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Specific Features of the Electron Paramagnetic Resonance Spectrum in the Vicinity of the Convergence of the Transitions of Gadolinium Centers in $Pb_5(Ge_{1-x}Si_x)_3O_{11}$

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Abstract—An anomalous electron paramagnetic resonance spectrum of the transitions $-1/2 \longleftrightarrow +1/2$ of four Gd^{3+}–Si dimer clusters in the $Pb_5(Ge_{1-x}Si_x)_3O_{11}$ crystals doped with gadolinium has been found in the vicinity of the orientation of the magnetic field along the optic axis of the crystal. It has been assumed that this spectrum is caused by rapid transitions between the spin packets of the initial resonances due to the cross-relaxation. A computer simulation of the spectrum has been carried out. The results obtained adequately describe the experiment.

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1. In the recent study [1] of $Pb_5(Ge_{1-x}Si_x)_3O_{11}$ solid solution crystals doped with gadolinium, it was found that the trigonal electron paramagnetic resonance (EPR) spectrum of single Gd^{3+} ions observed in $Pb_5Ge_3O_{11}$ is split into four spectra with strongly broadened lines. It was shown that these spectra are associated with the triclinic Gd^{3+}–Si dimer centers; the Gd^{3+} ions of these complexes substitute for the Pb^{2+} ions; and the Si^{4+} ions are located in the positions of the nearest germanium spheres. Models of the localization of silicon ions were proposed for all the observed Gd^{3+}–Si centers. It is obvious that the presence of silicon ions in more distant germanium spheres also disturbs the spectrum of Gd^{3+} ions. It is the existence of a large number of variants of the substitution $Si^{4+} \longrightarrow Ge^{4+}$ in these spheres that is responsible for the strong broadening of the transitions of the triclinic dimer centers.

In [1], it was ignored that the EPR spectrum in the region of the resonances $-1/2 \longleftrightarrow +1/2$ of Gd^{3+}–Si centers in the vicinity of the orientation $\mathbf{B} \parallel \mathbf{C}_3$ ($\mathbf{B}$ is the magnetic induction) demonstrates an anomalous shape and behavior with a deviation from $\mathbf{B} \parallel \mathbf{C}_3$ and that, in a wide vicinity of the coincidence of the transitions $\pm 1/2 \longleftrightarrow \pm 3/2$, there is an additional signal [2–5]. This work is devoted to the study of the aforementioned features in the EPR spectrum of Gd^{3+} centers in single crystals of the $Pb_5(Ge_{0.85}Si_{0.15})_3O_{11}$ solid solutions.

2. We studied $Pb_5(Ge_{0.85}Si_{0.15})_3O_{11}$ single crystals grown by the Czochralski method from the charge containing 0.01 mol % gadolinium [1]. The fraction of silicon in the charge during the growth coincided, within the limits of experimental error, with the results of comparison of the peak intensities of the X-ray luminescence lines of lead and germanium in crystals with silicon and without it. The structure of the $Pb_5Ge_3O_{11}$ single crystal, which undergoes a second-order ferroelectric structural transition $P3 \longleftrightarrow P\bar{6}$ at a temperature of 450 K, was investigated in [6, 7]. The EPR spectra were recorded on a Bruker EMX Plus X-band (3 cm) EPR spectrometer at temperatures in the range from 100 to 450 K. The temperature of the sample was measured and maintained constant with an accuracy of ±1 K.

3. The change in the shape of the first derivative of the absorption spectrum in the region of the transitions $-1/2 \longleftrightarrow +1/2$ of Gd^{3+}–Si centers with a deviation from the orientation $\mathbf{B} \parallel \mathbf{C}_3$ is illustrated in Fig. 1. The character of the orientation changes of the spectrum does not depend on the microwave power, even though at a power higher than 1 mW the saturation effects similar to those observed in other transitions become noticeable. It should be noted that, in the magnetic field range shown in Fig. 1, there are unresolved transitions $-1/2 \longleftrightarrow +1/2$ of four triclinic centers ($Gd_{Si}1$, $Gd_{Si}2$, $Gd_{Si}3$, and $Gd_{Si}4$ in the notation used in [1]), each represented by three signals of the structurally equivalent but differently oriented complexes. The spectra of the Gd^{3+}–Si dimer centers are resolved for the orientation $\mathbf{B} \parallel \mathbf{C}_3$ only in the case of the transitions $\pm 3/2 \longleftrightarrow \pm 5/2$ and $\pm 1/2 \longleftrightarrow \pm 3/2$, and the splitting of signals from the three structurally equivalent centers is observed only for the $Gd_{Si}4$ center.

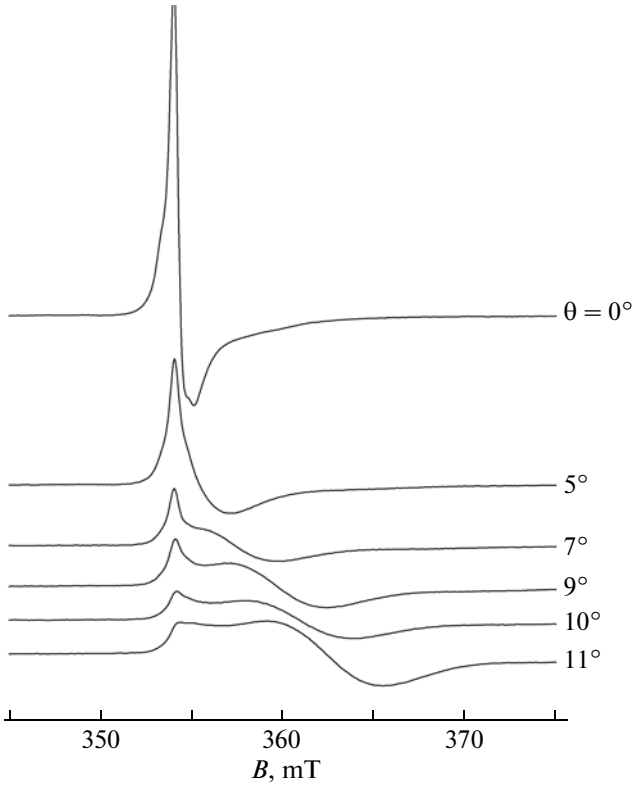

Fig. 1. Dependence of the spectrum shape (the first derivative of the absorption signal) in the region of the transitions $-1/2 \longleftrightarrow +1/2$ on the polar angle θ of the polarizing magnetic field in the *zy* plane ($\mathbf{z} \parallel \mathbf{C}_3$) at 300 K.

Another argument in favor of the fact that the observed spectrum (Fig. 1) is caused by the transitions of Gd^{3+}–Si complexes is that the spectrum (the second derivative of the absorption, Fig. 2) contains two pairs of satellites, which can be explained by the hyperfine interaction with nuclei of the odd isotopes ^{157}Gd and ^{155}Gd. The orientation behavior of the spectrum at temperatures of 105 and 450 K is not qualitatively different from the behavior observed at room temperature and shown in Fig. 1.

The EPR spectrum of the $Pb_5(Ge_{0.85}Si_{0.15})_3O_{11}$ single crystal exhibits another specific feature, namely, an additional signal *X* (Fig. 3), which arises near the intersection of the angular dependences of positions of the transitions $\pm1/2 \longleftrightarrow \pm3/2$ (Fig. 4). In this case, the shape of the spectrum does not depend on the microwave power. It should be noted that each of the signals in Fig. 3 is the sum of transitions of at least three centers ($Gd_{Si}1$, $Gd_{Si}2$, $Gd_{Si}3$), which is clearly seen from Fig. 4.

A similar signal in the spectrum of the Gd^{3+} trigonal center in the $Pb_5Ge_3O_{11}$ single crystal doped only with gadolinium was detected and examined in [2–5]. The emergence of this signal is explained by selective averaging of the spin packets of two signals ($\pm1/2 \longleftrightarrow \pm3/2$) of the Gd^{3+} centers as a result of the spin–lattice transitions between the states involved in the formation of these resonances. The main mechanism of the inhomogeneous signal broadening, which provides a symmetrical structure of the spin packets, was considered to be the modulation of spin Hamiltonian parameters of the b_{21} and c_{21} types due to static fluctuations of both the longitudinal and transverse components of the local electric field [8]. These parameters are not involved in the Hamiltonian of the trigonal center, but form spin packets of the broadened lines. It is important to note that an additional signal can be observed only in a small vicinity ($\Delta\theta \approx \pm1°$, $\Delta\theta = \theta - \theta_0$) of the coincidence of the signal positions at the polar angle θ_0.

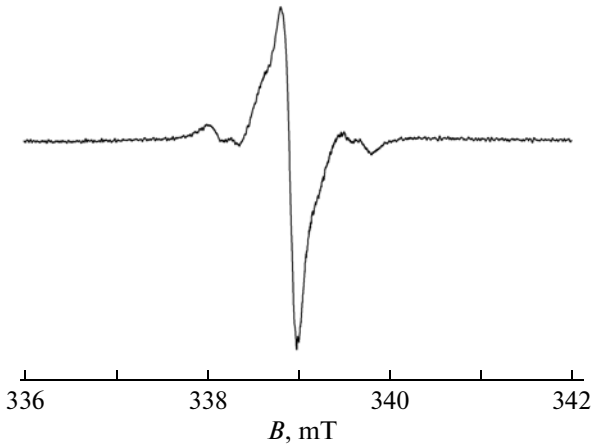

Fig. 2. Second derivative of the absorption spectrum in the region of the transitions $-1/2 \longleftrightarrow +1/2$ in the $Pb_5(Ge_{0.85}Si_{0.15})_3O_{11} : Gd^{3+}$ crystals for the orientation $\mathbf{B} \parallel \mathbf{C}_3$ at 105 K.

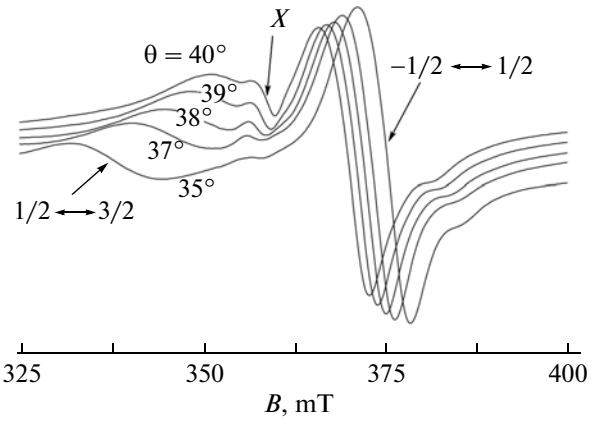

Fig. 3. Dependence of the EPR spectrum shape in the region of crossing of the transitions $\pm1/2 \longleftrightarrow \pm3/2$ on the polar angle θ in the *zy* plane at 300 K. Signals of the transitions $-1/2 \longleftrightarrow -3/2$ are not seen because of the dominant (in intensity) signals of the transitions $-1/2 \longleftrightarrow +1/2$.

It can be seen from Fig. 3 that, in the $Pb_5(Ge_{0.85}Si_{0.15})_3O_{11}$: Gd crystal, the additional signal X is detected in a considerably wider range of polar angles. The intensive transition $\pm1/2 \longleftrightarrow \pm1/2$, which in this region completely overlaps the signal $-1/2 \longleftrightarrow -3/2$ (Fig. 4), makes impossible the observation of the X signal at $\theta > 41°$. Taking into account this fact, the estimation of the range of formation of an additional signal gives the value of no less than $\Delta\theta \approx \pm8°$. It is clearly seen from Fig. 4 that the signal X arises precisely in the vicinity of the coincidence of positions of the transitions $\pm1/2 \longleftrightarrow \pm3/2$.

The wide angle range of observation of the additional signal X in the spectrum of the $Pb_5(Ge_{0.85}Si_{0.15})_3O_{11}$ single crystal is not surprising. This range is determined by the large inhomogeneous width of interacting signals $\pm1/2 \longleftrightarrow \pm3/2$, as well as by the existence of a sequence of coincidences of these transitions of three centers $Gd_{Si}1$, $Gd_{Si}2$, and $Gd_{Si}3$ (Fig. 4).

For the orientation $\mathbf{B} \parallel \mathbf{C}_3$, the transitions $-1/2 \longleftrightarrow +1/2$ of all the centers $Gd_{Si}1$, $Gd_{Si}2$, $Gd_{Si}3$, and $Gd_{Si}4$ are observed in a narrow range of magnetic fields, while the signals from the equivalent but differently oriented centers are degenerate. In this respect, we can make assumption that the anomalous shape of the spectrum in this region is caused by the interaction of the existing resonances (magnetization transfer between the observed transitions [9–11]). It should be noted that an attempt to simulate the spectrum by means of the summation of noninteracting components for the orientation $\mathbf{B} \parallel \mathbf{C}_3$ has failed. Since the considered resonances belong to different centers, the desired interaction can be the cross-relaxation excitation transfer rather than the spin–lattice relaxation, as in the case of the convergence of the transitions $\pm1/2 \longleftrightarrow \pm3/2$ [2, 4, 5]. Incidentally, the authors of [3] made an attempt to explain the appearance of the additional signal between the transitions $\pm1/2 \longleftrightarrow \pm3/2$ of the Gd^{3+} centers in lead germanate precisely by the cross-relaxation through the field of soft phonons.

4. In this respect, we made an attempt to describe the observed spectrum by assuming the existence of cross-relaxation with the Gaussian line between twelve transitions $-1/2 \longleftrightarrow +1/2$ of the Gd–Si centers. The calculation was performed with the LabView 8.6 software. In the procedure of computer simulation of the spectrum, we used the expression [9, 10] obtained for the description of the spectrum of a spin system that has several closely spaced resonances with infinitely narrow lines and undergoes transitions between the states corresponding to these resonances,

$$I(B) = \mathrm{Re}\{\mathbf{W} \cdot \hat{A}(B)^{-1} \cdot \mathbf{l}\}, \qquad (1)$$

where I is the absorption intensity, B is the magnetic induction, $\mathbf{W}$ is the vector with the components equal to the probabilities of noninteracting resonances, and

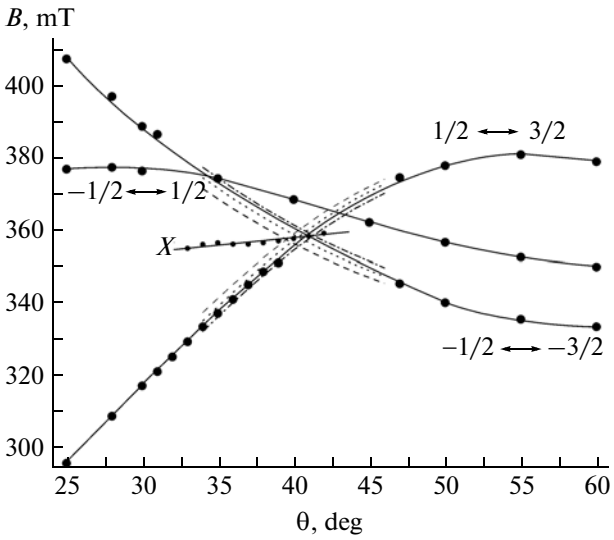

Fig. 4. Experimental orientation behavior of the X signal and transitions of the Gd–Si centers. Dashed, dotted, and dot-dashed curves show the calculated (parameters [1]) behavior of the transitions $\pm1/2 \longleftrightarrow \pm3/2$ of the $Gd_{Si}1$, $Gd_{Si}2$, and $Gd_{Si}3$ centers, respectively.

$\mathbf{l}$ is the unit vector. The matrix $\hat{A}(B)$ for the case of two resonances has the form

$$\hat{A}(B) = \begin{vmatrix} ig\beta(B_i - B) - 1/2\tau & 1/2\tau \\ 1/2\tau & ig\beta(B_j - B) - 1/2\tau \end{vmatrix}, \qquad (2)$$

where B_i and B_j are the positions of noninteracting resonances, g is the g-factor, β is the Bohr magneton, and $1/2\tau$ is the probability of the transition between resonances i and j per unit time.

We used two variants of the calculation. In the first variant, the simulation of the EPR spectrum consisted in constructing the twelfth-order matrix $\hat{A}(B)$ for spectrum (1). In contrast to (1), the form of twelve signals from four centers was assumed to be Lorentzian with the width ΔB_{pp}^L. The inclusion of the inhomogeneous broadening in the calculation by means of the introduction of spin packets in this case appeared to be impossible because of the necessity of forming a high-order matrix and, consequently, the very long time of operation of the program.

In the second variant, in contrast to (1) and (2), it was assumed that the initial lines consist of Lorentzian spin packets with intensities that have the Gaussian distribution

$$Y(B) = \sum_{n=-m}^{m} \frac{I_0 \exp(-(n/\sigma_1)^2)}{1 + \left[(B - B_0 - n)/\frac{\sqrt{3}}{2}\Delta B_{pp}^L\right]^2}, \qquad (3)$$

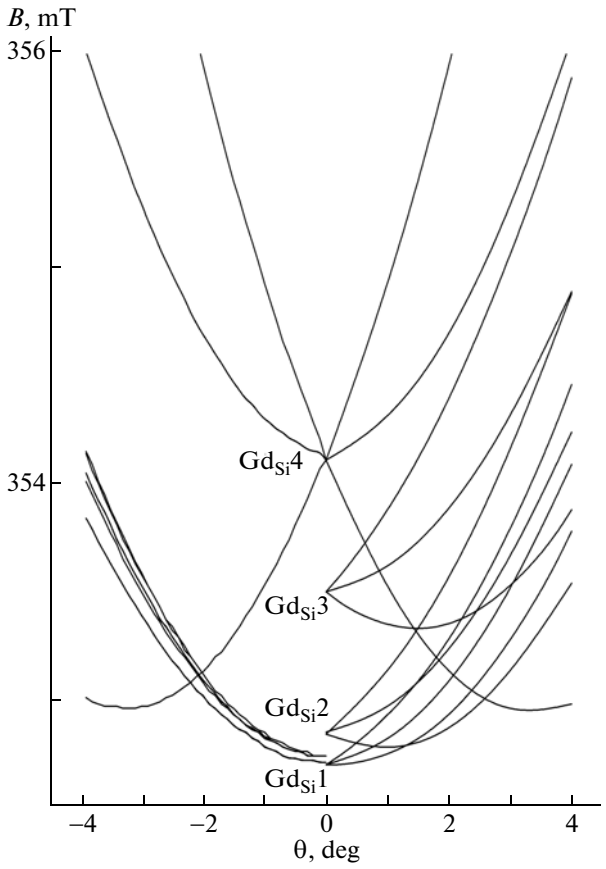

Fig. 5. Calculated and hypothetical orientation behavior of the positions of the transitions $-1/2 \longleftrightarrow +1/2$ of the $Gd_{Si}1$, $Gd_{Si}2$, $Gd_{Si}3$, and $Gd_{Si}4$ centers.

where B_0 is the resonance position of the initial line, ΔB_{pp}^L is the width of the line between the peaks of the first derivative, $2m + 1$ is the number of spin packets, and σ_1 is the parameter characterizing the inhomogeneous broadening. We took into account only the pair interaction of the spin packets with each other, and the total number of spin packets was $12(2m + 1) = 156$. A further increase in the number of spin packets was limited by the finite speed of the program. In this case, the expression for the shape of the EPR spectrum modified by the cross-relaxation takes the form

$$I(B) = \sum_{i=0}^{k}\sum_{j=0}^{k}\sum_{n_1=-m}^{m}\sum_{n_2=-m}^{m} \mathrm{Re}(\mathbf{W}\cdot\hat{A}(B)^{-1}\cdot\mathbf{I}) \times \exp(-(n_1/\sigma_1)^2)\exp(-(n_2/\sigma_1)^2), \quad (4)$$

where $k + 1$ is the total number of initial signals, i and j are the numbers of the initial signals, and n_1 and n_2 are the numbers of the spin packets in the corresponding signals.

In both variants of the simulation of the spectrum, the probability of the cross-relaxation process was specified in the form

$$\frac{1}{2\tau} = \frac{1}{2\tau}\exp\left(-\left(\frac{B_{n_2} - B_{n_1}}{\sigma_2}\right)^2\right), \quad (5)$$

where σ_2 is the parameter of the line width of the cross-relaxation, and B_{n_1} and B_{n_2} are the positions of noninteracting spin packets.

The finding of the initial positions of required signals, which consisted in calculating the orientation behavior of the transitions $-1/2 \longleftrightarrow +1/2$ with the use of the spin Hamiltonian parameters [1] led to the results presented on the left-hand side of Fig. 5. Nine signals from the $Gd_{Si}1$, $Gd_{Si}2$, and $Gd_{Si}3$ centers appeared to be almost completely degenerate. This is associated with the fact that, in [1], because of the large line width, the authors could not observe splittings of the transitions of these centers with a deviation from the orientation $\mathbf{B} \parallel \mathbf{C}_3$ and, consequently, could not estimate the values of parameters of the b_{21} and c_{21} types. However, it is obvious that these parameters differ from zero, even though their values are less than those characteristic of the $Gd_{Si}4$ center. It should be noted that the shift of the transition of the $Gd_{Si}4$ center toward higher magnetic fields with respect to the signals from the $Gd_{Si}1$, $Gd_{Si}2$, and $Gd_{Si}3$ centers for the orientation $\mathbf{B} \parallel \mathbf{C}_3$ and the rate of splitting of this transition with a deviation from $\mathbf{B} \parallel \mathbf{C}_3$ are determined precisely by the values of b_{21} and c_{21}. In this respect, the calculations were carried out using the hypothetical orientation behavior, which accounts for the above considerations and is presented on the right-hand side of Fig. 5. Since the quantity $dB/d\theta$ for high-field signals in Fig. 5, on the average, is significantly greater than that for low-field signals, the influence of the mosaicity of the crystal on the width of the transitions should be substantially different. In order to account for this effect, as well as to compensate for the insufficient number of spin packets in the simulation, the width of spin packets of the high-field signals was assumed to be many times greater than that for the low-field signals. Of course, this approach cannot be considered to be entirely correct; however, in this situation, it proved to be the only one possible.

The first variant of the simulation of the shape of the observed spectrum at $\theta = 1°$ gave the result presented in Fig. 6 for the parameters $\Delta B_{pp}^L = 0.45$ mT, $1/2\tau_0 = 0.3$ MHz, and $\sigma_2 = 1$ mT. In our opinion, the quality of the description of the experimental spectrum is quite satisfactory. The ignoring of the inhomogeneous broadening effects in the computational procedure should lead to the transformation of the obtained parameters into the effective ones, which account for the absence of the aforementioned mechanism of inhomogeneous broadening in the calcula-

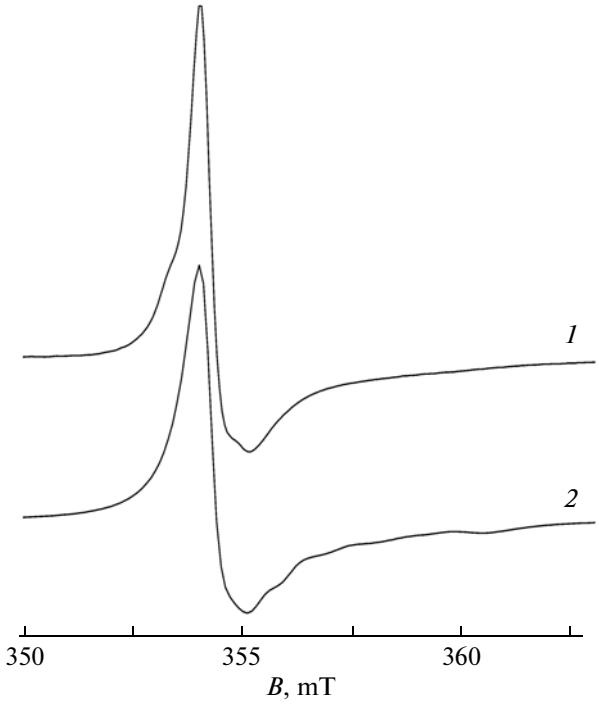

Fig. 6. EPR spectrum shape in the region of the transitions $-1/2 \leftrightarrow +1/2$ (300 K, $\theta = 1°$): (*1*) experiment and (*2*) the result of the calculation of the first variant.

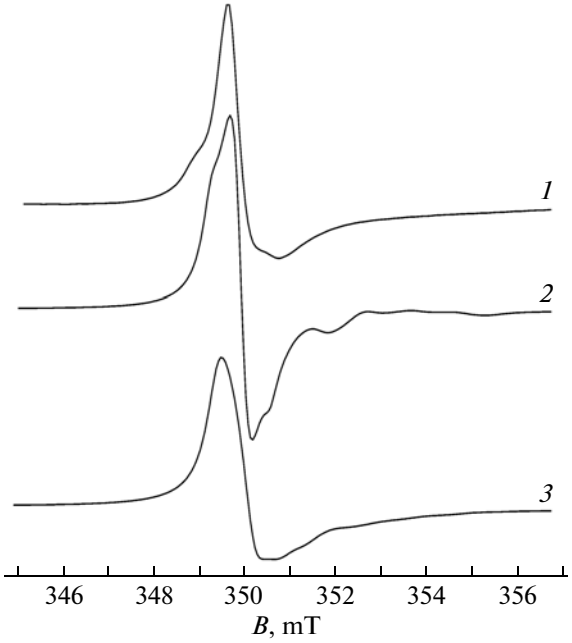

Fig. 7. EPR spectrum shape in the region of the transitions $-1/2 \leftrightarrow +1/2$ at 300 K and $\theta = 1°$: (*1*) experiment, (*2*) calculation without taking into account the cross-relaxation, and (*3*) calculations with taking into account the cross-relaxation according to expression (4).

tions. For example, it should be expected that the homogeneous broadening will be overestimated. Naturally, an attempt to construct the spectrum consisting of twelve lines, which is observed at $\theta = 10°$ (Fig. 1), was unsuccessful.

The results obtained taking into account only the pair cross-relaxation interaction of spin packets both inside the line and between the spin packets of different EPR transitions (expression (4)) are presented in Fig. 7. The calculated spectra were obtained with the following parameters: the number of spin packets in the line $2m + 1 = 13$, $\Delta B_{pp}^{L} = 0.4$ mT, $\sigma_1 = 1.2$ mT, $1/2\tau_0 = 60$ MHz, and $\sigma_2 = 7$ mT. As can be seen, the spectrum shape simulated without inclusion of the cross-relaxation is far from experimental (Fig. 7), whereas the description of the experiment taking into account the cross-relaxation is satisfactory, even if slightly worse than in the first variant of the calculation. In our view, the values of the parameters obtained in the simulation of the spectrum are quite reasonable.

Figure 8 presents the result of the simulation of the spectrum in this approximation for the orientation $\theta = 10°$ (see Fig. 1). The parameters $1/2\tau_0$ and σ_2 were considered to be independent of the orientation of the magnetic field, and the values of ΔB_{pp}^{L} and σ_1 had to be increases by a factor of several tens for an acceptable description of the experimental spectrum. Most likely, this is associated with the fact that, in the calculation, the number of spin packets forming an individual EPR line was not sufficient. Moreover, the quality of the simulation of the spectrum substantially depends on the shape of the initial spectrum (positions and intensities of noninteracting components). Unfortunately, this information so far has not been obtained experimentally.

5. We have observed an anomalous behavior of the electron paramagnetic resonance spectrum in the region of the convergence of the transitions $-1/2 \leftrightarrow$

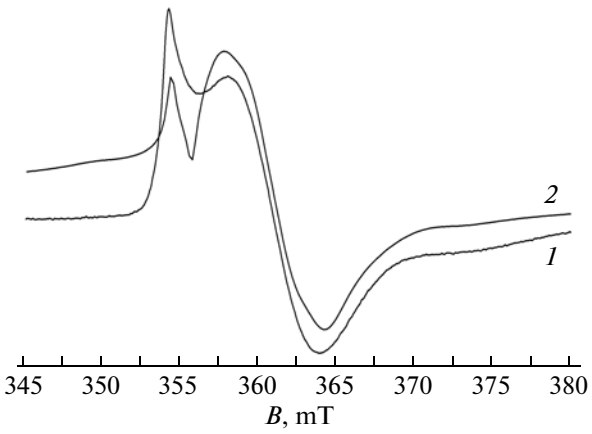

Fig. 8. EPR spectrum shape in the region of the transitions $-1/2 \leftrightarrow +1/2$ (300 K, $\theta = 10°$): (*1*) experiment and (*2*) simulation using expression (4).

+1/2 of four triclinic gadolinium dimer complexes in the $Pb_5(Ge_{1-x}Si_x)_3O_{11}$ crystals in the vicinity of the orientation of the magnetic field $\mathbf{B} \parallel \mathbf{C}_3$, as well as an additional signal between the transitions $\pm 1/2 \longleftrightarrow \pm 3/2$ in the vicinity of the coincidence of their positions ($\theta \approx 40°$). The simulation of the EPR spectrum in the vicinity of the orientation $\mathbf{B} \parallel \mathbf{C}_3$ has been performed by assuming the existence of rapid transitions between the resonances due to the cross-relaxation. The obtained results, in our view, provide a strong argument in favor of the observation of the cross-relaxation effects in $Pb_5(Ge_{1-x}Si_x)_3O_{11}$. The additional EPR signal observed near the polar angle $\theta \approx 40°$ can be explained by the averaging of the central part of the spin packets of two transitions ($\pm 1/2 \longleftrightarrow \pm 3/2$) of the Gd^{3+} centers as a result of the spin–lattice transitions.

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