics. The Mössbauer spectra of this alloy have been already measured in sixties [8], however orientation of hyperfine fields and strength of the EFG is still not exactly known [9,10]. The invariants offer strict description of the spectra components at temperatures close to the transition temperature and thus spectra measured in the wide temperature range can simultaneously be analysed. This results in information on the hyperfine interactions in poorly resolved spectra.

2. Example of UFe₄Al₈

Mössbauer measurements were performed on the powdered sample of UFe₄Al₈ (reported in [11]) at different temperatures. The spectra shown in Fig. 1b were simultaneously analysed using the set of four components. The line positions and intensities can be given explicitly by invariants $S_0$, $S_1$, $S_2$ constructed from the EFG tensor $V$ and the HMF pseudovector $B$ [3]:

$$S_0 = a \sqrt{\text{Tr} V^2},$$
$$S_1 = a m^T \cdot V \cdot m,$$
$$S_2 = a \sqrt{m^T \cdot V^2 \cdot m},$$

where

$$a = e Q c / E_g$$

is the proportionality constant between the EFG components (in [V/m²] in SI units) and the invariants expressed conveniently for applications in [mm/s]. $Q$ is the nuclear quadrupole moment, $e$ is the elementary charge, $c$ is the speed of light, $E_g$ is the energy between the ground and the excited state, $m = B / B$. Because of presence of weak intensity components, constraints were applied to their center shifts according to the Debye model. The isomer shift at $T=0$ was a free parameter for each component. Constraints were also applied to the areas under subspectra and $T^{3/2}$ dependence of the EFG components on temperature. The invariants $S_0$, $S_1$, $S_2$ extracted from the spectra at temperatures 12, 35 and 80 K are shown in Fig. 1c for the main component (Fe(8f)). The measurements were also performed at higher temperatures close to the magnetic transition temperature (not shown). However, observed shape of the spectra indicate that simple approximation which uses constant number of subspectra is not sufficient.

All possible values of hyperfine parameters $B$, $V_{zz}$, $\eta$, $\theta$, $\phi$, corresponding to a point in Fig. 1c, were next extracted by a method similar to those presented in [2]. We note that the treatment described in [2] does not include situation when invariants are closely related to condition:

$$2S_0^4 + 18S_1^2 - 3S_0^2 (S_1^2 + 4S_2^2) = 0$$

shown by the lines in Fig. 1c. This case corresponds to the axially symmetric EFG and full discussion of the data treatment will be published elsewhere. The results obtained for all possible values of $V_{zz}$, $\eta$, $\theta$, $\phi$ are shown in Fig. 1d.

Low temperature measurements indicate presence of six line patterns, in agreement with earlier reports [5,6,11]. However, room temperature spectra consist of a slightly asymmetric doublet. It is hard to expect that Goldanski-Karyagin effect can be responsible for the asymmetry because...
A tetragonal axis of symmetry is perpendicular to the local two-fold axis of iron. More likely explanation can be searched in distribution of EFG originated due to chemical disorder in the crystal. One cannot also exclude presence of small amount of other phases, for example FeAl. That is why four components were used for simultaneous fit shown in Fig. 1b.

The method of invariants and constrained simultaneous fit allowed us to decompose the spectra into the main and other components. Although invariants are not single valued functions of hyperfine parameters, the results obtained for the main component in UFe₄Al₈ (Fig. 1d) are located within relatively narrow ranges. The Vzz component of the EFG is negative and the angle between the Vzz axis and the hyperfine magnetic field is close to π/2. No systematic changes of the orientation of hyperfine field with respect to the EFG axes were detected in the temperature range 13-80K.

Figure 1 a) Local structure of Fe at 8f site in UFe₄Al₈, b) Mössbauer spectra of Fe in UFe₄Al₈ and results of simultaneous fit (weak-area components are reduce practically to horizontal lines in the figure c). Invariants S₀, S₁, S₂ of the main component (different temperatures are indicated by different colors, however the symbols overlap). Dashed lines indicate the region of all physically possible values of the invariants. Orange lines correspond to values of axially symmetric EFG, see eq. (3), d) All possible values of Vzz, η, θ, φ parameters for the S₀, S₁, S₂ invariants shown in c) (θ and φ in radians). Blue, green and red colours correspond to T=12, 35 and 80 K, respectively.

3. Example of γ-FeMn

Chemical disorder in cubic alloys causes breaking of local symmetry and creation of nonzero EFG. This was demonstrated in the case of bcc Fe-V alloys [12]. Similar situation may be present in
disordered fcc Fe-Mn alloys. In case of magnetic order, number of different local environments is large. For exemplary estimation let us assume that local magnetization in fcc Fe-Mn is oriented along one of (111) directions. If the EFG gradient is next assumed to depend on the chemical configuration of the nearest neighbours (screened Coulombic pseudopotential [13]), one finds $2^{12}$ different chemical configurations and 8 different orientations of the local hyperfine fields (see example in Fig 2a) which makes $8 \cdot 2^{12} = 32768$ different local environments for which diagonalisation has to be performed for correct calculation of the mixed hyperfine interactions. The problem, however, may be greatly simplified if the invariants are calculated. For all considered configurations only 160 different sets of invariants $(S_0, S_1, S_2)$ exist. These invariants, once calculated, may be used in the fitting procedures. Efficiency of this procedure is shown in Fig.2 which displays excellent fit performed for the spectra measured in a wide temperature range (for details see [14]).

**Figure 2** a) Example of local environment of iron at fcc binary alloy and HMF vector along (111) direction. b) Selected Mössbauer spectra of γ-FeMn fitted simultaneously at wide temperature range.

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