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Paramagnetic centers in chromium-doped scandium orthosilicate

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The EPR spectrum of single crystals of scandium orthosilicate doped with chromium was studied in the X-band. In the crystallographic and local coordinate systems, the parameters of the spin Hamiltonians of two Cr³⁺ centers that have replaced scandium in the nonequivalent triclinic positions and demonstrate orthorhombic symmetry in the principal axes are determined. The spectrum of the Gd³⁺ center localized in one of scandium position was discovered and studied, and the parameters of the fine structure of its ground state were determined. In the studied crystals, EPR signals of unidentified paramagnetic centers also were observed.

Keywords: scandium orthosilicate, impurity ions, paramagnetic resonance.

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1. Introduction

Scandium orthosilicate Sc₂SiO₅ is a structural analog of yttrium silicate Y₂SiO₅, which, when doped with chromium ions, is considered as the active medium of solid-state lasers, working in the near-infrared area, as well as a saturable absorber for passive Q switching, and with an admixture of ions Ce³⁺ shows effective scintillation properties. The crystal structure of Sc₂SiO₅ has been studied in [1,2], the luminescence and laser properties of scandium silicate have been studied by [3,4] authors, and the nuclear magnetic resonance ⁴⁵Sc in [5].

The electron paramagnetic resonance (EPR) of impurity chromium centers in Sc₂SiO₅ was studied by the authors [6,7]. In [6], it was found that Cr³⁺ ions (electronic spin $S = 3/2$) enter the crystal, replacing Sc³⁺ ions in two physically non-equivalent triclinic positions; in addition, the values of ground state splittings in zero magnetic field were determined in the work. The presence of two non-equivalent Cr³⁺ centers of extremely different intensities in Y₂SiO₅ was found in [8].

In a single crystal Sc₂SiO₅ the authors have measured the orientation behavior of the EPR spectra of two impurity centers of the isotope ⁵³Cr³⁺, determined the parameters of the tensors of the fine structure of the ground state in the principal axes (local coordinate systems), values of isotropic hyperfine interactions were obtained, and it was found that, for some orientations, the probability of forbidden hyperfine transitions becomes comparable to the probability of allowed transitions. In works [6,7] samples of Sc₂SiO₅:Cr, besides intense Cr³⁺ transitions, exhibited a large number of weak, unidentified EPR-signals (Fig. 1).

The present work presents a detailed study of the dependence of the EPR-spectrum of Sc₂SiO₅:Cr on the magnetic

field orientation, determination of the spin Hamiltonian (SH) parameters of Cr³⁺ centers in both crystallographic and local coordinate systems, as well as an attempt to identify other observed paramagnetic centers.

2. Samples and measurement procedure

In this work, scandium silicate single crystals with a chromium concentration (with natural isotope content) of the order of 1 wt% in the charge are investigated. The crystals were grown by Kuban State University staff using the Czochralski method from an iridium crucible in a

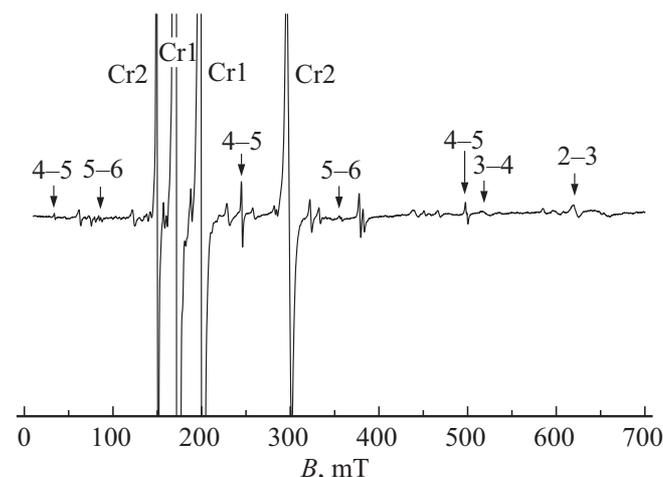


Figure 1. The EPR spectrum of the crystal Sc₂SiO₅ with chromium admixture at 9700 MHz at $\mathbf{B} \parallel \mathbf{b}$. The intense signals belong to the transitions of the two centers Cr³⁺. The arrows mark the identified signals of the center Gd³⁺.

nitrogen atmosphere at a pulling rate of 1.5 mm/h at temperatures above 1970°C [6].

Sc_2SiO_5 crystals have a monoclinic space group $C2/c$ (C_{2h}^6). In the $I2/c$ cell, the lattice constants are $\mathbf{a} = 0.997$ nm, $\mathbf{b} = 0.643$ nm, $\mathbf{c} = 1.206$ nm and the angle between \mathbf{a} and \mathbf{c} axes is 103.94° [1]. All atoms in the structure have symmetry 1 ($C1$): silicon is in a distorted oxygen tetrahedron, Sc^{3+} ions occupy two non-equivalent positions with coordination numbers 6 ($M1$) and 7 ($M2$). Each atomic position is multiplied by the symmetry elements of the cell (inversion and axis $C_2 \parallel \mathbf{b}$) up to four. In this connection, if the paramagnetic ion is localized in any of the three positions ($M1$, $M2$, Si), two magnetically non-equivalent spectra will be observed in the EPR. If the magnetic field is in the \mathbf{ac} plane or at $\mathbf{B} \parallel \mathbf{b}$ (\mathbf{B} — magnetic field induction) the two spectra become equivalent.

The orientation behavior of the EPR spectra at room temperature was measured on a Bruker EMX Plus three-centimeter band spectrometer in fields up to 1.5 T. The samples in the resonator of the spectrometer were attached to a holder fixed to the rod of the standard automatic goniometer and capable of rotating around the perpendicular axis of the rod. The directions of crystallographic axes in the samples were preliminary determined on an X-ray diffractometer.

3. Cr^{3+} centers in scandium orthosilicate

The results of measurements of the orientation behavior of the resonant positions of the signals of the two centers Cr^{3+} (Cr 1 and Cr 2) in two orthogonal planes are shown in Fig. 2, 3. The splitting of the signals (double dots in Fig. 2) is due to a small deviation of the magnetic field from the \mathbf{ac} plane, the value of which, according to our estimates, does not exceed one degree. The averaged values of the transition positions were used in the optimization procedure for the spin Hamiltonian parameters. In the azimuthal dependence (Fig. 2), in addition to the intra-doublet transitions (1–2) and (3–4) in the high fields, inter-doublet (2–3) were also observed, which provided high accuracy in determining the values of the zero field splitting.

The polar angular dependence (Fig. 3) was measured in the \mathbf{zx} plane, $\mathbf{z} \parallel \mathbf{b}$, the \mathbf{x} axis ($\varphi = 0^\circ$ in Fig. 2) is close to \mathbf{c} according to X-ray data. Comparison of our results with [7] showed that the angle between the axis \mathbf{x} and the axis D_1 (D_1 and D_2 — the optical indicatrix axis, the angle between D_1 and \mathbf{c} is 66.2° [9]) is -60.2° and hence, \mathbf{x} is 6° away from \mathbf{c} .

In the above coordinate system, the first two terms of the Hamiltonian (1) were used to describe the spectrum of chromium centers of triclinic symmetry with spin $S = 3/2$. Optimization (fitting) of the SH parameters of the Cr^{3+} centers was carried out by minimizing the RMS deviation of the calculated and measured transition frequencies in the resonant fields of Figs. 2, 3. The results of the fitting procedure with the isotropic g -factor in the coordinate

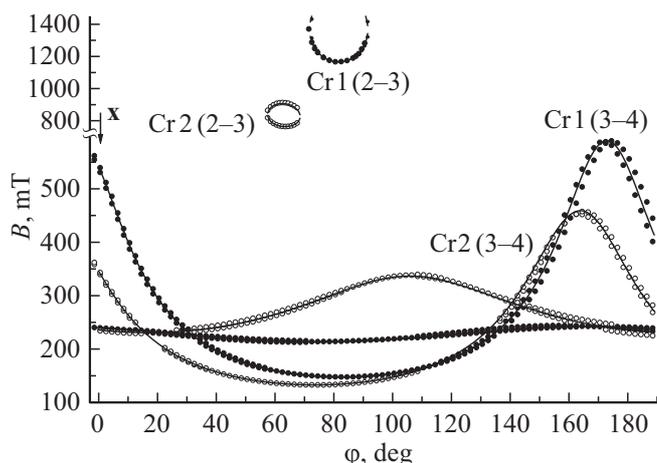


Figure 2. Angular dependence of the positions of the transitions of the two Cr^{3+} centers in the \mathbf{ac} plane at 9630 MHz, points (for Cr 1 — black) — experiment, curves — calculation with the parameters of Table 1. The double points are caused by the splitting of signals due to the magnetic field deviation from the plane \mathbf{ac} . High-field rings are formed by inter-doublet transitions (2–3) of the chromium centers.

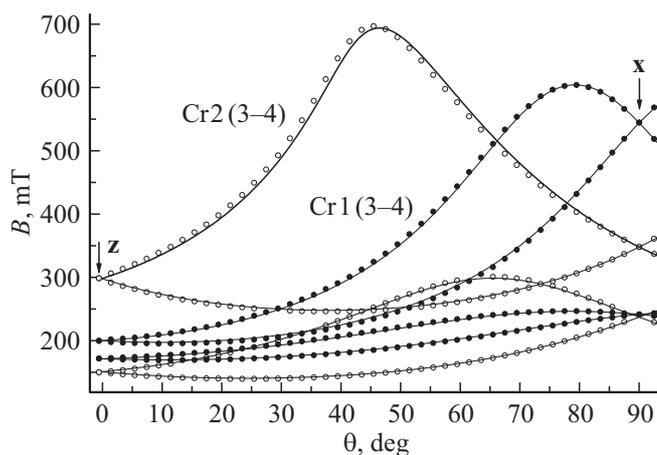


Figure 3. Orientation behavior of the transition positions of the two centers of Cr^{3+} in the \mathbf{zx} plane, points (for Cr 1 — black) — experiment, curves — calculation with the parameters of Table 1. The \mathbf{x} axis is approximately parallel to \mathbf{c} .

system \mathbf{xyz} are shown in Table 1. The SHs of the two magnetically non-equivalent Cr^{3+} centers (for both Cr 1 and Cr 2) differ only by the signs of b_{21} and c_{21} .

Table 1 also shows the parameters of SH $\text{Sc}_2\text{SiO}_5:\text{Cr}^{3+}$ in the local coordinate system (in principal axes) obtained by rotating the coordinate system to maximize the parameter b_{20} . In the same place, the Euler angles of the system of principal axes with respect to \mathbf{xyz} are given. In this case, the second-rank fine structure tensor becomes diagonal, and the other components of the tensor practically vanish. As can be seen in the principal axes, the obtained parameters of the SH are in good agreement with the results [7].

Table 1. SH parameters of the two Cr³⁺ centers in Sc₂SiO₅ at room temperature. (Zero field splitting — Δ , b_{nm} , c_{nm} and RMS deviation — F (GHz); Euler angles — α, β, γ (deg); N — the number of transition positions used in the optimization procedure. The double signs of the parameters b_{21} and c_{21} correspond to the two magnetically non-equivalent centers)

Centers	Cr 1			Cr 2		
	$\mathbf{z} \parallel \mathbf{b}$	In principal axes [this work]	In the principal axes [7]	$\mathbf{z} \parallel \mathbf{b}$	In the main axes [this work]	In the main axes [7]
g	1.970	1.970	1.9592	1.970	1.970	1.9534
b_{20}	−4.75	32.08	32.80	−10.94	19.74	19.7
b_{21}	±15.46	−8.1 · 10 ^{−3}	—	±28.39	−5.1 · 10 ^{−3}	—
b_{22}	−19.50	16.89	17.58	−17.40	14.41	14.43
c_{21}	±106.75	2.3 · 10 ^{−3}	—	±42.72	−0.6 · 10 ^{−3}	—
c_{22}	4.26	−3.1 · 10 ^{−3}	—	7.64	0.7 · 10 ^{−3}	—
F(N)	58(203)	—	—	81(182)	—	—
Δ	67.16		68.7	42.84		42.8
$\alpha \pm$	262.8	82.8	—	253.6	73.6	—
β	126.2		—	111.8		—
γ	272.1		—	287.2		—

The obtained parameters b_{20} (Table 1) radically differ in magnitude from $b_{20}(\text{Cr 1}) = 22.9$ GHz and $b_{20}(\text{Cr 2}) = 14.1$ GHz, given in expressions (14), (15) of [6] (other parameters of the fine structure may differ due to different choice of axes \mathbf{xy}). The reason for this mismatch was the erroneous statement [6] that these parameters were obtained in the coordinate system $\mathbf{z} \parallel \mathbf{b}$, whereas it was done in some coordinate system for a magnetic field lying in the plane \mathbf{ac} . After the transition to the major principal (in resulting from the maximization of b_{20}), the parameter values b_{20}, b_{22} [6] deviate from the data in Table 1 by no more than 0.5 GHz. In addition, it is noticed that in Fig. 9 in [6] the magnetic field was not rotated exactly in the plane, as evidenced by the mismatch of positions of the signals in the orientations differing by 180°, which explains the poor quality of the description of the experiment.

In work [8] it was reported that the ratio of peak signal intensities of Cr 1 and Cr 2 in scandium silicate is about 4. Comparison of the integral transition intensities taking into account to the probabilities allowed us to conclude that the ratio of Cr 1/Cr 2 concentrations is about 10.

4. Gd³⁺ centers in scandium orthosilicate

Figs. 4, 5 show the angular dependences of the positions of all measurable EPR signals (except the transitions of the centers Cr 1 and Cr 2) in two planes (\mathbf{xy} and \mathbf{xz}), in which the centers Cr³⁺ were studied (Sect. 3). Measurements of the spectrum behavior (especially in the fields of 150–350 mT) are complicated by the presence of intense

transitions of Cr³⁺ centers (see Fig. 1), as well as the strong dependence of the signal intensity on the magnetic field orientation. The same figures show (as curves) the results of the numerical diagonalization of the spin Hamiltonian matrix for the center with $S = 7/2$ [10]:

$$\begin{aligned}
 H_{\text{sp}} = & (\mathbf{BgS}) + \frac{1}{3} \sum_m (b_{2m}O_{2m} + c_{2m}\Omega_{2m}) \\
 & + \frac{1}{60} \sum_m (b_{4m}O_{4m} + c_{4m}\Omega_{4m}) \\
 & + \frac{1}{1260} \sum_m (b_{6m}O_{6m} + c_{6m}\Omega_{6m}), \quad (1)
 \end{aligned}$$

where g — g -factor, β — Bohr magneton, O_{nm}, Ω_{nm} — Stevens spin operators, b_{nm}, c_{nm} — fine structure parameters [10].

The calculation was carried out with the parameters of Table 2, obtained by minimizing the standard deviation of the calculated and measured transition frequencies without the sixth-rank term in (1). Fitting was performed using more than 400 positions of signals measured in two planes and attributed by us to transitions of two magnetically nonequivalent Gd³⁺ centers with $S = 7/2$ and $g = 1.990$. The numbers of energy levels between which the transitions occur are shown in Fig. 1, and the zero-field splittings in Table 3.

The error of the given parameters was defined as their change leading to the condition $f_n/2 > \max(|f_{n0}|, |\delta|)$ for the most sensitive transitions, where f_n and f_{n0} — the current and optimal individual deviations [11]. The error in determining the resonance conditions $\delta = 15$ MHz used

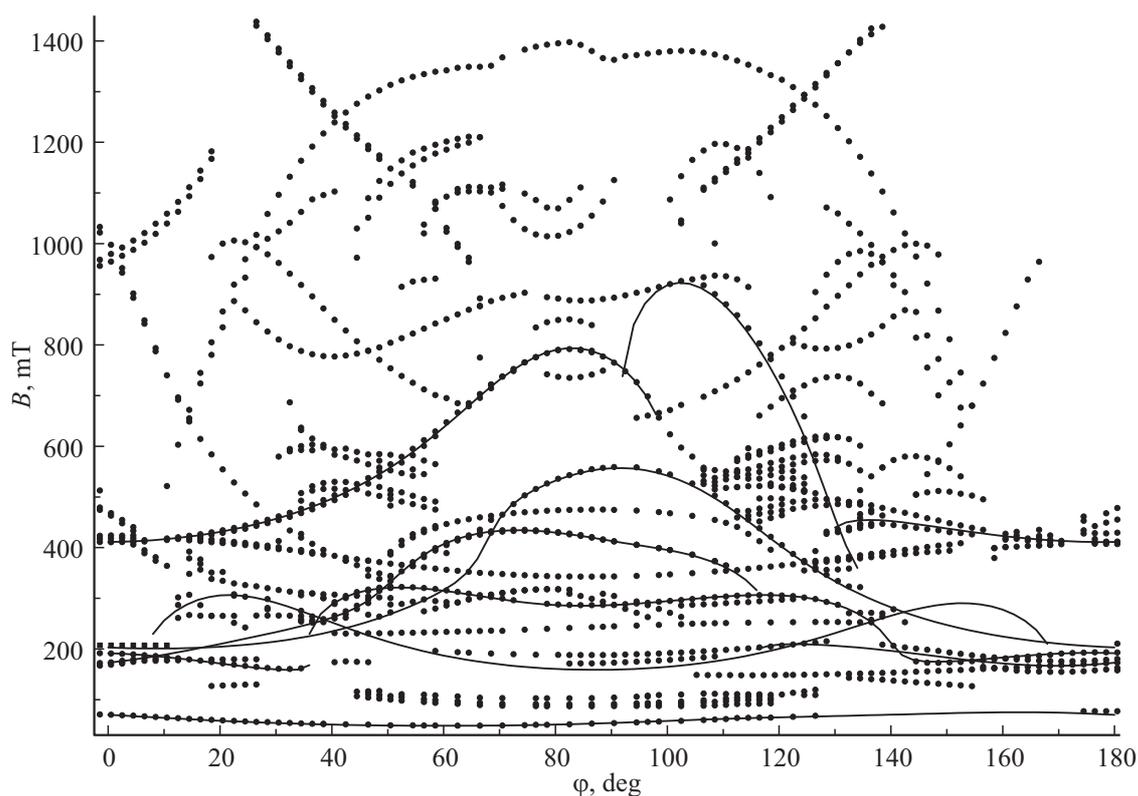


Figure 4. Angular dependence of the positions of the observed EPR signals in the ac plane at a frequency of 9630 MHz. Curves — results of calculating the behavior of the transitions of the identified center Gd^{3+} with the parameters of Table 2. The positions of the signals of the Cr^{3+} centers are not given.

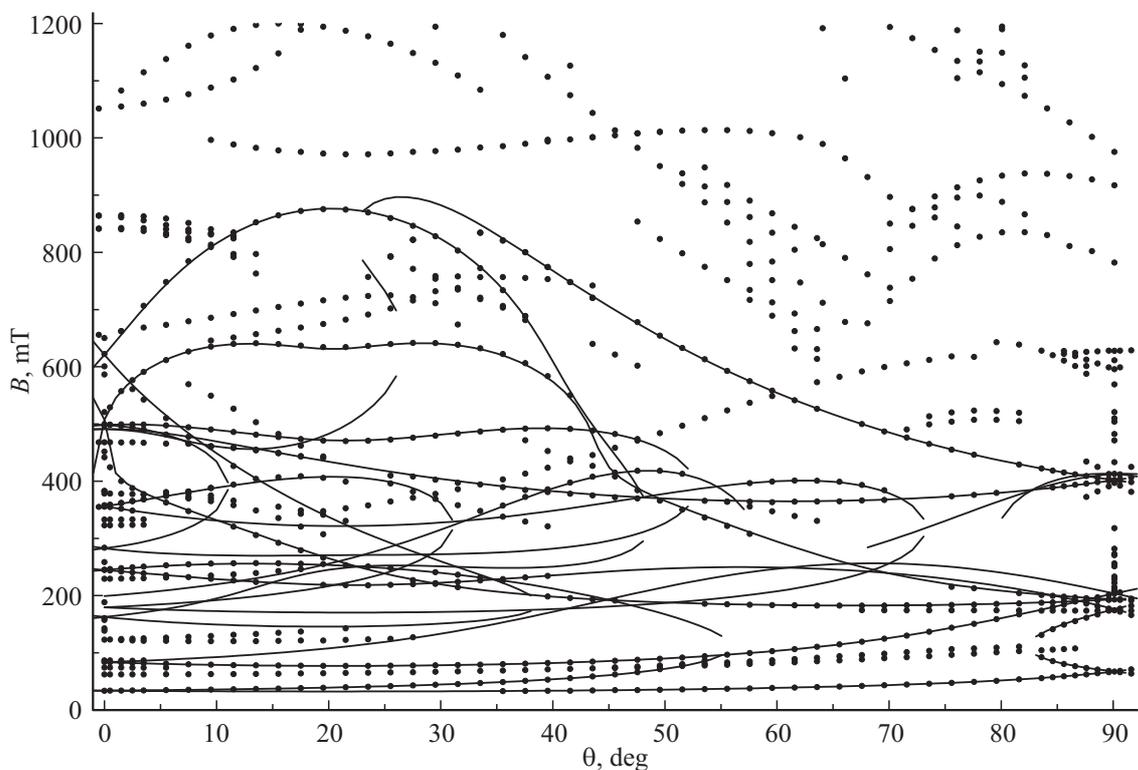


Figure 5. Orientation behavior of positions of measurable EPR signals in the zx plane. The x axis is approximately parallel to c . Curves — results of calculating the behavior of the transitions of the identified center Gd^{3+} with the parameters of Table 2. The positions of the signals of the Cr^{3+} centers are not given.

Table 2. Parameters of the SH center Gd^{3+} in Sc_2SiO_5 at room temperature in the coordinate system $z \parallel \mathbf{b}$ and in the principal axes of the second-rank tensor. (b_{nm}, c_{nm} , standard deviation — F (MHz); N — the number of transition positions used in the optimization procedure. Double signs of parameters b_{nm} and c_{nm} with odd projections correspond to two magnetically non-equivalent centers)

Parameters	$z \parallel \mathbf{b}$	In principal axes
b_{20}	2860(7)	3480
b_{21}	$\pm 5430(15)$	—
b_{22}	2880(15)	2470
c_{21}	$\pm 3200(20)$	—
c_{22}	166(15)	—
b_{40}	6(4)	0
b_{41}	$\pm 60(15)$	36
b_{42}	45(15)	15
b_{43}	$\pm 10(35)$	113
b_{44}	13(15)	40
c_{41}	$\pm 36(18)$	40
c_{42}	$-10(15)$	-26
c_{43}	$\mp 100(40)$	-370
c_{44}	85(30)	64
F(N)	60(438)	—

Table 3. Splitting in zero magnetic field of Gd^{3+} centers in Sc_2SiO_5 at room temperature (GHz)

Energy levels	Gd^{3+}
$\pm 1/2 \leftrightarrow \pm 3/2$	14.38
$\pm 3/2 \leftrightarrow \pm 5/2$	12.62
$\pm 5/2 \leftrightarrow \pm 7/2$	20.11

in this procedure does not include errors in measuring the orientation of the magnetic field, so that the given errors are underestimated.

The coordinate system XYZ , in which the value of the axial parameter b_{20} of the Gd^{3+} centers takes the maximum value, is given by the following direction cosine matrix:

$$\begin{array}{ccc}
 & X & Y & Z \\
 \mathbf{x} & 0.9407 & -0.0323 & -0.3377, \\
 \mathbf{y} & -0.0797 & -0.9886 & -0.1275, \\
 \mathbf{z} & -0.3298 & 0.1468 & -0.9326,
 \end{array}$$

in this case, the second-rank tensor of the fine structure becomes diagonal with $b_{20}/b_{22} > 1$ (Table 2), i.e. rhombic.

Other parameters of the second-rank SH in the principal axes do not exceed units of MHz.

The fourth-rank tensor of the fine structure in the XYZ coordinate system (see Table 2) shows a noticeable dominance of the components b_{43} and c_{43} . Rotating around the Z axis by an angle of about 12° makes the components b_{40} and b_{43} equal 0 and 450 MHz, respectively, with the RMS value of the other parameters 23 MHz. Because of the large (relative) error of the SH parameters b_{4m} (see Table 2), the orientation of the principal axis of trigonal pseudo-symmetry of the fourth-rank tensor [12] determined in this way is rather approximate. Unfortunately, a comparison of the directions of the principal axes of the tensors of the second- and fourth-ranks of the observed Gd^{3+} centers with the structure of the nearest environment of scandium positions $M1$ and $M2$ does not allow us to determine the localization of these gadolinium ions, due to the very low symmetry of oxygen polyhedra.

Figs. 1 and 4,5 show that the EPR-spectrum of $Sc_2SiO_5:Cr$ is not exhausted by transitions of Cr^{3+} and Gd^{3+} centers, there are many more signals, including those in high magnetic fields. It is very likely that among the observed signals, there are transitions of the Gd^{3+} center localized at a different scandium position, the angular dependences of the positions of which are mainly located under the intense signals of the Cr^{3+} centers. The high-field signals in Figs. 4,5 most likely belong to transitions of Fe^{3+} centers with spin $S = 5/2$, which are usually well observed at room temperature and have larger zero-field splitting than Gd^{3+} centers.

In order to verify these assumptions, it is necessary to make accurate measurements on scandium silicate crystals containing only gadolinium and only iron impurities. Such measurements will also solve the question of the principal axes of the fine structure tensors of Gd^{3+} centers.

5. Conclusion

The ability to detect very small amounts of gadolinium in yttrium or scandium silicate crystals at room temperature allows us to estimate (due to the similarity of their chemical properties) the total concentration of uncontrolled impurity ions of the rare-earth series. This fact is very important in the study and development of quantum memory materials, because the rapid increase with temperature of the spin-lattice relaxation rate of even a small amount of rare-earth ions can affect the relaxation of active centers.

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Conflict of interest

The authors declare that they have no conflict of interest.

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