Mössbauer studies of single crystal γ-Mn-Fe

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Abstract Mössbauer measurements were performed on single crystals γ-$Mn_{60}Fe_{37}Cu_3$ in an external field of 1.3 T at room temperature. The hyperfine field distribution can be described as a vector sum of the external and internal fields. In addition, anisotropic response of magnetic moments was detected. The anisotropy, due to Fe atoms, has Fe-rich surroundings.

Key words γ-Mn-Fe alloys • iron alloys • manganese alloys • Mössbauer spectroscopy

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Introduction

Face-centered cubic Mn-Fe alloys with an Fe concentration up to 70 at.% order antiferromagnetically below the Néel temperature. The Néel temperature has a maximum around 50% Mn and decreases steeply with increasing concentration of iron [8]. The alloys with Fe content below 27 at.% undergo tetragonal lattice deformation at magnetic transition. The lattice structure remains unchanged for higher Fe content. The magnetic structure for alloys with a tetragonal lattice was unambiguously determined by the magnetic neutron diffraction. Both, atomic magnetic moments and the wave-vector of antiferromagnetic modulation, are oriented along [100] direction (see Ref. [8]); this magnetic structure is abbreviated by 1Q.

Among continuum of possible AF structures the most probable ones for cubic symmetry are: 1Q, 2Q and 3Q with magnetic moments parallel to [100], [110] and [111] directions, correspondingly [5]. For the first two types of structure, there exist 3 types of antiferromagnetic domains which differ in the directions of the AF modulation wave-vectors and of the magnetic moments. For example, in the case of 1Q structure there are three type of domains with magnetic moments and AF wave-vector parallel to [100], [010] and [001] directions, respectively. It is the presence of these domains which makes neutron diffraction technique unable to distinguish the type of magnetic structure which is realized in cubic alloys. Therefore, details of the magnetic structure of the γ-Fe-Mn are still much debated.

Mössbauer measurements of γ-Fe-Mn indicate that the average hyperfine field extrapolated to $T = 0$ K is weakly dependent on the concentration. The temperature dependence of the hyperfine field does not follow temperature variations of the average magnetic moment [2]. Although our experiment is sensitive to the direction of magnetic field, the presence of antiferromagnetic domains makes the Mössbauer spectra in zero external field insensitive to

the magnetic structure. However, each of the structure exposed to external magnetic field would, in principle, produce different Mössbauer pattern. Measurements in the field up to 9 T applied along [100] crystallographic direction excludes the possibility of presence of 1Q structure [6]. This paper presents experimental results of measurements carried out on single crystals of the γ-$Mn_{60}Fe_{37}Cu_3$ alloy exposed to an external magnetic field parallel to different crystallographic directions [100], [110] and [111].

Samples

A single crystal γ-$Mn_{60}Fe_{37}Cu_3$ alloy was grown by the Bridgman method. A small amount of Cu was added to stabilize fcc structure. Three flat samples of thickness of about 0.5 mm were cut with their surfaces parallel to (100), (110) and (111) crystal planes, respectively. The samples were thinned by grinding to a thickness of about 50–60 micrometers. In the next step, the samples were thinned by electrochemical methods to thickness suitable for Mössbauer transmission experiment. To avoid selective etching of the elements, we use solvents, as an electrolyte, which cause an effect of electrochemical polishing. Obtained samples have thickness in the range 30–35 μm and surface from 5 to 10 mm^2. The effective thicknesses of the samples were in the range 4÷4.7. Neutron diffraction was used to verify whether the grinding and polishing processes did not destroy the single-crystal structure. The measurements were performed at a 3-axis spectrometer at the MARIA reactor at Świerk. Diffraction of the beam with wavelength 1.5 Å was observed from the (200) and (110) planes, parallel to the samples surfaces. These results confirmed that the thinned samples are still single crystals.

Mössbauer measurements

Mössbauer measurements were performend in constant acceleration mode at room temperature with unpolarized monochromatic radiation. For measurement in magnetic field, the samples were placed in a hole of the permanent rare earth magnet producing an axial field of 1.3 T. The field was parallel to the $\boldsymbol{k}$ vector of the radiation and perpendicular to the sample surface. An example of the spectrum for $\boldsymbol{k}$ and $\boldsymbol{B}$ perpendicular to the (100) planes is shown in Fig. 1. Two other spectra measured with $\boldsymbol{k}$ and $\boldsymbol{B}$ perpendicular to the (110) and (111) planes, respectively, have a slightly different shape and the differences between the spectra are shown in Figs. 2c and 2d. The observed differences reflect anisotropy of the hyperfine field distribution induced by external field acting in different crystal directions.

One expects that this anisotropy will not be observed when the external field vanishes. To demonstrate this behavior, measurements in zero applied field were performed. The differences between the spectra are shown in Figs. 2a and 2b. We see that when magnetic field is absent, the shape of the spectrum does not depend on the orientation of the $\boldsymbol{k}$ vector of the radiation with respect to the crystal axes.

All measured spectra are not symmetric in the velocity coordinate, Fig. 1. Precisely, we mean that the spectrum is
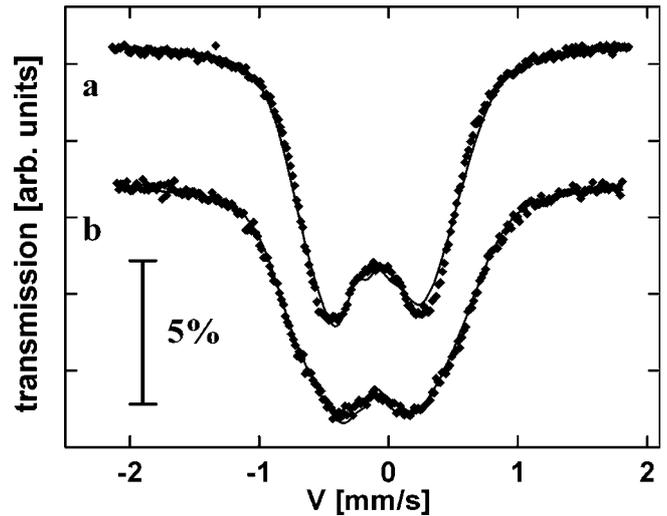

Fig. 1. Mössbauer spectra measured on a single crystal with (100) planes parallel to the $\boldsymbol{k}$ vector of the radiation (a) in zero external field and (b) in external field 1.3 T applied perpendicular to the sample surface. Solid lines correspond to the model of rigid magnetic moments for 3Q structure, see text.

not symmetric with respect to v_{CS}, v_{CS} is the center shift of the spectrum. Small asymmetry seen in the spectrum indicates that there is a correlation between the local hyperfine field and other hyperfine parameters (isomer shift (*IS*) or/and quadrupole splitting (*QS*)).

Because atoms in γ-Fe-Mn are distributed randomly among crystal sites, one expects the presence of distribution of hyperfine interactions due to local chemical disorder. Thus we assume that the alloy is pseudobinary and there is a binomial distribution of hyperfine magnetic field and isomer shift.

$$(1) \qquad p(B_k,IS_k) = n!(k!(n-k)!)^{-1}c^k(1-c)^{n-k}$$

where $B_k = B_0 + \Delta B \cdot k$, $IS_k = IS_0 + \Delta IS \cdot k$, $k = 1,2,...n$. For the fcc crystal structure $n = 12$, and c was equal to the concentration of Fe. Distribution of the isomer shift was introduced to explain the small asymmetry in the spectra, and for simplicity a linear correlation between local hyperfine field and isomer shift was assumed. *QS* was assumed to be zero, and will be discussed later. Since the Fermi contact interaction results in hyperfine field antiparallel to the Fe magnetic moment [4, 12], the hyperfine field vectors $\boldsymbol{B}_k$ were antiparallel to directions of the magnetic moment, irrespective of the model used. All three magnetic structures in the case of zero applied field results in the same shape of the spectrum shown by the line in Fig. 1a. When external field $\boldsymbol{B}_{ext}$ is applied to the sample, the spectrum corresponds to the sum of components with hyperfine fields equal to the vector sum $\boldsymbol{B}_k + \boldsymbol{B}_{ext}$. We assume that the magnetic moments did not change their orientations under applied field (we will call it the "rigid magnetic structure"). Our assumption is in agreement with Mössbauer measurements in the field up to 9 T [6], with magnetic susceptibility measurements in fields up to 1 T [3, 8] and with the observed minute anisotropy of the magnetic susceptibility [10]. In the data analysis of all spectra measured in different crystallographic directions, only one set of hyperfine parameters B_0, ΔB, IS_0, ΔIS, was taken for
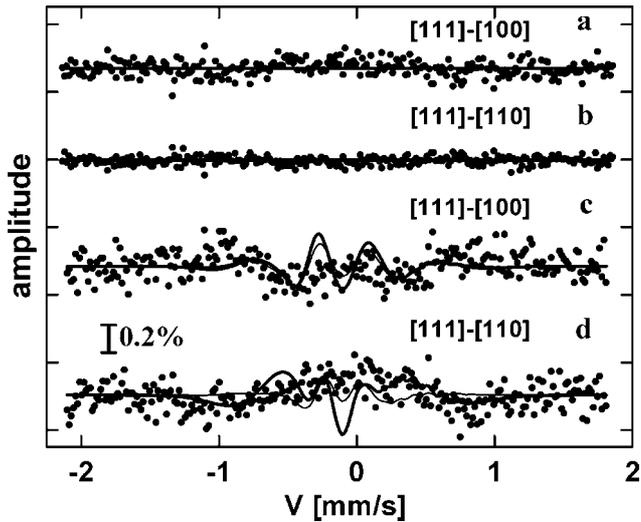
Fig. 2. Differences between the spectra measured under different orientation of the external magnetic field B_{ext} (and k) vector with respect to the crystallographic directions: (a, b) $B_{ext} = 0$ T; (c, d) $B_{ext} = 1.3$ T. Abbreviation [111]–[100] means that the spectrum measured with B_{ext} and k parallel to the [100] was subtracted from that measured with B_{ext} and k parallel to the [111]. Solid lines correspond to the models of rigid magnetic moments (thin lines) and varied populations (thick lines), respectively, for 3Q structure, see text.

characterization of a given structure. The spectra computed for 3Q structure are shown as solid lines in Fig. 1. We see good agreement between the experimental spectra and the solid lines representing the microscopic model.

Similar evaluation was performed for two other magnetic structures (1Q and 2Q). The quality of agreement between the experimental and model spectra is similar although the lowest value of χ^2 obtained for 3Q structure could indicate that this structure is preferred. The fitted parameters ΔB, ΔIS, which may have physical interpretation of the change of hyperfine field and isomer shift, respectively, caused by the exchange of Fe by Mn atom in the first coordination shell of Fe atom, are $\Delta B = 0.57$ T, $\Delta IS = 0.02$ mm/s.

Having performed best simultaneous fits of the spectra for the given magnetic structure (1Q, 2Q or 3Q), the experimental and theoretical spectra were compared. Rather poor agreement of the experiment and model of rigid magnetic structure (Fig. 2) indicates that the magnetic moments must respond to the applied field and the reaction depends on the direction in which the field is applied. Following these ideas of [6], we test the possibility of changing the population of magnetic moments oriented along directions predicted by 1Q, 2Q or 3Q structures. In the simulations, it was assumed that the change of populations does not create ferromagnetic moment – the fact known from the susceptibility measurements [3, 8]. In all cases better agreement was obtained with enhanced population of the moments perpendicular to the applied field. The best agreement, obtained again for the 3Q structure, is, however, still poor, see Fig. 2.

Discussion

Absorption line amplitudes depend on the thickness and may create nonzero differences seen in Figs. 2c and 2d.

However, because the observed differences in the spectra appear only when magnetic field is applied, one may safely conclude that the role of thickness is negligible in the observed effects.

In paper [2], it was reported that for polycrystalline γ-Fe-Mn alloys in the concentration range of 10–50 at.%. Fe, the average hyperfine field measured well below the Néel temperature does not depend on the concentration. Above the Néel temperature, $T_N = 519$ K, the spectrum for γ-Fe-Mn with 50.9 at.%. Fe measured at $T = 543$ K consists of a broadened single line of FWHM equal to about 0.4 mm/s [2]. Those authors report that natural width, measured on the hematite calibration sample, was equal to about 0.3 mm/s. We thus estimate that the broadening due to hyperfine interactions (IS or QS) above the Néel temperature is in the range of 0.1 mm/s. From $\Delta IS = 0.02$ mm/s and eq. (1) the FWHM of the IS distribution is 0.045(5) mm/s, which, consistently, does not exceed the above estimation. This result indicates also that one should expect a slight concentration dependence of isomer shift, not yet reported for γ-Fe-Mn. Indeed, from eq. (1) we estimate that in the concentration range 20–60% the average isomer shift should change by about 0.09 mm/s, the value which is below the natural width and to our knowledge was not reported.

The positive value of the correlation between IS and hyperfine field $dIS/dB = \Delta IS/\Delta B = 0.037$ mm/s/T indicates that the larger hyperfine field, the larger isomer shift is present on the nucleus. It is known from experiment that the isomer shift of isolated ^{57}Fe impurity in Mn is negative, -0.230 ± 0.012 mm/s with respect to the α-Fe [9]. Similarly, Mn impurity in bcc Fe also decreases the isomer shift of its nearest neighbors to $-(0.01 \div 0.02)$ mm/s [1, 11]. Because there is quite good overall agreement of the measured spectra and the model of rigid magnetic moments (see Fig. 1), the obtained value $\Delta B = 0.5$ T may be interpreted as a change of hyperfine field when Fe atom is replaced by Mn in the iron nearest neighborhood. In the concentration range 50–70% Fe, we thus expect a change of the average field by 1.2 T. We have no experimental data to check this room temperature estimation, however, there is a trend reported for zero temperature of increasing field with increase of the Fe concentration [2] which agrees with our prediction.

A quadrupole splitting of -0.019 mm/s was determined for γ-Fe$_{55.8}$Mn$_{44.2}$ at $T = 4.2$ K [6]. It is known that QS increases with decreasing temperature because of lattice vibrations [7]. Moreover, for an alloy one expects that because of various orientations of the local electric field gradient axes, the average QS is zero. These are reasons why in our analysis zero QS was assumed. We note that asymmetry of the room temperature spectra could be fully explained as resulting from the correlation between the IS and hyperfine magnetic field.

Small systematic deviations observed in Fig. 1 between the experimental points and the fitted lines are probably due to approximate only correctness of the assumed binomial distribution, eq. (1), of the hyperfine field and a possible influence of Cu atoms which was not considered at all. However, the discrepancies observed in Figs. 2c and 2d cannot be explained by this way because in the difference of spectra, the components with the largest probabilities only are dominating. We see that both models, of the rigid

magnetic moments and the model with varying domain population, do not describe correctly the behavior of the moments in the external magnetic field. We note that the outer maxima (or minima) of the differences seen in Figs. 2c and 2d are located at velocities which correspond rather to the tails than to the maximum absorption of the spectrum from Fig. 1b. This indicates that the anisotropic behavior must be a property of iron atoms which has a large hyperfine field, i.e. the Fe atoms with nearest coordination shell rich in Fe.

Summary

Mössbauer technique was employed to investigation of the effect of an external magnetic field on the Fe moments in the single crystal of γ-Fe-Mn-Cu. The observed hyperfine magnetic field distribution corresponds to the presence of the variety of chemical environments of Fe atoms. The asymmetry observed in the spectra indicates a correlation between the hyperfine magnetic field and the isomer shift. We argue that the more Fe-rich environment, the larger is the hyperfine field present on the Fe nucleus.

The modifications of the hyperfine fields of Fe, introduced by the applied external field, consist of a vectorial addition of the external field to the hyperfine field. The vector sum also explains the observed broadening of the spectra caused by the external magnetic field. All three magnetic structures, $1Q$, $2Q$, $3Q$ produce fits of quality similar to that presented in Fig. 1.

The shape of the spectra depends on the direction of the external field applied to the crystal. This small effect cannot be explained neither by the assumption that magnetic moments are rigid, nor by the various population of domains. It is argued that iron moments, which have iron-rich surroundings, are responsible for the observed in-field anisotropy.

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