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Ferromagnetic Resonance of Nickel Nanoparticles in an Amorphous Oxide Matrix

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Abstract—The formation of a ferromagnetic phase in the thermal decomposition of a layered lithium–aluminum double hydroxide with intercalated nickel–EDTA complexes was studied using ferromagnetic resonance (FMR) spectroscopy. The FMR spectra were simulated based on a superparamagnetic narrowing model. Data on the size and shape of the resulting nickel nanoparticles were calculated.

INTRODUCTION

The properties of nanosized particles are of considerable interest in heterogeneous catalysis. In the last few years, ferromagnetic resonance (FMR) spectroscopy has been used in increasing frequency, along with other techniques, for studies of magnetic oxide and metal nanoparticles [1]. This technique is highly sensitive, and its sensitivity is higher than the sensitivity of EPR spectroscopy by two or three orders of magnitude, all other factors being the same. This provides an opportunity to study early steps in the generation of a ferromagnetic phase, and these studies may be very useful for studying the synthesis of catalysts.

A so-called superparamagnetic effect is well known for ferromagnetic nanoparticles of sizes of about 1–10 nm [1, 2]. The magnetic moment of a particle is small, so that thermal changes in its direction play an important role. The FMR spectrum of these particles depends on their size. The Brownian rotation of the magnetization vector of a nanoparticle effectively averaged magnetic anisotropy fields and, as a consequence, narrowed the FMR line.

Previously, oxide and metal nanoparticles were studied by FMR spectroscopy [1–6]. De Biasi and Devezas [7] proposed a model; based on this model, Berger and coauthors [8–10] calculated the FMR spectra of iron oxide nanoparticles in silicate and borate glass matrices. Calculations of this kind give information on the shape and size of the ferromagnetic nanoparticles in a sample. However, the above model cannot be used for calculations under conditions of a strong magnetic anisotropy, which is characteristic of nonspherical particles or magnetically hard materials, such as cobalt. Yulikov *et al.* proposed a model [11] in order to extend the above approach [7–10] to systems with a strong magnetic anisotropy. The calculation is based on the idea that, in the occurrence of rapid changes in the direction of a magnetization vector, the speed of magnetization rotation in an external magnetic field and a magnetic anisotropy field should be averaged, as distinct from the above approach [7–10], according to which a local anisotropy field is averaged.

In this work, we used FMR spectroscopy to study magnetic nickel nanoparticles that are formed in the thermal decomposition of the layered lithium–aluminum double hydroxide with intercalated nickel–EDTA complexes $[LiAl_2(OH)_6]_2[NiEDTA] \cdot 4H_2O$. Previously, it was found that the thermal decomposition of this compound at temperatures higher than 340°C resulted in the formation of nanosized nickel particles distributed in an X-ray amorphous matrix of lithium aluminate and a carbon-containing phase [12, 13]. This solid phase was studied by small-angle X-ray scattering analysis and high-resolution electron microscopy. It was found that the nickel particles exhibited a narrow size distribution, and the average diameter was 3–5 nm. The resulting composites containing nickel nanoparticles were sufficiently stable against oxidation in air at room temperature. Therefore, it was of interest to study both the magnetic properties of nanosized nickel particles having a narrow size distribution and the formation of these particles in the thermal decomposition of $[LiAl_2(OH)_6]_2[NiEDTA] \cdot 4H_2O$ with the use of FMR spectroscopy.

EXPERIMENTAL

Samples of $[LiAl_2(OH)_6]_2[NiEDTA] \cdot 4H_2O$ synthesized by the ion exchange of chloride ions in $[LiAl_2(OH)_6]Cl \cdot nH_2O$ for $[NiEDTA]^{2-}$ [12, 13] were used in the experiments. The process of thermal decomposition was performed in a tube reactor under conditions of continuous pumping. A temperature gradient across the sample and temperature fluctuations were no

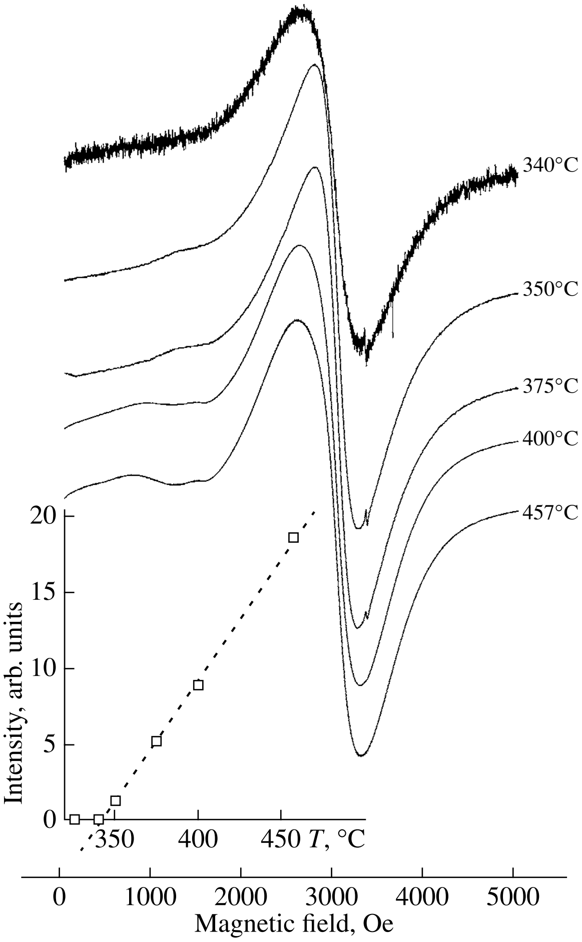

Fig. 1. FMR spectra of samples prepared by the decomposition of $[LiAl_2(OH)_6]_2[NiEDTA] \cdot 4H_2O$ at various temperatures. Insert: the dependence of the FMR signal intensity on the temperature of decomposition.

more than 5°C. The temperature was controlled with a programmed temperature regulator. A sample placed in a quartz cell was evacuated to a pressure of about 1–4 Pa; next, it was heated to a required temperature for 1 h at a certain rate and exposed for 2 h at this temperature. After completion of the decomposition process, the sample was cooled in the reactor with continuous evacuation until the reactor temperature had decreased to room temperature.

The FMR spectra were measured on a Bruker ER-200D EPR spectrometer at room temperature. A Radiopan SE/X 2547 EPR spectrometer with a high-temperature attachment, which made it possible to heat the sample in the resonator to ~400°C, was used for measurements at elevated pressures.

When thermal decomposition was performed directly in the resonator of the spectrometer, an ampule with the sample was evacuated to a pressure of about 1–4 Pa with the use of a fore pump. Next, the sample was heated to a certain temperature with continuous evacuation, exposed at this temperature for a required time, and rapidly cooled to 20°C. The FMR spectrum was recorded at 20°C, and the procedure was repeated. The above procedure was chosen because the temperatures at which a ferromagnetic phase was formed in the test sample were higher than the Curie temperature of nickel; this fact did not allow us to perform *in situ* measurements.

RESULTS AND DISCUSSION

Figure 1 demonstrates the magnetic resonance spectra of samples prepared at various decomposition temperatures of the parent substance.

A ferromagnetic signal was not detected in the FMR spectrum up to $T \approx 340$°C. In the sample decomposed at 340°C, a weak absorption line with $g \approx 2.2$ and a width of about 650 Oe was detected. As the decomposition temperature of the parent substance was increased, the line width decreased to ~500 Oe; the resonance position was shifted upfield by 30–50 Oe, and the intensity increased. In this case, over the range 340–457°C, the line intensity was approximately proportional to the temperature of decomposition (Fig. 1, insert). The FMR line shape was the same at decomposition temperatures of 350–375°C; this fact is indicative of the same nickel particle size distribution. At a decomposition temperature of ~400°C, the shape of the absorption line changed: the low-field wing was distorted, and the line width increased. This behavior of the spectrum can be explained based on the assumption that the average particle size began to increase at this temperature. The FMR line width of a powder depends on the effective magnetic anisotropy field [14]. As the size of the ferromagnetic particles increases, the effective averaging of a magnetic anisotropy due to thermal fluctuations of the direction of a magnetization vector should weaken and, correspondingly, the experimentally observed absorption line width should increase.

The experimentally observed narrowing of an FMR line as the decomposition temperature was increased from 340 to 350°C suggests that irregularly shaped particles, probably with a defect crystal structure, were formed at the early stage of ferromagnetic phase formation at a low decomposition temperature. All of the above facts should result in the broadening of an absorption line in the case of a lower decomposition temperature, as well as in a downfield resonance shift.

A narrow (~10 Oe in width) low-intensity line with a g-factor of ~2.00 can be seen in the magnetic resonance spectra of some samples against the background of an FMR line. This line was due to the EPR signal of coke deposits at some distance from the ferromagnetic particles. For coke deposits close to nickel particles or on the surface of these particles, this line will be fully broadened by local magnetic fields. As estimated, the regions that give the above signal should lie at a distance of about four or five linear particle sizes from the nearest ferromagnetic particles.

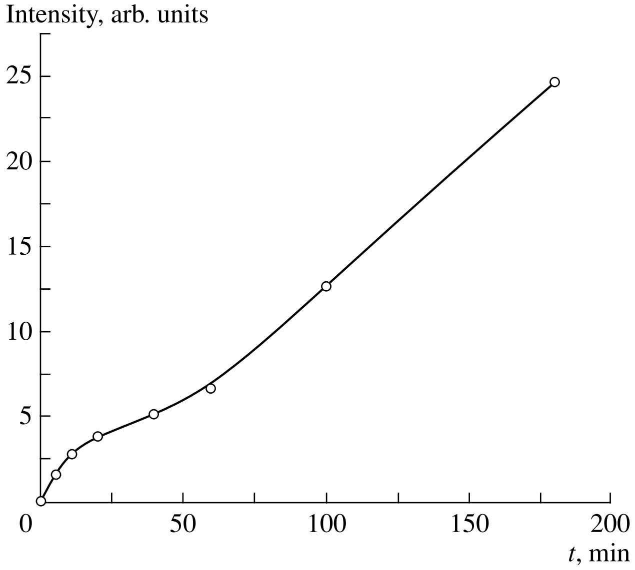

Fig. 2. Dependence of the intensity of the FMR line of a sample of $[LiAl_2(OH)_6]_2[NiEDTA] \cdot 4H_2O$ subjected to thermolysis (385°C; ~1–4 Pa) on the time of decomposition.

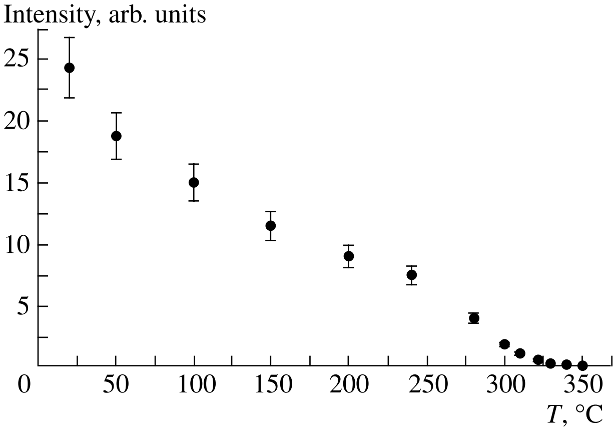

Fig. 3. Dependence of the intensity of the FMR line of a sample prepared by the decomposition of $LiAl_2(OH)_6]_2[NiEDTA] \cdot 4H_2O$ at 400°C on the temperature at which the spectrum was measured.

Figure 2 demonstrates the dependence of FMR signal intensity on the time of vacuum decomposition at 385°C. It can be seen in Fig. 2 that the FMR signal intensity continuously increased with decomposition time and did not reach saturation. We can conclude that a considerable portion of nickel was not transformed into a ferromagnetic state at the decomposition temperature and in the allotted time. The shape of the absorption line remained practically unchanged with decomposition time. At decomposition times longer than 100 min, an additional low-field feature, which corresponded to the formation of a small amount of coarser particles in a "pure" ferromagnetic state, appeared in the spectrum.

Figure 3 demonstrates the dependence of the intensity of absorption on the temperature at which the spectrum was measured for a sample prepared at a decomposition temperature of 400°C. This dependence is characteristic of particles that exhibit superparamagnetic properties [1], and it suggests that the particle size was no greater than 10–12 nm. The Curie temperature of the resulting nanoparticles (600–620 K) measured using FMR spectroscopy was close to the corresponding value for bulk nickel (627.4 K [15]). It is well known that the Curie point for nickel particles 1–2 nm in size can be shifted toward lower temperatures by more than 100 K [16].

We performed a numerical calculation of the spectrum of a sample prepared at a decomposition temperature of 400°C. The simulation in terms of an approach proposed previously [11] allowed us to describe adequately the line shape (Fig. 4). In this case, we found that the particles should be oblate ellipsoids in shape with a deviation from sphericity of about 20%. In our calculation, we also considered the fact that a portion of the nickel particles can be much coarser and have an irregular shape. The insert in Fig. 4 demonstrates the particle-size distribution obtained from calculations. The fraction of coarser "ferromagnetic" particles is shown separately. According to our calculations, the coarse particles are film fragments with a great perimeter-to-thickness ratio. Note that, although the weight fraction of these particles is significant, their number should be very small, and a detailed microscopic study is required for detecting them in a sample. The resulting

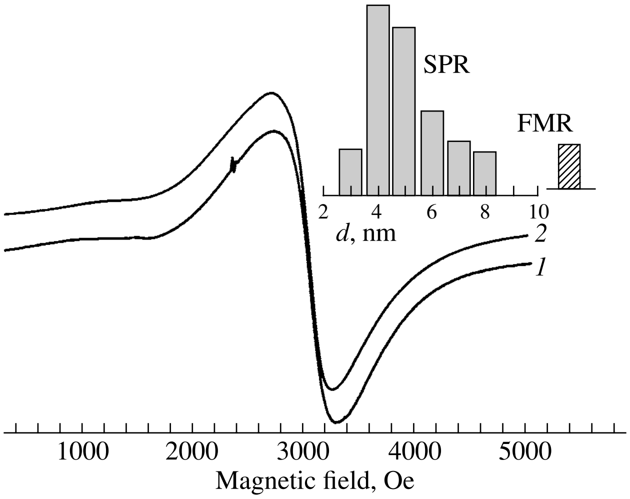

Fig. 4. (*1*) FMR spectrum of a sample prepared by the decomposition of $[LiAl_2(OH)_6]_2[NiEDTA] \cdot 4H_2O$ at T = 400°C and (*2*) the result of a numerical simulation of the above spectrum. Insert: particle size distribution by weight corresponding to the numerical calculation (SPR); the fraction of coarse particles in a pure ferromagnetic state is shown separately.

distribution, which has a maximum at 4–5 nm, corresponding to superparamagnetic particles, is consistent with published data [13].

CONCLUSIONS

In this work, we studied the formation of ferromagnetic nickel nanoparticles in the course of thermolysis of $[LiAl_2(OH)_6]_2[NiEDTA] \cdot 4H_2O$ using FMR spectroscopy. Data on the early stage of formation of a ferromagnetic phase were obtained. It was found that the Curie temperature of nanosized (4–5 nm) nickel particles is close to the Curie temperature of bulk nickel. A numerical simulation of the FMR spectra of these systems was performed, and information on the shape and size of nickel particles was obtained, which both was consistent with data obtained using other methods and supplemented these data.

Thus, FMR spectroscopy is of interest as an investigation technique for nanosized ferromagnetic particles. In particular, it can be used as an investigation technique for the synthesis of heterogeneous catalysts with a ferromagnetic active component. This technique provides additional information on both the size and shape of the nanoparticles formed, as well as on the early stages of generation of a ferromagnetic phase.

ACKNOWLEDGMENTS

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