Hyperfine Interaction Parameters in $Fe_{28}Al_{72}$:
^{57}Fe Mössbauer Spectroscopy and *Ab Initio* Study

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The paper discusses a theoretical model that associates the shape of the Mössbauer spectrum with the configuration of atoms in local surroundings of the Mössbauer nuclide. Using the model we analyse the Mössbauer spectra of $Fe_{72}Al_{28}$ alloys after various heat treatments. Basing on the model calculations the hyperfine structure parameters describing an effect of an Al atom in the first and the second coordination shell of ^{57}Fe atom are evaluated. Using these parameters the values of hyperfine magnetic field and isomers shift for the atomic configurations present in stoichiometric Fe_3Al are estimated and compared with the results of *ab initio* calculations.

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1. Introduction

It is well established that physical and mechanical properties of Fe–Al alloys are related to their atomic ordering [1]. The Mössbauer spectroscopy offers a sensitive microscopic point-probe to identify the nature of ^{57}Fe-atom configurations responsible for various hyperfine fields observed in Fe–Al alloys [2, 3]. In the paper we describe model of the Mössbauer spectra analysis taking into account different configurations of atoms in local surroundings of the Mössbauer nuclide. The influence of neighboring atoms on the hyperfine interactions at ^{57}Fe-atom is taken into account using the additive model described in [4, 5]. Basing on the model calculations the hyperfine structure parameters describing an effect of an Al atom in the first and the second coordination shell of ^{57}Fe atom are evaluated. Using these parameters the values of hyperfine magnetic field and isomers shift for the atomic configurations present in stoichiometric Fe_3Al are estimated and compared with the results of *ab initio* calculations.

2. Experimental

The materials investigated were multicomponent Fe28Al alloys of nominal composition 71.64 at.% Fe, 28 at.% Al and small amounts of other additives (Mo–0.2, C–0.1, Zr–0.05, B–0.01 at.%) introduced in order to improve their thermal and mechanical properties. The alloys were produced by vacuum induction melting. The samples were examined in seven different states defined in Table I.

The Mössbauer spectroscopy measurements in the standard transmission geometry were carried out for thin foils (about 40 μm thick) of samples at room temperature using a constant acceleration drive. The source was ^{57}Co(Rh) with an activity of about 50 mCi (one spectrum was measured with source of activity 50 mCi).

TABLE I

The thermal treatment of the investigated samples.

Abbreviation	Treatment
FC	homogenization 48 h at 1000 °C in air, slow cooling with furnace
Q-air	homogenization 48 h at 1000 °C in air, quenching in air
Q-oil	homogenization 48 h at 1000 °C in air, quenching in oil
Q-air/500°0.5 h	Q-air + annealing at 500 °C for 0.5 h/slow cooling with furnace
Q-oil/500°0.5 h	Q-oil + annealing at 500 °C for 0.5 h/slow cooling with furnace
Q-air/500°2 h	Q-air + annealing at 500 °C for 2 h/slow cooling with furnace
Q-oil/500°2 h	Q-oil + annealing at 500 °C for 2 h/slow cooling with furnace

For the numerical analysis of the spectra, specially created software was used which implemented a theoretical model appropriate to solve the problem. The Mössbauer spectra were deconvoluted into a complex of sextets of lines. Each Zeeman sextet was related to a specific atomic configuration (m, n) in two nearest neighboring shells of ^{57}Fe, appearing with probability $P(m, n)$ (in DO_3 structure $m_{max} = 8$ and $n_{max} = 6$). The influence of the nearest neighboring shells is determined by the number of various atoms in these shells, but not by their space arrangement. The positions of lines in each sextet are calculated via respective hyperfine parameters related to the specific atomic configuration (m, n): the hyperfine magnetic field $H(m, n)$, isomer shift $IS(m, n)$ and quadruple splitting $QS(m)$ (the latter is assumed to be a function of m solely). In order to reduce the number of free parameters, the following constraints have been imposed: according to literature suggestions [4, 5], $H(m, n) = H(0, 0) - m\Delta H_I - n\Delta H_{II}$ where $H(0, 0)$, ΔH_I and ΔH_{II} are constant values. $IS(m, n)$ is calculated as a linear function of the hyperfine field $IS(m, n) = IS_0 + \beta H(m, n)$. Such a correlation was re-

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ported in literature for mean values of H and IS [4, 6] as well as for respective local value of H and IS [6]. The model assumes also that the hyperfine interactions of further coordination shells lead to a broadening of the spectrum lines and that the broadening (in relation to natural width of line Γ_0) depends on the distance of a given line from the centre of spectrum $\Delta\Gamma = \delta|\nu_i|\Gamma_0$ where ν_i is the i-th line position. The probability $P(m,n)$ is approximated as a product $P(m,n) = p_{\mathrm{I}}(m)p_{\mathrm{II}}(n|m)$ where $p_{\mathrm{I}}(m)$ is the probability of finding m atoms of Al in the first coordination shell of the Mössbauer probe and $p_{\mathrm{II}}(n|m)$ is the conditional probability of finding n atoms of Al in the second shell given the presence of m atoms Al in the first coordination shell. For further reduction of free parameters and to obtain smooth changes of $p_{\mathrm{II}}(m|n)$, the conditional probability is approximated by binomial distribution $p_{\mathrm{II}}(m|n) = C_n^6 p_m^n (1 - p_m)^{6-n}$ where p_m is a parameter different for different m. All the experimental spectra, of samples after different heat treatment, were fitted simultaneously. The searched values of parameters $H(0,0)$, ΔH_{I}, ΔH_{II}, IS_0, β, δ and $QS(m)$ were assumed to be common for all the spectra fitted together.

The electronic structure calculations were performed using the WIEN2k code [7] based on the full-potential linearized augmented plane wave (FP-LAPW) method with the local orbitals added for correction of linearization errors [8]. The fully relativistic and scalar-relativistic formalism was used for core and valence states, respectively. The LSDA-GGA exchange-correlation (XC) potential was used in the form given in [9]. Atomic muffin-tin spheres radii were taken 1.99 a.u. for Al and 2.12 a.u. for Fe in bcc-Fe and Fe_3Al. Basing on the *ab initio* electronic spin density the hyperfine field was calculated using the relativistic formula of Blügel et al. [10].

3. Results and discussion

Despite the relatively strong constraints imposed on the model parameters, very good fits were obtained. The determined values of the common parameters are presented in Table II.

TABLE II

The determined values of some hyperfine structure parameters.

ΔH_{I} [T]	ΔH_{II} [T]	$H(0,0)$ [T]	IS_0 [mm/s]	β [mm/s T^{-1}]
3.29	1.19	33.6	0.353	-0.00926

From the *ab initio* calculations for Fe_3Al compound we have obtained IS $= 0.002$ mm/s and $H = 31.4$ T for Fe(0,6), and IS $= 0.136$ mm/s and $H = 24.6$ T for Fe(4,0). The calculated values of IS and H for Fe(4,0) are close to those estimated on the basis of experimental data given in Table II ($\mathrm{IS}_{\exp} = 0.164$ mm/s and $H_{\exp} = 20.4$ T). Although the magnitude of calculated hyperfine field exceeds the estimated value by 4 T but it is to be reduced by the oppositely directed orbital contribution. For Fe(0,6) the discrepance between the *ab*

initio and experimental values of IS and H is significant probably due to the nonstoichiometry and disorder of investigated samples. The disagreement can also be related to the low probability of the Fe(0,6) configuration as estimated from the Mössbauer spectra analysis. According to the phase diagram for the Fe–Al system [11], if the concentration of Al is close to 28 at.%, the DO_3 phase is the equilibrium phase. Indeed, the X-ray diffraction (XRD) patterns related to all investigated Fe28Al samples indicated the presence of DO_3 phase in various amounts. In the completely ordered structure of DO_3, there are only two configurations of Al atoms in two first coordination shells of Fe atom, namely configuration ($m = 4$, $n = 0$) with frequency $P(4,0) = 2/3$ and configuration ($m = 0$, $n = 6$) with frequency $P(0,6) = 1/3$. The Fe28Al alloy is not stoichiometric, so even in the completely ordered phase, some additional configurations besides the mentioned above have to exist. In the case of our samples, the ideally ordered structure is impossible to obtain because the samples are not in the equilibrium state, they have a non-stoichiometric composition and contain defects and antiphase domains. Becasue of this, one may expect a number of various atomic configurations (m,n). Indeed, the experimentally obtained $P(m,n)$ distributions are quite complex, however they always contain peaks at $(4,0)$ and $(0,6)$. It is especially seen in the diagram of $P(m,n)$ determined for furnace cooled sample.

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