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Alternative approach for evalution of Mössbauer spectra of nanostructured ferromagnetic alloys within generalized two-lewel relaxation model

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The simplest treatment of the complex ^{57}Fe Mössbauer absorption spectra of nanostructured Fe-Cu-Nb-B alloys within the recently-developed generalised two-level relaxation model has been successfully performed. This model applied for a system of superparamagnetic particles allows one to take into account the interparticle interaction in a simpler form and to describe qualitatively a specifically asymmetric shape of Mössbauer lines with sharp outer and smeared inward sides when the conventional two-level relaxation model fails. The approach is actually an alternative way in order to evaluate the Mössbauer spectra of nanostructured ferromagnetic alloys without taking into consideration a rather wide and diverse distribution over the particle sizes.

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We report the first experimental evidence for the success of the generalised two-level relaxation (GTLR) model recently introduced in order to understand Mössbauer spectra of nanostructured magnetic alloys [1]. Studies of these alloys by means of different techniques are of great interest for both fundamental and technological reasons. The most attractive are the structural and magnetic properties of these alloys so that the ^{57}Fe Mössbauer spectroscopy appears to be an excellent tool for characterisation of the iron-based nanostructured materials [2 – 6]. These materials are produced by the partial devitrification of amorphous alloys and consist structurally of nano-sized crystalline bcc-iron grains (NG) with a long-range order and the residual amorphous matrix that exhibits short-range order. As a result, the Mössbauer spectra of the materials look like a superposition of the well-resolved hyperfine magnetic structure corresponding to NG and strongly broaden magnetic component with lower average hyperfine field which is usually associated with the amorphous phase (see Fig.1). In spite of a large amount and diversity of the experimental spectra of various nanostructured materials, there still remain principal difficulties and even contradictions in the treatment of data.

The most popular approach for evaluation of Mössbauer spectra of nanostructured ferromagnetic alloys is taking into consideration continuous distributions of the hyperfine field H_{hf} [7], which should describe, first of all, a distribution over the particle sizes in such inhomogenious materials. This method has allowed researchers to restore the temperature dependencies of the H_{hf} average values and widths of their distribution for NG and amorphous phase as well as to justify the presence and evaluate the parameters of so-called interface zones between NG and matrix [2, 6]. However, the results obtained within the method suffer often some ambiguousness. First, the widths of H_{hf} distribution requires for their explanation a rather wide distribution over particle's size, which is often not confirmed by complementary methods. On the other side, the sizes of NG in the nanostructured materials are regarded to be rather small (for instance, the average size of particles in the $Fe_{86-x}Cu_1Nb_xB_{13}$ alloys was estimated to be of about 2–4 nm from transmission electron microscopy measurements [8]) so that the particles should demonstrate superparamagnetic relaxation at finite temperatures.

The simplest way to describe the relaxation effects on the Mössbauer lineshape is to use the two-level relaxation (TLR) model [9], within which only two energy states corresponding to opposite directions of the particle's magnetic moment along the easy magnetisation axes are considered, so that jumps from one state to the other are determined by the energy barrier U_0 between them (Fig.2, left). The Neel formula is used to describe the temperature-dependent transition rate [10]:

$$p = p_0 \exp\left(-U_0/k_B T\right) \qquad (1)$$

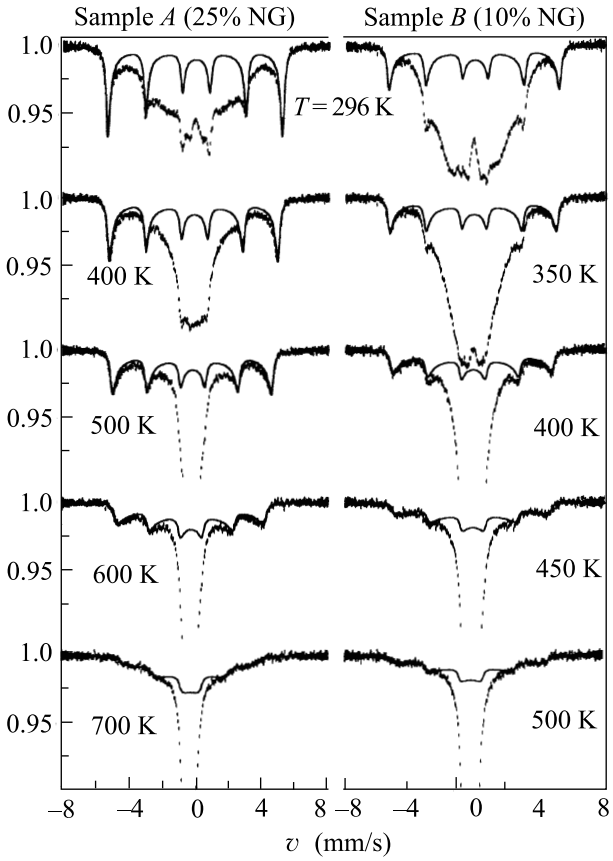

Fig.1. Temperature evolution of ^{57}Fe Mössbauer spectra (bars) of the nanostructured ferromagnetic $Fe_{79}Cu_1Nb_7B_{13}$ alloys with different content of nanograins: 25% NG (left) and 10% NG (right). Solid lines are calculated within the generalized two-level relaxation model for the outermost hyperfine magnetic component corresponding to NG of the same size with different energy distribution widths σ

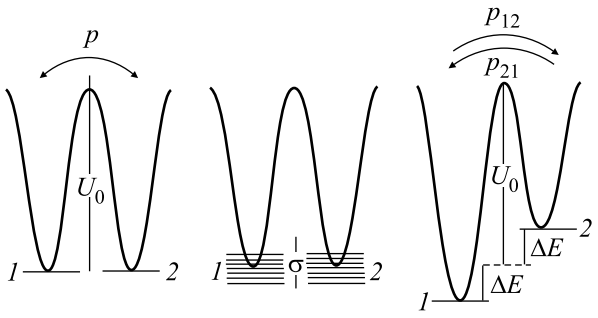

Fig.2. Two-level relaxation model for a single superparamagnetic particle (left), generalized two-level relaxation model for a particle interacting with enviroment (center); two-level scheme for a particle interacting with enviroment at given ΔE (right)

where p_0 is slightly dependent on temperature. According to the model, if the relaxation rate is comparable or larger than the natural Mössbauer linewidth Γ_0 (that is just the case for the iron nano-sized particles at room temperatures and higher ones), the relaxation is to reveal itself in the Mössbauer spectra with temperature increasing as a remarkable broadenning of spectral lines followed by shifts of the widely broaden lines to the centrum of the spectra and a collapse of the magnetic hyperfine structure into a single central line or quadrupole doublet at higher temperatures [1, 9].

At the first glance, the temperature evolution of Mössbauer spectra of nanostructured ferromagnetic alloys (like those shown in Fig.1) just exhibits behaviour of the kind, that is why some investigators has tried to evalute the spectra within the relaxation effects [4]. The pressing point here is just the consequence of the two-level relaxation model that at any stage of relaxation in the transition region from a well resolved hyperfine magnetic structure to its collapse the broadenning of spectral lines should be principally of Lorentzian type, i.e., the relaxation should result in the appearance of long Lorentzian tails in the spectrum, which could be easily registered by means of carefull fitting the spectrum. Earlier [6], we have performed such a detailed analysis of the Mössbauer spectra of nanostructured $Fe_{86-x}Cu_1Nb_xB_{13}$ alloys using powerful DISCVER method [11], but failed to find any traces of the conventional relaxation effects (i.e., the presence of additional Lorentzian tails in the spectra) up to higher temperatures where the collapse effect occurs.

However, the most striking feature of Mössbauer spectra of nanostructured ferromagnetic alloys is a specifically asymmetric shape of the spectral lines with sharp outer and smeared inward sides, and even stairs-like shape at higher temperatures (see Fig.1), which is experimentally observed in almost each second work published in the field (see, e.g., [2–6] and references therein). Lines of this unusual form have been observed earlier in many studies of systems with superparamagnetic particles [12, 13] and could not fit the conventional two-level relaxation model without taking into account a rather wide distribution over the particle sizes, i.e., over the magnetic anisotropy energies U_0 and relaxation parameters p_0 [14]. Note that a much more complicated multilevel relaxation model with a log-normal particle size distribution has successfully described the Mössbauer spectra of real fine particle systems, but no qualitative distinction between effects of the two factors on the line-shape evolution with temperature has been given [15].

A qualitatively new explanation for Mössbauer line-shapes of the kind has been recently suggested in theoretical work [1] where a generalisation of the TLR model has been performed. In the present study we

have applied this GTLR model for a qualitative treatment of the Mössbauer spectra of the nanostructured $Fe_{79}Cu_1Nb_7B_{13}$ alloys with average NG size of about 4 nm and different NG content, measured in the temperature range from 300 K to 700 K. Because of great importance of qualitative consequences of the new GTLR model for superparamagnetic relaxation as a whole and for studies of nanostructured magnetic materials in particular we will stay below within the simplest possible assumptions taken in [1].

The principal postulate of the GTLR model is that the relaxation between the particle's states with opposite directions of its magnetic moment never occurs as a transition between the states of the same energy because even weak interaction with the enviroment should inevitably smear out the energy levels (Fig.2, center). In a system like nanostructured ferromagnetic alloys with a great number of degrees of freedom, the energy levels of each particle at a certain time prove to be separated by a certain gap ΔE (Fig.2, right) and the average value σ of distribution over ΔE may be rather large and comparable to temperature. Such a separation of the energy levels results in different values of the relaxation rates, $p_{12}(\Delta E)$ and $p_{21}(\Delta E)$, from one state to the other and vice versa, followed by a difference in equilibrium populations of these states from the detailed balance principle. As a result, the shape of Mössbauer absorption spectrum and its temperature evolution changes drastically [1, 9].

Following the assumption of the conventional TLR model that the hyperfine field at the nucleus can only be reversed during the relaxation and results obtained in [1], one can easily derive the following expression for the cross-section of gamma-quantum absorption for a given ΔE:

$$\varphi(\omega, \Delta E) = -\frac{\sigma_a \Gamma_0}{2} \sum_{\alpha} |C_\alpha|^2 \mathrm{Im} \frac{\bar{\omega} + i\bar{p} + (\Delta p/\bar{p})\omega_\alpha}{\bar{\omega}^2 - \omega_\alpha^2 + \bar{p}^2 - 2i\Delta p I \omega_\alpha} \tag{2}$$

where $\bar{\omega} = \omega + i(\Gamma_0/2 + \bar{p})$, $\alpha = (M, m)$ labels the hyperfine transitions between the ground and excited states with nuclear spin projections m and M onto the direction of the hyperfine field, $\omega_\alpha = M\omega_e - m\omega_g$, $\omega_{e,g} = g_{e,g}\mu_N H_{hf}$, μ_N is the nuclear magneton, $g_{g,e}$ is the nuclear g factor for the ground and excited states, C_α determines the intensity of the corresponding transition, σ_α is the effective absorber thickness,

$$\bar{p} \equiv \bar{p}(\Delta E) = \frac{p_{12}(\Delta e) + p_{21}(\Delta e)}{2}$$

and (3)

$$\Delta p \equiv \Delta p(\Delta E) = \frac{p_{21}(\Delta E) - p_{12}(\Delta E)}{2}.$$

It is clearly seen that in the absence of interaction ($\Delta E = 0$, $\bar{p} = p$, $\Delta p = 0$) Eq. (2) is reduced to the well-known expression for the absorption spectrum within the conventional TLR model [9].

From the physical point of view the ΔE values must be random variables spread over a certain interval, and the simplest ΔE distribution function can be chosen in the Gaussian form:

$$P(\Delta E, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(\Delta E)^2}{2\sigma^2}\right). \tag{4}$$

Then, the averaged absorption cross-section is naturally determined by the energy distribution width σ:

$$\bar{\varphi}(\omega) = \int_{-\infty}^{\infty} \varphi(\omega, \Delta E) P(\Delta E, \sigma) d(\Delta E). \tag{5}$$

Using Eqs. (2)–(5) one can easily calculate the absorption spectrum within the GTLR model providing that the relaxation parameters $p_{12}(\Delta E)$ and $p_{21}(\Delta E)$ are given, i.e., the values of energy maximum and minima shown in Fig.2 (right) should be determined. In the simplest case of weak interaction ($\Delta E \ll U_0$) the relaxation parameters can be written in the form:

$$p_{21,12}(\Delta E) = p \exp(\pm \Delta E / k_B T) \tag{6}$$

where p is defined by Eq. (1). In this case, as clearly seen from comparison of Eqs. (1)–(6), the averaged absorption spectrum $\bar{\varphi}(\omega)$ is completely defined by only three parameters p_0, U_0 and the ratio of the energy distribution width to temperature, $\sigma/k_B T$. As have been already shown in [1], the relaxation Mössbauer spectra calculated within this scheme differ drastically from those of the TLR model, and the most salient feature of the GTLR spectra is just the appearance of asymmetrically shaped lines with extended inward wings.

Since the asymmetrical lineshape is clearly seen in the spectra of nanostructured $Fe_{79}Cu_1Nb_7B_{13}$ alloys shown in Fig.1, we have tried to fit the data within the GTLR model. However, in order to analyze spectra of such a high level of complexity in details one needs first to develop a strategy of analysis and corresponding computer programm like DISCVER [11], which, of course, takes time. That is why at this first stage of analysis we have decided to restrict ourselves with fitting the only, most distinguishable contribution into the spectra with the highest value of hyperfine field which obviously comes from nanocrystalline grains. We have performed simultaneous fitting of the whole temperature series of spectra for each sample over the outermost velocity ranges including only outer lines of magnetic sextet corresponding to NG. The adjustable parameters in

the course of fitting were p_0 and U_0, the same for all spectra of each sample, as well as hyperfine field, isomer shift and σ for each spectrum of the sample. In order to avoid unphysical solutions due to the restrictions on the fitting velocity ranges, the variable parameter was also the spectral area of only one spectrum of the series while others were bonded by the ratios of total areas of corrresponding spectra, which were estimated independently with rather good accuracy [6].

Results of the analysis are shown as solid curves in Fig.1 and temperature depedencies of the values of hyperfine field H_{hf} and energy distribution width σ for both the samples studied are displayed in Fig.3. As clearly seen, Fig.1 demonstrates a good description of

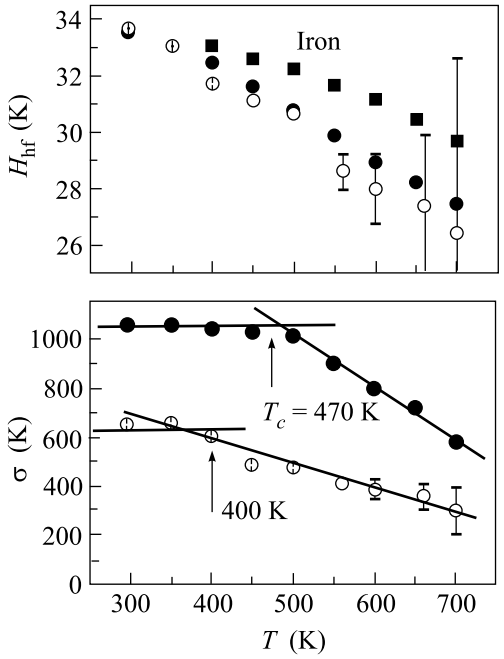

Fig.3. Temperature dependences of the hyperfine fields (top) and energy distribution widths σ (bottom) obtained from the fitting outermost velocity ranges of the spectra shown in Fig.1: sample A with 25% NG (closed circles) and sample B with 10% NG (open circles). Rectangles (top) correspond to the bulk values of hyperfine field in pure iron. The indicated Curie temperatures of the amorphous matrix in the samples were estimated by the Mössbauer thermal scan method [8]

the outermost lines of all the spectra as well as almost complete accordance between the calculated curves and resolved magnetic hyperfine structure (with lines of strongly asymmetrical shape mentioned above) at temperatures higher than the Curie temperature of amorphous phase for both the samples. Remembering that solid lines in Fig.1 are calculated within the GTLR model for the only hyperfine magnetic component corresponding to NG of the same size, one can understand that in this case there is no need to introduce a broad distribution of particle's size at least for this NG phase even at higher temperatures, because the relaxation of interacting particles can result in the specific broadening of the spectral lines. In any case it is clear that although the GTLR model does not deny principally the particle's distribution over sizes, taking into account the interparticle interaction should strongly modify the shape of the distributions obtained by conventional methods.

There is one more interesting result of physical meaning. As Fig.3 shows, despite of considerable difference between the temperature evolution of Mössbauer spectra for two samples studied, the hyperfine field values for nanograines in these samples are practically the same up to higher temperatures and slightly deviate from the temperature dependency of bulk values of hyperfine field in pure iron. In the same time, the difference in the temperature evolution of the spectra for two samples as well as the forms of this evolution mentioned above seem to be governed by the temperature dependency of energy distribution width σ characterizing interparticle interactions. At least, it is obviously seen in Fig.3 that the $\sigma(T)$ dependencies exhibit remarkable changes in the interactions just above the Curie temperature of amorphous phase for both the samples, which again evidences for an essential interrelation between the magnetic behaviour of NG and amorphous matrix.

As for the relaxation parameters p_0 and U_0, they apppeared to be equal to $(1.0 \pm 0.8) \cdot 10^{11}\,\mathrm{s}^{-1}$ and $1100 \pm 300\,\mathrm{K}$, respectively, just indicating that the fast relaxation regime is realized for nanograins in both the samples down to the room temperature. Moreover, large mean-square errors in these parameters justify this conclusion, because in the case of fast relaxation the absorption cross-section becomes slightly dependent on the relaxation rate p, i.e., on p_0 and U_0. Indeed, the fast relaxation regime from physical viewpoint means very fast fluctuations between the energy states of a particle so that the nucleous should 'feel' only the stochastically averaged hyperfine field defined by the difference of the equilibrium polpulations, $w_1(\Delta E)$ and $w_2(\Delta E)$, of the states at a given ΔE:

$$\bar{H}_{hf}(\Delta E) = [w_1(\Delta E) - w_2(\Delta E)]H_{hf}. \qquad (7)$$

As follows from the detailed balance principle,

$$w_1(\Delta E) - w_2(\Delta E) = \Delta p/\bar{p} = \tanh(\Delta E/k_B T), \qquad (8)$$

and Eq. (5) for the absorption cross-section in the GTLR model is reduced to the form independent of the parameter p [1]:

$$\bar{\varphi}(\omega) = \frac{\sigma_a \Gamma_0^2}{4} \sum_\alpha |C_\alpha|^2 \times$$

$$\times \int_{-\infty}^{\infty} \frac{1}{[\omega - \omega_\alpha \tanh(x)]^2 + \Gamma_0^2/4} P(x, \sigma/k_B T) d(x). \quad (9)$$

As seen from this equation, the spectrum in the fast relaxation regime represents a continuous distribution of hyperfine magnetic sextets with lines of natural width and relative intensities defined by the $P(x, \sigma/k_B T)$ probability function. Then, one can easily see that the lineshapes in the GTLR model are asymmetric and fully determined by the ratio of energy distribution width σ to temperature. Realisation of the fast relaxation regime in our case may only mean that nanograins in the samples studied are really small and would demonstrate the superparamagnetic behavior even at room temperature if they were isolated, however, the interparticle interaction makes them stay in the locally ferromagnetic state up to essentially higher temperatures.

In conclusions, the generalised two-level relaxation model proved to be rather efficient in describing specific shapes of Mössbauer spectra of nanostructured ferromagnetic alloys. It actually represents a new approach to analysis of the spectra taking into consideration the interparticle interaction in a simple form which can be easily used by experimentators. However, the GTLR model must be extended to the case of time-dependent energy shifts ΔE which should be correlated over mutually interacting superparamagnetic particles. Besides that, a detailed quantitative analysis of Mössbauer spectra of nanostructured ferromagnetic alloys obviously requires the development of efficient computational procedure taking into account both the relaxation of interacting particles and their distribution over sizes.

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