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Electron Paramagnetic Resonance of Gd^{3+} Ions in the $Pb_{1-x-y}Gd_xCu_yS$ Narrow-Gap Semiconductor: Effects of Resonance Transitions on Conductivity

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Abstract—Crystals of the narrow-band semiconductor $Pb_{1-x-y}Gd_xCu_yS$ ($x = 1.1 \times 10^{-3}$, $y = 2.5 \times 10^{-3}$) at temperatures $T = 5$–300 K demonstrated unusual dependences of the shape of the lines of the electron paramagnetic resonance (EPR) spectra of paramagnetic centers of Gd^{3+} on temperature and microwave power in the resonator of EPR spectrometer. Analysis of the shape parameters of the resonance lines recorded in the X band showed that one of the causes of the unusual changes in the observed EPR spectra of Gd^{3+} centers is a nonuniform distribution of the acceptor impurity of copper with the formation of regions with different concentrations of free charge carriers. Apparently, in these regions, resonance transitions between the spin states of Gd^{3+} centers differently affect the kinetic characteristics of free charge carriers, which lead to different contributions to the quasi-resonant absorption of microwave power.

Keywords: lead chalcogenide, narrow-gap semiconductor, electron paramagnetic resonance, Gd^{3+} ion, EPR line shape, conduction electrons

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INTRODUCTION

The basic component of the semiconductor compound $Pb_{1-x-y}Gd_xCu_yS$ to be considered, which determines its physical properties, is galena (PbS). It belongs to the group of lead chalcogenides ($A^{IV}B^{VI}$), represented by narrow-gap direct-gap semiconductors PbS, PbTe, and PbSe with a rock salt (NaCl) structure. The physical properties of materials in this group [1] (narrow band gap (0.23–0.42 eV), low effective mass, high mobility of free charge carriers with low effective mass and high static permittivity) are prerequisites for creating materials with new properties based on them.

In particular, the introduction of paramagnetic ions into the crystal lattice of lead chalcogenides allows one to obtain diluted magnetic semiconductors (DMSs), in which the spin moments of the resulting paramagnetic centers interact with the spin moments of free charge carriers (electrons or holes). Due to spin-orbit interaction [2, 3], the states of free carriers belonging to the conduction band and the valence band are mixed.

As a result, the synthesized DMSs under certain conditions can exhibit effects that depend on the spin moments of free charge carriers and give rise to magnetically controlled transport properties in them.

To date, the effects giving rise to magnetically controlled transport properties have been studied in sufficient depth in two-dimensional nanostructures created in direct-gap semiconductors with a relatively wide band gap [3]. However, the role of the spin dynamics of impurity paramagnetic ions in the formation of magnetically controlled transport properties of bulk materials remains studied to a much lesser extent. This is apparently explained by the fact that the most effective method for studying the dynamic properties of paramagnetic centers is the electron paramagnetic resonance (EPR) method. However, in two-dimensional nanostructures, the total number of paramagnetic centers is usually insufficient to detect signals using the classical EPR method. In such structures, resonance transitions between spin states of magnetic centers have been mainly studied by detecting EPR signals from changes in conductivity [4]. In this case, the shapes of the signals from resonance transitions turned out to be distorted and did not allow one to determine the parameters of the observed interactions with sufficient accuracy. It could be expected that, in lead chalcogenides, at high mobilities of free charge

carriers and a smaller energy interval between the valence and conduction bands, the effects of spin dynamics in EPR spectra can also manifest themselves in three-dimensional systems. Indeed, our synthesized galena crystals with gadolinium impurity ($1.1 \times 10^{-3} \le x \le 1.5 \times 10^{-3}$) [5] showed an unusual dependence of the shape of the EPR spectrum lines of cubic Gd^{3+} centers ($S = 7/2$) on the microwave power in the spectrometer resonator. At sufficiently low temperatures ($T < 15$ K) and high powers of the electromagnetic wave, except for the relatively narrow seven lines characteristic of Gd^{3+} ions, significantly wider additional lines were observed, the positions of which virtually coincided with the positions of the indicated narrow lines. These additional lines had an unusual "inverted-bell" shape and could have been caused by resonance transitions between spin states of only a certain fraction of the Gd^{3+} centers, which are influenced by conduction electrons scattered at these centers. The fact is that, in crystals of the lead chalcogenide group, Gd^{3+} is introduced by non-isovalent cationic substitution and imparts an excess positive charge to the lattice of the doped semiconductor. Compensation of this charge in lead chalcogenides can occur in different ways. The most effective mechanism is the one that leads to the formation of donor defects with zero activation energy (in galena, such defects are sulfur vacancies, which supply two free electrons to the conduction band [1]). This is why Alekseeva et al. [6] and Zayachuk and Dobryanskii [7] came to the conclusion that the gadolinium impurity in lead telluride crystals exhibits donor properties. By analogy, it can be assumed that the gadolinium impurity in galena behaves in approximately the same way. This means that the vicinity of the impurity ion Gd^{3+} contains electrons that are weakly bound to it and probably influence the processes of scattering of free electrons. Therefore, in this work, along with the gadolinium impurity, an additional copper impurity was introduced into galena, acting here as an acceptor impurity [8]. The purpose of introducing the additional acceptor-type impurity was to study possible changes in the shape of the observed EPR signals under the influence of holes appearing in the $Pb_{1-x-y}Gd_xCu_yS$ crystal and to obtain additional information about the mechanisms of the processes responsible for the effects observed in our previous work [5].

EXPERIMENTAL

The studied $Pb_{1-x-y}Gd_xCu_yS$ single crystals ($x = 1.1 \times 10^{-3}$, $y = 2.5 \times 10^{-3}$) were grown by the vertical Bridgman method in a Donets-2 induction crystal growing apparatus in quartz crucibles with a conical lower end. Gadolinium and copper impurities were introduced into the batch in the form of fine metal powders. To ensure stoichiometry, the required amount of sulfur was introduced into the prepared batch. The batch of the specified composition was loaded into a quartz crucible and annealed at $T = 250$°C under vacuum pumping conditions (2.3×10^{-4} mm Hg), after which the crucible was sealed. The heating system provided a temperature gradient in the crystallization zone of 250 deg/cm. The speed of the crystallization front was 1.0 cm/h.

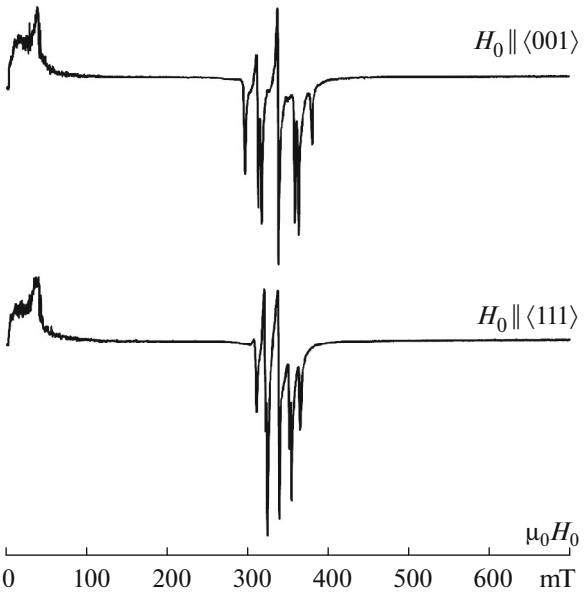

Fig. 1. EPR spectra of a single-crystalline sample of $Pb_{1-x-y}Gd_xCu_yS$, which were recorded in the orientations $\langle 001 \rangle \parallel \vec{H}_0$ and $\langle 111 \rangle \parallel \vec{H}_0$ at $f_{mw} = 9419 \pm 1$ MHz, $T = 5$ K, and $P_{mw} = 2$ mW.

Samples for the studies were pricked out of the grown crystalline boules using a scalpel and had dimensions of $4 \times 2 \times 2$ mm^3. The cleavage surfaces of the prepared samples were glossy and flat and coincided with the crystallographic planes (001). These samples were mounted on a vertical quartz holder so that rotation of the holder around the axis allowed the sample to be installed in the spectrometer resonator in three main directions corresponding to the cases $\vec{H}_0 \parallel [001]$, $\vec{H}_0 \parallel [110]$, and $\vec{H}_0 \parallel [111]$.

The studies were carried out using the EPR method in the X band at temperatures of 5–300 K with an ER200SRC spectrometer (EMX/plus, Bruker) equipped with an ITC503S temperature controller (Oxford Instruments).

Figure 1 presents the experimental EPR spectra of the studied single-crystalline $Pb_{1-x-y}Gd_xCu_yS$ sample, which were recorded in the range of strengths of constant external magnetic field $0 \le H_0 \le 700$ mT in two orientations ($\langle 001 \rangle \parallel \vec{H}_0$ and $\langle 111 \rangle \parallel \vec{H}_0$). Both spectra were recorded in the range of strengths of constant external magnetic field $0 \le H_0 \le 700$ mT at a tem-

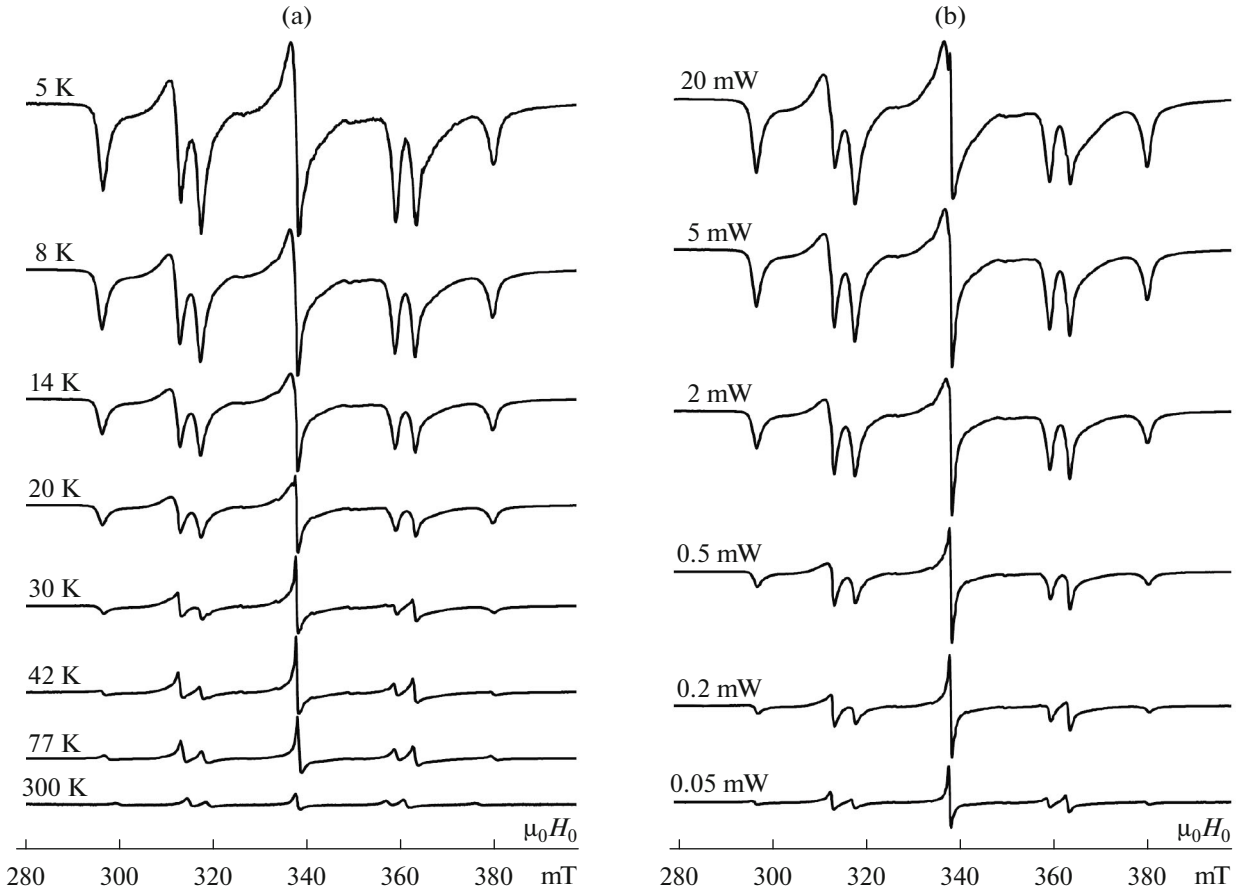

Fig. 2. EPR spectra of a single-crystalline sample of $Pb_{1-x-y}Gd_xCu_yS$, which were recorded in the orientation $\langle 001\rangle \parallel \vec{H}_0$ at $f_{mw} = 9419 \pm 1$ MHz: at $P_{mw} = 5$ mW and various sample temperatures (a), and at $T = 14$ K and various microwave powers in the spectrometer resonator (b).

perature of $T = 5$ K and a microwave power of $P_{mw} = 2$ mW at a frequency of $f_{mw} = 9419 \pm 1$ MHz. In the middle part of each spectrum, there is a group of seven lines, which is the EPR spectrum of the paramagnetic centers of gadolinium in the studied $Pb_{1-x-y}Gd_xCu_yS$ sample. The number of lines, their relative positions, and relative intensities indicate that they characterize Gd^{3+} ions ($S = 7/2$), which replaced the Pb^{2+} cation and found itself in the center of a coordination octahedron of six sulfur ions S^{-}. In the weak-field part of each spectrum, there are bursts of non-resonant absorption, which indicate the presence of microscopic inclusions of metallic lead in the bulk of the studied sample [9].

Figure 2 shows the EPR spectra of the $Pb_{1-x-y}Gd_xCu_yS$ sample, which were recorded in the orientation $\langle 001\rangle \parallel \vec{H}_0$ at $P_{mw} = 5$ mW and some selected values of sample temperature (left), and at $T = 14$ K and several values of microwave power in the spectrometer resonator (right). The vertical scale of representation of spectra is the same for spectra in each of the groups of spectra, but is different for spectra of different groups. Figure 2 demonstrates that the shape of spectra in each of the two groups depends very strongly on either temperature, or the power P_{mw}. At a fairly low power ($P_{mw} \le 0.05$ mW) and a sufficiently high temperature ($T \ge 42$ K), the shape of the lines turns out to be Dysonian. However, at $P_{mw} \ge 0.2$ mW and $T \le 30$ K, the line shape are more complex, and in the central line of the uppermost spectrum of the right group can be seen to consists of least two lines (wide and narrow).

Naturally, when looking at the shapes of lines in Fig. 2, a suspicion arises about the incorrect adjustment of the automatic frequency control (AFC) system of the spectrometer resonator. Therefore, test recording of spectra was made with a targeted detuning of the AFC system within the limits that were possible for the EPR spectrometer used. However, no noticeable changes were found in the EPR spectra recorded at the power and temperature values shown in Fig. 2. Moreover, in the spectra with the AFC sys-

tem turned off, small changes were found only at high microwave power values of $P_{mw} = 20$ mW.

RESULTS AND DISCUSSION

It is known [10] that the spectrum of Gd^{3+} ions ($4f^7$, $S = 7/2$, ground multiplet ^8S) in the crystal field of the cubic symmetry group consists of seven EPR lines with relative integral intensities in an approximate ratio of 7 : 15 : 12 : 16 : 12 : 15 : 7. The positions of these lines change depending on the orientation of the crystal relative to the direction of the external constant magnetic field $\vec{H}_0$. The angular dependences of the positions of the fine structure lines in the EPR spectrum of Gd^{3+} centers of the cubic symmetry are described by the spin Hamiltonian (SH)

$$H_S = \beta_e g S H_0 + \frac{1}{60} b_4 (O_4^0 + 5O_4^4) + \frac{1}{1260} b_6 (O_6^0 - 21O_6^4), \quad (1)$$

represented in a Cartesian coordinate system with axes parallel to the crystallographic axes ⟨001⟩. In SH (1), β_e is the Bohr magneton, g is the spectroscopic splitting factor (g-factor), and b_4 and b_6 are parameters of the fine structure of the EPR spectrum. In this work, for the studied center Gd^{3+} at $P_{mw} \le 0.05$ mW, the values of the SH(1) parameters were obtained (Table 1). These parameters describe with high accuracy the experimental angular dependences shown in Fig. 3 by circles. These angular dependences correspond to the rotation of the external magnetic field vector $\vec{H}_0$ in the crystallographic plane [110]. Here, ϑ is the angle between the vector $\vec{H}_0$ and the crystallographic direction ⟨001⟩; $\vartheta = 0°$ corresponds to the orientation $\vec{H}_0 \parallel \langle 001 \rangle$, and $\vartheta = 54.3°$, to the orientation $\vec{H}_0 \parallel \langle 111 \rangle$. The spectrum lines are labeled *1*–*7*.

Comparing the parameters from Table 1 with those obtained in our previous work [5], one can conclude that the presence of the copper impurity in the studied $Pb_{1-x-y}Gd_xCu_yS$ crystal did not lead to a strong change in the fine structure parameters in SH(1). However, the noticeable increase in the g-factor indicates a decrease in the average concentration of free electrons [11] in the studied sample.

In this work, of the greatest interest are the dependences of the shapes of the observed EPR lines on the power and temperature of the sample. It is known that the shape of the EPR spectrum lines of a paramagnetic center depends on processes that affect the lifetime of this center in the spin states of its ground spin multiplet that are excited as a result of the resonant absorption of microwave power in the resonator. In EPR spectra of defect-free ionic crystals, a Lorentzian line shape is usually observed, which can be represented as the first derivative of the symmetric Lorentzian function

$$f_L = \frac{1}{\pi \Gamma_L} \frac{\Gamma_L^2}{\Gamma_L^2 + (H - H_r)^2}. \quad (2)$$

Here, Γ_L is the half-width of the line, and N_r is the resonance value of the external magnetic field related to this line. In semiconductor crystals with noticeable conduction, EPR lines of the Dysonian form are observed, which corresponds to the first derivative of the Dyson function

$$f_D = \frac{d}{dH}\left[\frac{1}{\pi}\frac{\Gamma_D + \alpha(H - H_r)}{\Gamma_D^2 + (H - H_r)^2}\right]. \quad (3)$$

Here, α is the asymmetry parameter, which is the ratio of dispersion and absorption signals. This asymmetry of EPR lines in conducting materials is most often caused by the skin effect and the nonuniform distribution of the microwave field in their bulk.

Figure 4 presents the results of the simulation of the EPR spectrum line shapes of the $Pb_{1-x-y}Gd_xCu_yS$

Table 1. Parameters of spin Hamiltonian (1) of Gd^{3+} centers in the $Pb_{1-x-y}Gd_xCu_yS$ crystal at three temperature values

T, K	SH parameter		
	g	b_4, MHz	b_6, MHz
5	1.9957 ± 0.0002	−60.1 ± 0.1	0.08 ± 0.05
77	1.9952 ± 0.0003	−58.9 ± 0.2	0.1 ± 0.1
305	1.9936 ± 0.0005	−56.8 ± 0.3	~0

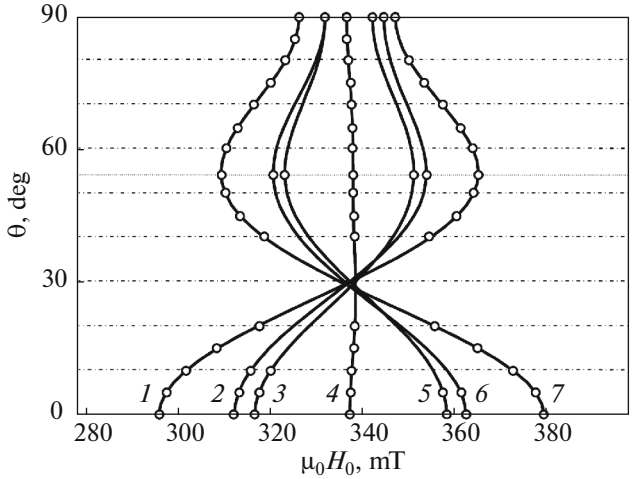

Fig. 3. Angular dependences of the resonance values of the external magnetic field in the studied sample of $Pb_{1-x-y}Gd_xCu_yS$, which were calculated with spin Hamiltonian (1) at $T = 5$ K, $f_{mw} = 9419$ MHz, and $P_{mw} = 0.05$ mW.

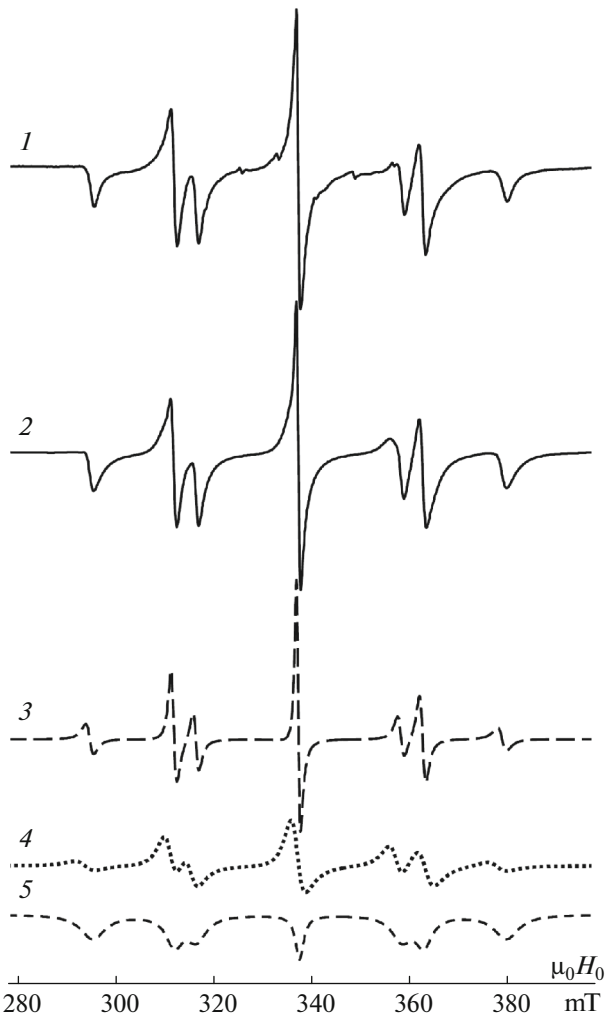

Fig. 4. Simulated EPR spectrum of a $Pb_{1-x-y}Gd_xCu_yS$ sample at $T = 15$ K, $f = 9418.7$ MHz, and $N_0 \| \langle 001 \rangle$.

sample, which was recorded at a temperature of 15 K and a microwave power in the resonator of 5 mW in the orientation $N_0 \| \langle 001 \rangle$. In this figure, spectrum *1* is the experimental spectrum, and spectrum *2* is the simulated spectrum. In addition to the seven lines of the Gd^{3+} ion, the experimental spectrum contains six weak hyperfine structure lines of the Mn^{2+} ion, a small amount of which entered the crystal under study together with the copper impurity.

The components of simulated spectrum *2* are three theoretical spectra required to describe the shape of observed spectrum *1*. Lines of spectra *3* and *4* are constructed in accordance with formula (3). To lines of spectrum *5*, not the first derivative of the Lorentz function, but the function itself corresponds, taken with a negative sign (the "inverted bell" shape). Table 2 presents the parameters of the shapes of lines of spectra *3*–*5*.

Data in Table 2 suggests the presence of at least three regions in the studied semiconductor crystal. Apparently, in these regions, the dynamics of the spin states of Gd^{3+} ions that are exposed to the influence of a resonant high-frequency field turns out to be different. In particular, this is indicated by the elevated value of the *g*-factor of Gd^{3+} centers, which points to a lower value of the average concentration of free electrons in the studied sample. Since the acceptor impurity of copper is usually distributed nonuniformly throughout the bulk of galena [8], the increased value of *g*-factor indicates the presence of regions with different concentrations of free charge carriers in the sample. Obviously, the kinetic parameters of free charge carriers in these regions must be different. Consequently, in these regions, the transfer of the excitation energy of Gd^{3+} ions into the crystal lattice by the mechanism of flip-flop transitions occurs in different ways. The completely unusual shape of the lines of theoretical spectrum *5* (especially the negative sign in front of function (2)) may suggest that the absorption of the electromagnetic wave power in the spectrometer resonator occurs not only by the magnetic dipole mechanism, but there is another mechanism that specifically affects the dynamics of the spin states of Gd^{3+} ions and depends on the values of the kinetic characteristics of free charge carriers. Conversely, since free carriers are bound to Gd^{3+} ions by the exchange interaction, their kinetic characteristics may be dependent on the pro-

Table 2. Line shape parameters of theoretical spectra *3*–*5* in Fig. 4

Spectrum	Parameter	Line number (in Fig. 3)						
		1	*2*	*3*	*4*	*5*	*6*	*7*
3	H_{res}, mT	294.8	311.8	316.2	337.2	358.1	362.6	378.8
	α	0.02	0.39	0.01	0.5	0.1	0.05	0
	Γ_D, mT	1.4	1.0	1.05	0.68	1.2	1.1	1.6
4	H_{res}, mT	293.8	311.0	315.4	316.8	357.6	363.1	377.8
	α	0.02	0.39	0.01	0.5	0.1	0.05	0
	Γ_D, mT	3.5	2.5	2.6	2.5	2.6	3.2	3.5
5	H_{res}, mT	295.3	312.2	316.3	337.5	358.6	362.7	379.6
	Γ_L, mT	6.0	4.0	5.0	2.0	5.0	4.0	6.0

cesses of resonant excitation of spin states of Gd^{3+} centers and their subsequent relaxation to the ground state. The latter may lead to quasi-resonant absorption of microwave power [12].

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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