Mössbauer spectra of hematite and magnetite nanoparticles in polymer composites

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Abstract. It is experimentally demonstrated that the shape of Mössbauer spectra of polymer composites based on single-domain magnetic particles depends more on an inter-particle interaction than on superparamagnetic properties of a separate particle. The characteristic features of the spectra of such systems with strong inter-particle interactions are separated, such as an asymmetric shape of lines with sharp outer and smeared inward sides and presence of central anomalously splitted doublet. It is shown that the three-level relaxation model, which takes into account the precession and diffusion of magnetization of single-domain particles between two local energy minima and one absolute energy maximum, allows to describe all characteristic features of the spectra of such systems.

1. Introduction

The particles of a magnetically ordered substance whose magnetization vector can spontaneously change its orientation due to a coherent rotation of its individual spins are called superparamagnetic. The results obtained from the investigation of the magnetic properties of these particles depend on a correlation between the time of measurement and that of magnetization vector relaxation. If the time of observation is much less than that of relaxation then the particles exhibit ferromagnetic properties, while in the opposite case the particles are superparamagnetic. The time of relaxation increases with the particle size. Therefore, the Mössbauer spectrum of a dispersed system of magnetic nanocrystals is usually a superposition of a Zeeman sextet, corresponding to the large-size ferromagnetic particles, with a superparamagnetic doublet, corresponding to the particles of smaller size. On the other hand, the time of relaxation in the system of interacting superparamagnetic particles can change due to correlation bonds arising between magnetization vectors of neighboring particles. This is the so called superferromagnetic state. Inserting of the magnetic nanoparticles in a polymer environment does not change the properties of the particles, but can change the parameters of inter-particle interaction. That is why qualitative interpretation and theoretical calculation of the polymer composites spectra is a difficult task.

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2. Qualitative features of the interacting single-domain nanoparticles spectra

We investigated superparamagnetic behavior of a dispersed $\alpha$-Fe$_2$O$_3$ powder with mean size of about 19 nm, prepared from aqueous solution of Fe(NO$_3$)$_3$$\cdot$9H$_2$O. Ammonium solution was added dropwise to the solution of the iron salt at 50°C until the PH of the solution became 7.2. The precipitate was filtered, washed, dried, ground in a ball mill and calcinated in air at 400°C for 1 hour. Mössbauer spectra of film samples, prepared by precipitation of a dredge of the powder in alcohol (a) and in alcohol with a polymer addition (b) are shown in Fig.1.

One can see that sample (b) exhibits classical superparamagnetic behaviour with temperature increase from 77 to 300 K. In contrast, the superferromagnetic sample (a) reveals doublet at 300 K only. The blocking temperature, which is experimentally estimated as the temperature at which the magnetically split and the unsplit subspectra have equal areas, differs for two samples of the same powder by more than 200 K.

For direct demonstration of the influence of inter-particle interaction on the shape of Mössbauer spectra, the powder under investigation was poured loosely into a lucite container. One can see in Fig. 2a that there is no sign of superparamagnetic component. After that, the container with powder was filled with water and a superparamagnetic doublet was observed in the spectrum measured at the same temperature (Fig. 2b). The effect is reversible and after the water has been dried out the spectrum came back to its initial form. For a qualitative analysis of specific features of such spectra it is convenient to use the approach based on the introduction of the continuous distributions of the hyperfine field $P(H_{hf})$. The result of such a calculation of the spectrum of loosely poured particles using of the MSTools software package [4] is shown in Fig. 3c. One can see in Fig. 3a that even within this model-free approach without any restrictions on distribution $P(H_{hf})$ besides Lorentzian shape of lines (linewidth 0.12 mm/s) it is impossible to describe asymmetric shape of lines with sharp outer and smeared inward sides. It may be recognized from a magnitude of standard deviations between the experimental and calculated spectra (Fig. 3b), which increase systematically at the outer sides of the lines. Another characteristic feature of the spectra of interacting particles is the presence of anomalously split doublet at temperature above the blocking one. The splitting can not be explained by a quadrupole hyperfine interaction in the presence of the electric field gradient on the nucleus because it disappears at lower temperatures.
Figure 2. Mössbauer spectra at $T = 300$ K of dispersed $\alpha$-$\text{Fe}_2\text{O}_3$ loosely poured in a container (a) and after filling the container with water (b).

Figure 3. Representation of spectra of loosely poured $\alpha$-$\text{Fe}_2\text{O}_3$ (a) as a continuous distribution of the hyperfine field on nucleus (c) and a magnitude of error of such approach (b).

3. Theoretical model

As it was shown above, the theoretical model for calculation of Mössbauer spectra of polymer composites of single domain magnetic particles has to take into account the inter-particle interaction. So, the model has to allow one to take into consideration physical mechanisms of formation of such features of hyperfine structure as asymmetric shape of lines with sharp outer and smeared inward sides and the presence of central anomalously split doublet.

The simplest way to describe the Mössbauer spectra of superparamagnetic particles is to use two-level relaxation model, within which only two states corresponding to opposite directions of the particle’s magnetic moment along the easy magnetization axes are considered, so that only jumps from one state to the other are possible. The energy density of such particles may be represented as

$$E(\Theta) = -K\cos^2\Theta$$

(1)

where $K$ is the constant of axial magnetic anisotropy and $\Theta$ is the angle between the easiest magnetization axis and the magnetization vector. Temperature dependence of the transition rate is determined by the energy barrier between these equal states and is described by the Neel formula:

$$p = p_0 \exp(-KV/k_BT)$$

(2)

where $p_0$ is slightly dependent on temperature $T$ and $V$ is volume of the particle. Temperature evolution of the spectra, calculated in accordance with two-level model demonstrates transition from a Zeeman sextet to a superparamagnetic doublet with temperature increasing, but the shape of lines remains essentially symmetrical as a result of assumption about equal population of two states, separated by energy barrier. The generalized two-level model of relaxation in the system of superparamagnetic particles was suggested [1], which postulates that the relaxation between the particle’s state with opposite directions of its magnetic moment never occurs as a transition between the states of the same energy because even weak interaction with environment should move apart two energy levels. As a result, the relaxation process always takes place between two states with different population, which leads to asymmetrical shape of spectral lines of sextet. However, this model can not describe anomalous splitting of the central doublet.

All characteristic features of the spectra of interacting particles are revealed within the framework of three-level relaxation model recently developed [2], taking into account precession and diffusion of
magnetization of single-domain particles between two local energy minima and the absolute energy maximum. The maximum in our case is induced by an interaction of the particle with environment. The interaction is written in the model as a rapidly fluctuating chaotic field \( h(t) \), so that

\[
E(\Theta) = -K \cos^2 \Theta - h(t)M
\]  

(3)

The assumption about existence of a nonzero mean-square amplitude of the chaotic field within interacting system of magnetic particles gives rise to appearance in a spectrum of a magnetic sextet with small hyperfine splitting slightly dependent on the particle size and temperature, which looks like anomalous doublet.

4. Mössbauer spectra of magnetite nanoparticles in polymer composites

The film composites of the magnetite \( \text{Fe}_3\text{O}_4 \) nanoparticles in the polyvinyl alcohol matrix were synthesized by the method described in [3]. The temperature evolution of experimental spectra of the composite with 4 nm particles (points) and resulting spectra (solid lines), calculated under Gaussian type of distribution of \( H_{hf} \) and effective doublet of lines with Gaussian type of broadening are shown at Fig. 4a.

![Figure 4. Mössbauer spectra of polymer composites of 4 nm magnetite nanoparticles (a) and theoretical spectra, calculated within the framework of three-level relaxation model under assumption of zero (b) and nonzero (c) root-mean-square amplitude of the chaotic field.](image)

It is evident that the experimental spectra show all characteristic features of inter-particle interactions. Theoretical spectra, calculated within the framework of three-level relaxation model [2] under assumption of zero (b) and nonzero (c) root-mean-square amplitude of the chaotic field \( h(t) \) are shown in columns (b) and (c), respectively. The last variant demonstrates all characteristic features of interacting particles spectra, so only the correspondent model can be recommended for fitting of the experimental spectra.

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