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Effect of short-term heat treatment in the hydrogen on magnetic properties of ZnO:Mn nanocrystals

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The magnetic properties of ZnO:Mn(2at%) nanocrystals synthesized by ultrasonic aerosol pyrolysis were studied. It has been established that short-term thermal treatment in hydrogen does not affect the magnetization of the synthesized sample, which had ferromagnetic and paramagnetic components. The sample, which underwent heat treatment in air at T = 850°C and acquired paramagnetic properties, after heat treatment in hydrogen again became ferromagnetic without a paramagnetic phase. It has been established by the EPR method that the structure of defects in the synthesized ZnO:Mn(2%) NCs is inhomogeneous. It changes after heat treatment in hydrogen. It is shown that the controlled thermal treatment of the samples, first in air and then in hydrogen, makes it possible to predictably change their magnetic properties. The results obtained are explained using the model of coupled magnetic polarons. During thermal treatment in hydrogen, the ratio of the number of oxygen vacancies V_o and interstitial Mn^{2+} ions changes in the samples.

Keywords: ZnO nanocrystals, ultrasonic aerosol pyrolysis, heat treatment, hydrogen, magnetic properties.

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Introduction

Dilute magnetic semiconductors (DMS), which include nanocrystalline (NC) ZnO doped with manganese, attract attention due to the possibility of their use in spintronics, as well as in many other areas of applied nanoelectronics. The experimental studies have shown that the ferromagnetic properties of such materials significantly depend on the technological conditions of production. Such properties are acquired during low-temperature synthesis (T<500°C) and at low concentrations of manganese dopant (Mn<4 at%) [1]. An important result of DMS studies was the establishment of the decisive role of defects in the formation of ferromagnetism. The exact mechanism for the appearance of ferromagnetism in oxides doped with transition metal atoms is currently under discussion. Several theoretical models have been proposed, of which the model of bound magnetic polarons (BMP) has the best agreement with the experimental results [2]. According to this model, ferromagnetism in ZnO:Mn NCs is due to the interaction between Mn^{2+} ions indirectly through intrinsic defects of the crystal lattice. In this case, defects such as oxygen vacancies (Vo) act as intermediaries in the exchange interaction between impurity defects - Mn^{2+} ions. The magnetic polaron in ZnO:Mn NCs is an electron bound to the Vo oxygen vacancy, which interacts with the 3d electrons of the Mn^{2+} ions. The magnetic moments of the Mn^{2+} ions are oriented in one direction during this interaction. This leads to the formation of local magnetic clusters, which determine the ferromagnetic properties of the sample.

It has been shown that the condition for ferromagnetic ordering in NCs DMS is not only the fact of presence but also the corresponding structure of defects [3, 4]. It has been established that such a structure of defects can be formed by milling of ZnO:Mn polycrystals in an inert medium [5]. Under such treatment, a defective near-surface layer with a large number of oxygen vacancies (Vo) is formed in the nanocrystals. The presence of impurity Mn^{2+} ions in this case creates conditions for their magnetic interaction and the appearance of ZnO:Mn ferromagnetism in samples at room temperature. A similar defect structure, which gives rise to ferromagnetic properties, was formed during the synthesis of ZnO:Mn

NCs by ultrasonic spray pyrolysis (USP) [6]. During this synthesis, a large number of defects appear in NCs and an inhomogeneous crystal structure is formed, consisting of a defect-free core and a defective shell [7].

Recently, many studies have shown that heat treatment (HT) in hydrogen improves the magnetic characteristics of DMS by changing the defective state of the samples [8]. For example, ZnO:Mn NCs (8 at %), obtained by chemical coprecipitation, after annealing in hydrogen at T = 700°C, had a significantly higher magnetization than after annealing in the air [9]. In [10] paramagnetic ZnO:Mn(2at%) NCs were obtained by annealing in air at T = 700°C. But after annealing in hydrogen, they also acquired ferromagnetic properties. At the same time, after repeated annealing in air, ZnO:Mn NCs again pass into a paramagnetic state. The possibility of restoring the ferromagnetic state of samples in the paramagnetic state by annealing in hydrogen was also established in [11].

Thus, much attention is paid to annealing in hydrogen in the study of DMS, because it makes it possible to controllably influence the defect state of samples and their physical properties. At the same time, short-cycle mode annealing, in which the defective state of NCs and their sizes increase slightly, is more effective. Such modes of annealing make it possible to carry out a reliable comparative analysis of the obtained results and to determine the key factors influencing the formation of ferromagnetic properties in the DMS.

The purpose of this work is to establish the influence of short-cycle mode annealing in the hydrogen on the structure of the defect state and the magnetic characteristics of ZnO:Mn NCs, obtained by the USP method.

I. Experiment

The USP method is based on the thermal decomposition of droplets of a solution of initial components as they pass through the heated zone of a furnace [12]. A feature of the synthesis by the UPA method is that the formation of the crystal structure of nanocrystals in it occurs inside the microdroplet under nonequilibrium conditions. Such synthesis leads to the formation of a large number of defects in ZnO:Mn NCs, which is a necessary condition for the formation of ferromagnetic properties when NCs are doped with Mn.

It was shown in [13] that the structure of defects in ZnO:Mn NCs is inhomogeneous during synthesis by the UPA method. The Mn impurity and defects associated with it, such as interstitial zinc (Zn_i), oxygen (Oi), oxygen (V_o), and zinc (V_{Zn}) vacancies, are predominantly located in the surface layer of the NC. It was found that in this synthesis, the process of doping ZnO NCs with Mn impurity is partial. Most of the Mn atoms are located in the amorphous intercrystalline medium, which surrounds the synthesized ZnO:Mn NCs. The impurity phases Mn_2O_3 and $ZnMn_2O_4$ are formed from these atoms during HT (annealing) in the air at T = 550°C. High-temperature HT (annealing) at T = 850°C leads to the decomposition of these phases and the diffusion of Mn atoms into the ZnO crystal lattice. A similar result was obtained in [14], where ZnO:Mn NCs were synthesized by chemical coprecipitation.

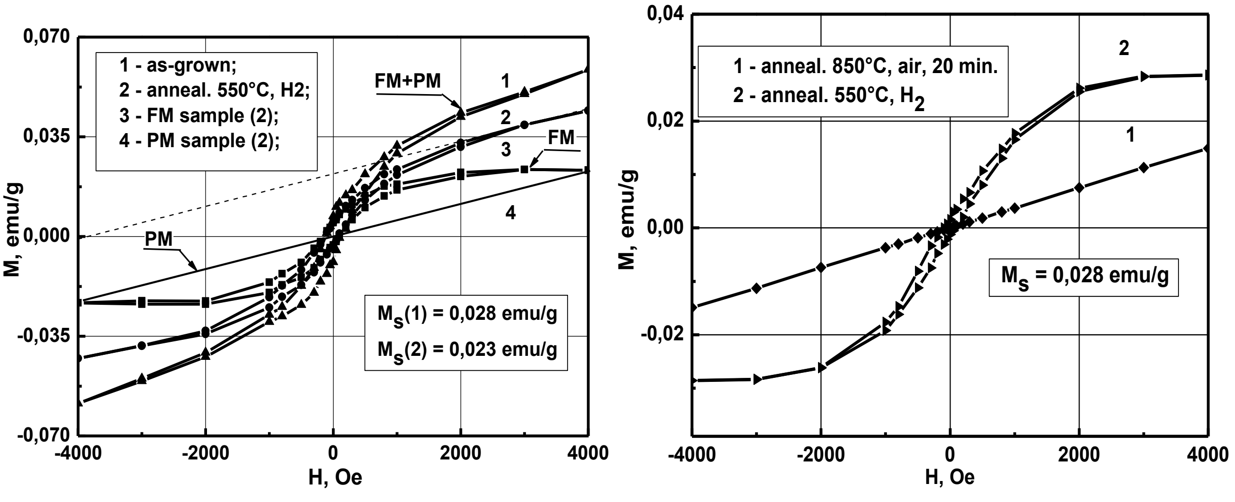
The ZnO:Mn NC samples with a manganese concentration of 2 at.% were obtained by the UPA method according to the technological regimes given in [12]. Aqueous solutions of zinc and manganese nitrates were used for the synthesis. The prepared solution of the components was sprayed into aerosol drops with a size of d=1÷2 μm. These drops were transported with the help of a carrier gas (air) through the reaction zone of the furnace heated to T = 550°C. Here, the processes of droplet drying and synthesis of ZnO:Mn NCs were implemented for a limited time (7–10 s). The synthesized product was accumulated on the filter at T = 250°C in the form of spherical granules.

The short-term HT in hydrogen has been conducted on the synthesized samples, as well as on the samples that underwent HT in the air at T = 850 °C for 20 min after synthesis. The HT in hydrogen has been conducted in a gas mixture consisting of nitrogen and hydrogen gases (N2 : H2 = 3 : 1) at T = 550˚C for 20 min. The samples were cooled outside the furnace in a stream of nitrogen gas. This cooling mode was used to preserve the concentration of intrinsic and impurity defects, which were formed during HT in hydrogen. The sizes of the obtained ZnO:Mn NCs were calculated by means of the Debye-Scherrer formula. They had the following values: synthesized samples - 34.9 nm; samples that underwent short-term HT in the air at T = 850°C - 63.7 nm [15]. Short-term HT of these samples in hydrogen did not lead to a significant increase in the NCs size.

The magnetic properties of the samples were studied by vibrational magnetometry. The EPR study of the samples was performed on a RADIOPAN SE/X 2543 radio spectrometer. When measuring the EPR spectra, the samples were studied under the same operating modes of the spectrometer and with equal sample weights. This made it possible to carry out a comparative analysis of the spectra in terms of intensity. When obtaining magnetic characteristics, NC samples were placed in sealed polyethylene ampoules, the magnetization of which was separated from the result obtained.

II. Results and discussion

The magnetic characteristics of the synthesized ZnO:Mn(2at%) NC sample before and after HT in hydrogen at T = 550°C are shown in Fig. 1a. The results obtained show that the magnetization of the synthesized sample decreases after HT. A similar result was also obtained in [8]. It should be noted that the magnetization curves of the samples before and after HT in hydrogen do not have a saturation state. This indicates that in addition to the ferromagnetic component, the magnetization also has a paramagnetic component. It is due to the presence of Mn^{2+} ions located between the nodes of the crystal lattice - interstitial Mn^{2+} ions. In this case, it is assumed that the Mn^{2+} ions occupying the crystal lattice nodes, replacing the Zn^{2+} ions, are not magnetically active. This conclusion is confirmed by the fact that the paramagnetic component disappears after prolonged HT of the sample at T= 850°C in air. Such HT leads to the disappearance of interstitial



a) b)

Fig.1. Magnetization curves of ZnO:Mn NC (2 at.%):
a – synthesized sample; 1 - before HT in hydrogen; 2 - after HT in hydrogen; 3 - ferromagnetic component of the sample (FM); 4 - paramagnetic component of the sample (PM);
b – sample annealed in air at T = 850˚C: 1 – after annealing in air, 2 – after HT in hydrogen.

ions and an increase in the concentration of Mn^{2+} nodal ions.

The amount of the paramagnetic phase is determined by the slope of the lines involved in these curves. The paramagnetic properties of the samples have a linear dependence on the magnetic field, and at zero magnetic field they disappear. Therefore, it is possible to separate the paramagnetic component from the experimental magnetization curves, as well as to determine the specific ferromagnetic (FM) component in the saturation state (Ms) and the specific magnetic susceptibility (χ_p) of the paramagnetic (PM) component (Fig. 1a). The latter is determined based on experimental data using the ratio χ_p = Mp/H, where Mp is the specific magnetization of the PM component. The analysis carried out in this way showed that the specific magnetization of the synthesized sample before HT is Ms (1) = 0.028 emu/g, and after HT in hydrogen it decreases to Ms (2) = 0.023 emu/g. It is known that the magnetization of the synthesized sample after HT of the sample in the air at T = 550°C decreases almost three times and has a value of Ms = 0.01 emu/g [15].

The magnetic susceptibility of the synthesized sample after HT in hydrogen also decreases from the value χ_p (1) = $7.35\mathrm{x}10^{-6}$ emu/g·Oe to the value χ_p (2) = $5.50\mathrm{x}10^{-6}$ emu/g·Oe (Table 1). The magnetic susceptibility χ_p is calculated according to the known Curie relation:

$$\chi_p = Np\mu 2/3kT, \qquad (1)$$

where Np is the number of magnetic moments (of Mn^{2+} ions), μ is the magnetic moment of Mn^{2+} ions in Bohr magnetons, k is the Boltzmann constant, and T is temperature.

Therefore, a decrease χ_p during HT in hydrogen can be a consequence of a decrease in the concentration of interstitial Mn^{2+} ions.

The magnetization curves of the sample annealed first in the air at T=850°C before and after HT in hydrogen are shown in Fig. 1b. It has been established that such HT has a significant effect on the magnetic characteristics of the sample. After annealing in air, the sample had only paramagnetic properties. The value of magnetic susceptibility χ_p = $3.53\mathrm{x}10^{-6}$ emu/g·Oe. But after HT of this sample in hydrogen at T = 550°C, it becomes ferromagnetic. The magnetization curve of the sample has a state of saturation, which corresponds to the value of the specific magnetization Ms = 0.028 emu/g. The magnetic characteristics of ZnO:Mn(2at%) NCs for different HT modes are given in Table 1.

Table 1

Magnetic characteristics of NCs ZnO:Mn (2at.%).

№	Type of samples	Magnetic parameters	
		Ms, emu/g	χ_p, emu/g·Oe
1	Synthesized sample ZnO:Mn (2at.%)	0.028	$7.35\mathrm{x}10^{-6}$
2	HT of sample (1) in hydrogen (T = 550°C)	0.023	$5.50\mathrm{x}10^{-6}$
3	HT of sample (1) in air (T = 850°C)	-	$3.53\mathrm{x}10^{-6}$
4	HT of sample (3) in hydrogen (T = 550°C)	0.028	-

It should be noted that, in [16], HT of paramagnetic ZnO:Mn (2 at.%) NCs was also carried out in a hydrogen atmosphere at a temperature of T = 500°C. After such HT, they acquired ferromagnetic properties, the value of the specific magnetization Ms = 0.016 emu/g. Thus, it is possible to conclude that the ferromagnetic properties lost during annealing in air can be restored by HT of the samples in hydrogen. In this case, the PM component in the magnetization of the samples disappears.

An explanation of the obtained results can be made based on the physical model of the BMP. The decrease in the magnetization of the synthesized sample after HT in hydrogen is due to a decrease in the number of participants in the magnetic interaction–oxygen vacancies and interstitial Mn^{2+} ions. Oxygen vacancies disappear during HT, but at the same time their number increases due to the destructive effect of hydrogen on the ZnO NC surface. At the same time, the number of interstitial Mn^{2+} ions decreases during such HT, since some of them take part in doping. As is known, hydrogen can activate the doping of ZnO NCs with manganese even at a low temperature T = 550°C [17]. From the fact that the magnetization curve of the sample after annealing in hydrogen does not have a saturation state (Fig. 1a), it can be concluded that during HT such a structure of defects is formed, in which the number of interstitial Mn^{2+} ions significantly exceeds the number of oxygen vacancies: $N(Mn^{2+}) > N(Vo)$. During the magnetic interaction, the Mn^{2+} ions and Vo combine and form magnetic clusters, which determine the ferromagnetic properties. The excess of Mn^{2+} ions not involved in this process forms the paramagnetic properties of the sample.

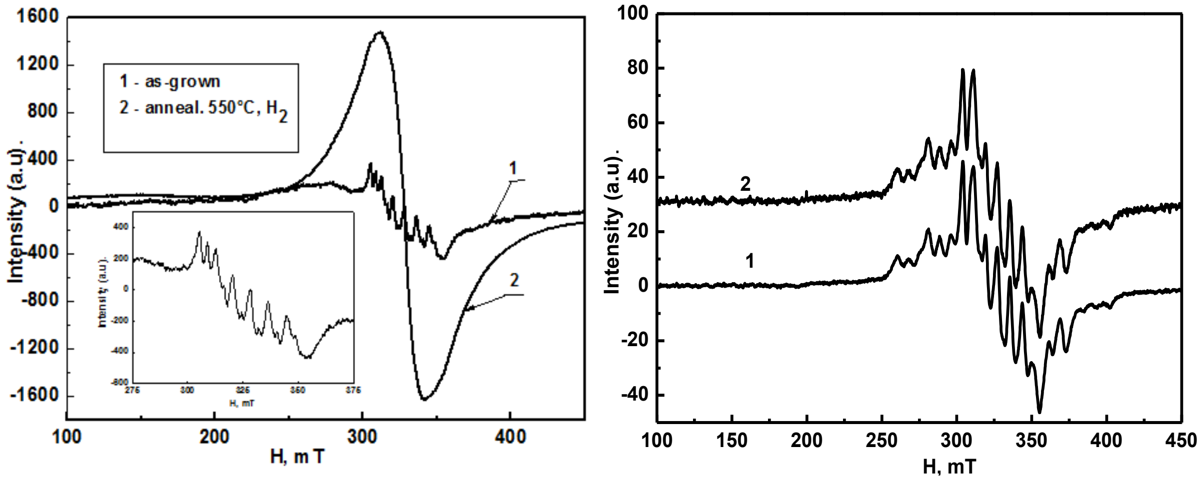
Short-term HT at T = 850°C in air leads to the formation of such a structure of defects, in which there are no oxygen vacancies, but there are a certain number of interstitial defects - Mn^{2+} ions, which determine the paramagnetic properties of the samples (Fig. 1b). The duration of HT in air (20 min) was established experimentally. An increase in this period led to a decrease in the number of interstitial Mn^{2+} ions, which negatively affects the formation of ferromagnetic properties during the next HT in hydrogen. As shown in [18], after long-term heat treatment of ZnO:Mn NCs at a high temperature in air, at which defects (interstitial Mn^{2+} ions) completely disappear, additional HT in hydrogen does not lead to the appearance of ferromagnetic properties in the samples. In our studies, the restoration of ferromagnetic properties in samples after HT in hydrogen at T = 550°C occurs because the ratio of the number of defects in the near-surface layer of NC changes in this case.

Under the action of hydrogen, a large number of oxygen vacancies arise in the nanocrystals, which exceeds the number of interstitial Mn^{2+} ions: $N(Vo) > N(Mn^{2+})$.

In accordance with the BMP model, the presence of these vacancies and interstitial Mn^{2+} ions remaining after short-term annealing of the samples in air at T = 850°C forms the conditions for the appearance of ferromagnetic properties. The magnetization curve of the samples has a saturation state (Fig. 1b). This is a sign of the absence of the PM phase in the samples. Thus, not only the number but also the ratio of the number of participants in the magnetic interaction determine the magnetic properties of the samples. A similar conclusion was also made in [19].

The EPR method is one of the effective methods for studying the structure of defects in nanocrystals. The EPR spectra of the synthesized ZnO:Mn NC sample before and after HT in hydrogen are shown in Fig. 2a. In the EPR spectrum of the sample before HT, the hyperfine structure (HFS) of the EPR spectrum of Mn^{2+} ions is recorded. It is located in the range of magnetic field H=300÷350 mT and consists of six lines. These Mn^{2+} ions replace Zn^{2+} ions at the nodes of the ZnO crystal lattice. According to the intensity of such lines, one can conclude about the efficiency of the doping process with Mn^{2+} ions of ZnO NCs. It should be noted that the HFS lines of the EPR spectrum of Mn^{2+} ions are superimposed on a broad background absorption line, which is due to the exchange interaction of Mn^{2+} ions. These HFS lines are structured, and each of them is double (Fig. 2a, inset). This is due to the fact that the Mn^{2+} ions are in different local environments and may indicate the presence of strain stresses in the wurtzite-type ZnO crystal lattice. Such Mn^{2+} ions are preferably located on the surface of ZnO NCs [13]. Thus, the performed analysis is an additional confirmation of the uneven location of the Mn dopant and associated intrinsic defects in the bulk of the NC.

The EPR spectrum of the sample after HT in hydrogen at T = 550°C becomes structureless, and its intensity increases significantly (Fig. 2a). Perhaps this is due to the presence of a large number of defects that arise as a result of the active action of hydrogen. Hydrogen on the NC surface can form oxygen vacancies (V_o), interstitial zinc (Zn_i), and hydroxyl groups (OH). It can also bind with intrinsic defects of NCs and with dopant ions, forming hydrogen complexes [20]. These complexes usually have unpaired electron spins and their own magnetic moment. Therefore, the EPR spectrum of this sample will have additional contributions that form a broad absorption line of high intensity. Thus, from the analysis of the EPR



a b

Fig. 2. EPR spectra of ZnO:Mn (2 at %) samples : a – synthesized sample; b – sample annealed in air at T = 850˚C (20 min.); 1 – before HT in hydrogen; 2 – after HT in hydrogen.

spectrum of samples after HT in hydrogen, it follows that it contains a group of defects that can participate in the formation of ferromagnetic properties.

Comparing the EPR spectra of the samples after HT in hydrogen (Fig. 2a, line 2 and Fig. 2b, line 2), we can conclude that the effect of hydrogen on the EPR spectra depends on the defective state of the samples. The crystal structure of the sample after annealing at T = 850°C in air has no structural defects, it is ordered. Therefore, the EPR spectra have only lines of the HFS of Mn^{2+} ions, which are superimposed on a broad line due to the exchange interaction of Mn^{2+} ions (Fig. 2b). The high intensity of the HFS lines indicates a significant amount of Mn^{2+} ions located at the nodes of the ZnO NC crystal lattice. The absence of a bifurcation of these lines is a sign of the absence of a defective near-surface layer in the NC. Annealing of this sample in hydrogen at T=550°C does not lead to a significant change in its EPR spectrum (Fig. 2b). This is explained by the fact that repeated short-term annealing at a low temperature cannot lead to significant structural changes. In this case, the sample acquires ferromagnetic properties.

In accordance with the BMP model, this is a consequence of the appearance in it of its own defects - oxygen vacancies. They determine the magnetic interaction between Mn^{2+} ions.

Conclusion

The studies performed have shown that the effect of short-term HT in hydrogen on the defect structure and magnetic characteristics of ZnO:Mn(2%) NCs depends on their defective state. Thus, HT in hydrogen of a synthesized sample, which has a disordered crystal lattice and a large number of surface defects, does not lead to significant changes in its magnetic characteristics. At the same time, HT in hydrogen of a sample that has previously been annealed in air and has an ordered crystal lattice leads to the appearance of ferromagnetic properties in the sample without a paramagnetic component.

The possibility of restoring the ferromagnetic properties of NCs lost during annealing in air is shown. Controlled HT of the sample, first in air and then in hydrogen, makes it possible to systematically change its magnetic characteristics. Spectral studies using the EPR method showed that the structure of defects in the synthesized ZnO:Mn(2%) NCs is inhomogeneous, after HT in hydrogen, it changes.

In accordance with the theoretical model of BMP, the results obtained are explained by the fact that during the maintenance in hydrogen there is a change in the structure of defects of ZnO: Mn NC (2%). It is concluded that the magnetic properties of the samples are determined not only by the number of defects, but also by the ratio of the number of intrinsic and impurity defects - oxygen vacancies and Mn^{2+} ions.

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Вплив короткотермінової термічної обробки у водні на магнітні властивості нанокристалів ZnO:Mn

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Досліджувались магнітні властивості нанокристалів ZnO:Mn(2ат%), синтезованих методом ультразвукового піролізу аерозолю. Встановлено, що короткотермінова термічна обробка у водні не впливає на намагніченість синтезованого зразку, яка мала феромагнітну та парамагнітну складові. Зразок, який пройшов термічну обробку на повітрі при T=850°C та набув парамагнітних властивостей, після термічної обробки у водні знову став феромагнітним без парамагнітної фази. Методом ЕПР встановлено, що структура дефектів синтезованих НК ZnO:Mn(2%) є неоднорідною. Вона після термічної обробки у водні змінюється. Показано, що контрольована термічна обробка зразків спочатку на повітрі, а потім у водні дозволяє передбачувано змінювати їх магнітні властивості. Отримані результати пояснюються з використанням моделі зв’язаних магнітних поляронів. Під час термічної обробка у водні у зразках відбувається зміна співвідношення кількості кисневих вакансій V_o та міжвузельних іонів Mn^{2+}.

Ключові слова: нанокристали ZnO, ультразвуковий піроліз аерозолю, термічна обробка, водень, магнітні властивості.