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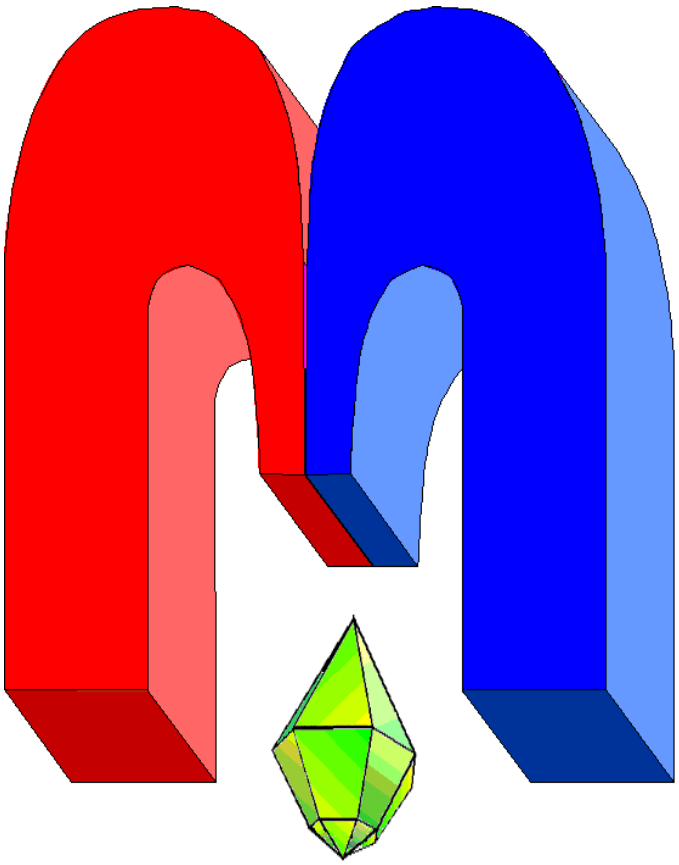

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

EMR searching of quantum behavior of magnetic γ-Fe_2O_3 nanoparticles encapsulated into poly(propylene imine) dendrimer†

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The superparamagnetic γ-Fe_2O_3 nanoparticles (average diameter of 2.5 nm) encapsulated in poly(propylene imine) dendrimer have been investigated by electron magnetic resonance (EMR). EMR measurements have been recorded in perpendicular and parallel configurations in the wide temperature range (4.2-300 K). It has been shown that the model based on the spin value $S = 30$, corresponding to the total magnetic moment of the nanoparticle, can be used to interpret the experimental results and the proof of the quantum behavior of γ-Fe_2O_3 nanoparticles.

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1. Introduction

Recently, interest in the study of nanoscale magnetic systems has increased significantly, which is caused by both wide technological applications of such systems (catalysis [1], storage [2], spintronics [3], MRI [4], magnetic fluids [5], biotechnology and biomedicine [6, 7]), and fundamental scientific interest [8, 9]. In the world of nanoscale magnetic systems, two classes of such objects can be distinguished: magnetic nanoparticles (NPs) and molecular nanomagnets (MNMs). The behavior of MNMs is known to be described by quantum mechanics, where calculations begin by considering the behavior of a single ion, while NPs behavior is described in terms of classical physics on the basis of parameters obtained for bulk materials. It seems interesting to develop a common approach for the consideration of nanoscale magnetic systems, which could provide a better understanding of their properties. Electron magnetic resonance (EMR) is an excellent tool to demonstrate the similarities in the behavior of NPs and MNMs, and its use can provide experimental evidences of quantum behavior of single-domain NPs. Some evidences in favor of the discrete nature of spin levels of NPs are already known in the literature. For example, a small signal is observed in the half-field of EMR spectra [10, 11], which, according to some authors, is attributed to forbidden transitions between states with $\Delta m = \pm 2$. Its appearance is interpreted as a proof of the quantum nature of the system and in such approach a nanoparticle is considered to be a giant exchange-coupled cluster with a total spin S.

In this paper, we try to find new arguments in favor of the quantum nature of NPs, and for this purpose we offer a new approach – to record EMR spectra of NPs in both (parallel and perpendicular) configurations, that is, when the H_1 field of the microwave radiation is parallel or perpendicular to the external magnetic H_0 field. These alternative configurations have different selection rules for the allowed transitions between the total spin projections, and therefore, provide the opportunity to "feel" the quantum nature of the system.

2. Results and discussion

In our previous paper [12], we investigated by EMR spectroscopy the behavior of superparamagnetic single-domain γ-Fe_2O_3 NPs (average diameter of 2.5 nm) encapsulated in poly(propylene imine) dendrimer of the second generation (Figure 1), using the classical theoretical approach [13].

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The typical EMR spectra (for configuration $H_1 \perp H_0$) are shown in Figure 2. As we can see, one basic signal with g-factor 2 is observed, which becomes broader and its resonance position is shifted to lower magnetic fields with the temperature decrease. The temperature dependence of the shift of the resonance position of this signal, $H_{res} - H_0$, is described by the following expression: $H_{res} - H_0 = h_a\,[1/L(\xi) - 3/\xi]$, where h_a is the anisotropic field of NP, $\xi = MVH_0/k_BT$, V is the volume, M is the magnetization of NPs, k_B is the Boltzmann constant, T is the absolute temperature, $H_0 = 3342$ G and $L(\xi)$ is the Langevin function. The best agreement between the experimental data and the theoretical dependence (Figure 3) [11] is obtained for the value of the anisotropic field $h_a = -1375$ G.

The magnetic measurements made using a SQUID magnetometer for this system (Figure 4) in the two cooling regimes of the sample – in the presence (FC) and in the absence of an external magnetic field (ZFC) have shown that there is a temperature-driven transition from superparamagnetic to ferrimagnetic state and the value of the effective magnetic moment of NPs is about $\mu_{eff} \approx 60\,\mu_B$.

Besides this basic signal ($g \sim 2$), EMR spectra demonstrate the presence of a small signal in the half-field around 1500 G (Figure 5), which has been attributed in the literature to 'partially' forbidden transitions between states with $\Delta m = \pm 2$, where m is the expectation value of S_z and S the total spin of the NP. If this interpretation is correct, then the intensity of this small signal should increase when the

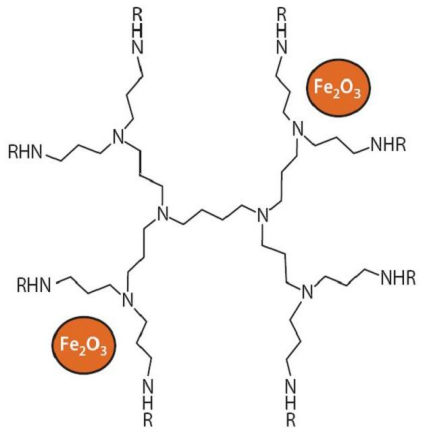

Figure 1. Schematic model of localization γ-Fe_2O_3 NPs into poly (propylene imine) dendrimer.

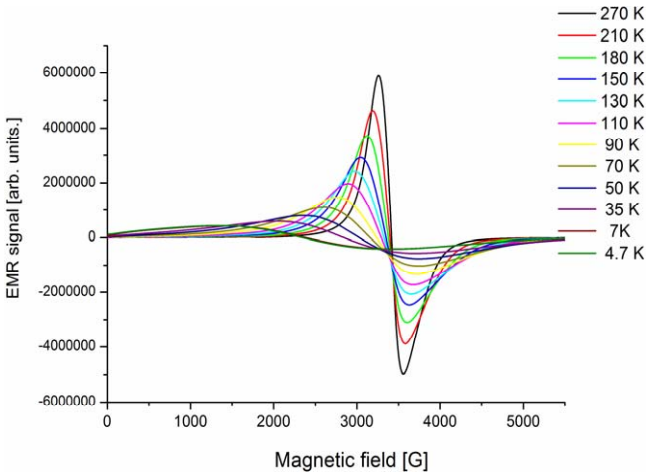

Figure 2. Temperature dependence of EMR spectra for γ-Fe_2O_3 NPs in dendrimer recorded at X-band in perpendicular configuration (ν = 9.64 GHz).

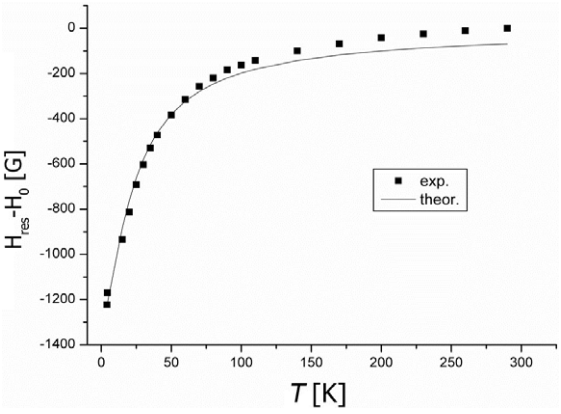

Figure 3. Temperature dependence of $H_{res} - H_0$ for γ-Fe_2O_3 NPs incorporated into dendrimer. The solid line shows the theoretical dependence.

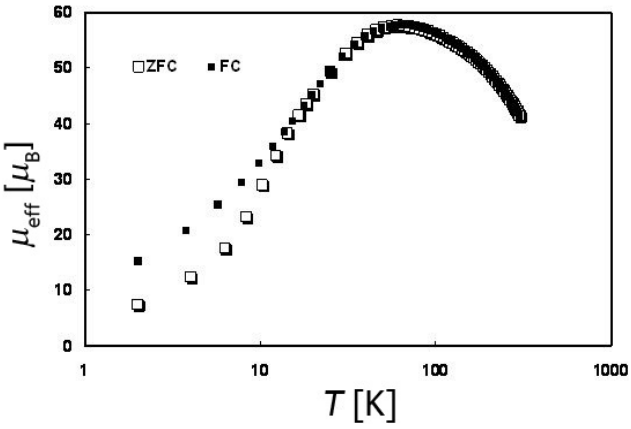

Figure 4. Variation of the effective magnetic moment of γ-Fe_2O_3 NP with temperature.

EMR spectra are recorded in a parallel configuration ($H_1 \parallel H_0$). EMR experiments carried out by us for this configuration, confirmed that it is indeed the case (Figure 6) and the intensity of the transitions in the half-field really increases. X-band EMR measurements were performed on a CW-EPR EMXplus Bruker spectrometer equipped with helium ER 4112HV cryostat, ER 4131VT temperature control system, and the ER 4116DM EPR- resonator (Bruker, Germany) was used. The spectra were recorded using the modulation frequency of 100 kHz and a microwave power for the perpendicular configuration was 25 μW and 20 mW for the parallel configuration. So, one can see that the proposed by us approach opens additional possibilities for the analysis of the properties of magnetic nanoparticles with using a model where each NP is treated as a quantum object with a large spin, similar to the approach that was successfully used to MNMs.

Thus, we can use the following spin Hamiltonian to calculate the EMR spectra:

$$H = \mu_B \hat{S} \cdot g \cdot \hat{H} + \hat{S} \cdot D \cdot \hat{S}, \quad (1)$$

where the first term gives the splitting of energy levels in the external magnetic field H, and the second term determines the fine structure of the levels of NP with spin S.

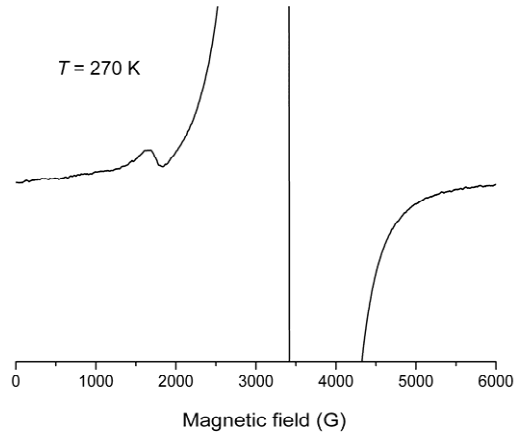

Figure 5. EMR spectrum of maghemite NPs in dendrimer at 270 K with a small signal at the half-field (~1500 G).

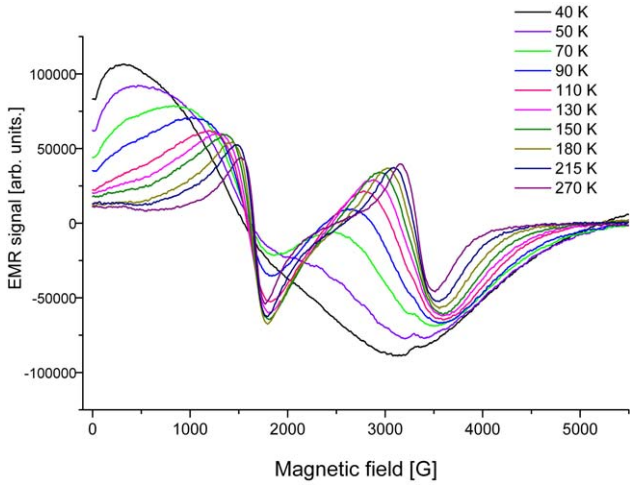

Figure 6. Temperature dependence of EMR spectra recorded at X-band in parallel configuration (ν = 9.39 GHz) for γ-Fe_2O_3 NPs encapsulated in dendrimer.

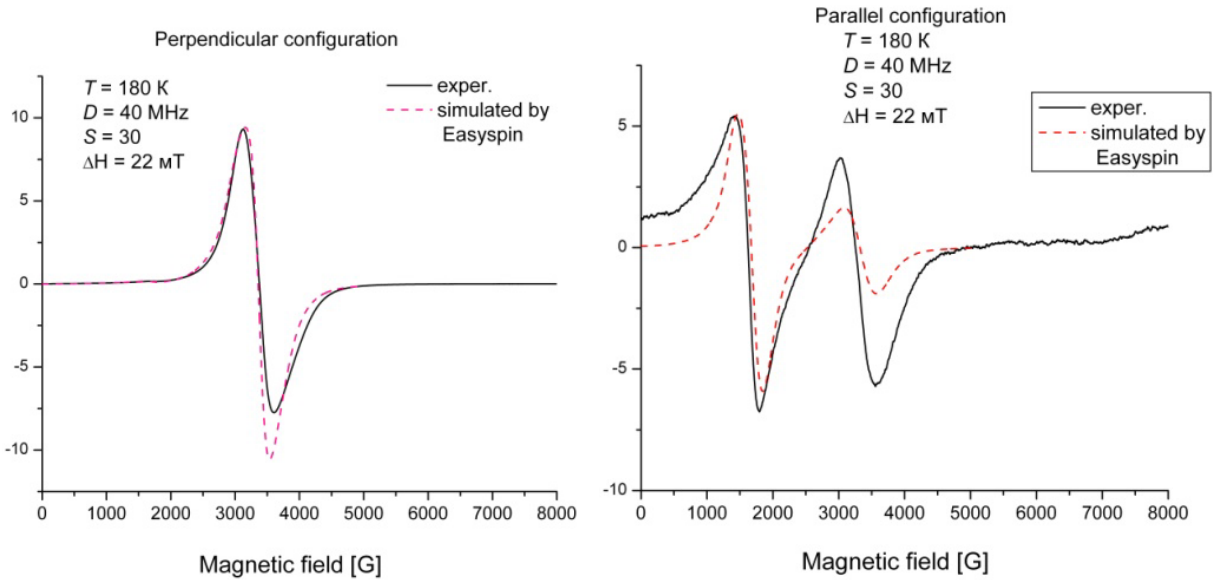

Figure 7. Experimental EMR spectra (continuous lines) acquired in the perpendicular and parallel configurations at 180 K, and simulated (dashed lines) spectra.

The value of spin S for NPs was estimated from magnetic measurements according to the expression $S = \mu/g\mu_B$ [14], and in our case $S \approx 30$.

Using the relation $D = -\gamma h_a/2S$ [14] together with the known values of the anisotropic field (h_a), and spin S value, we can obtain the estimated value of the fine structure parameter D for the NP, which is equal to $D \sim 64$ MHz. The simulation of EMR spectra for both magnetic field configurations was performed using the Easyspin program. The experimental and the simulated spectra at $T = 180$ K are shown in Figure 7. The best agreement between the experimental and theoretical spectra was obtained for the following parameters: $S = 30$, $D = 40$ MHz with individual Lorentzian line shape and line width $\Delta H = 220$ G. It is seen, that a fairly good qualitative agreement between the spectra is observed.

3. Summary

Thus, we can conclude that the obtained results demonstrate the possibility to analyze the magnetic properties of NP using the large spin value $S = 30$, and hence NP can be considered as a quantum object.

Acknowledgments

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