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Impurity paramagnetic centers in $\text{LiCaAlF}_6 : \text{Cr}$

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In $\text{LiCaAlF}_6 : \text{Cr}$ single crystals, paramagnetic resonance spectra of isolated Cr^{3+} centers and uncontrolled Mn^{2+} , Gd^{3+} , V^{2+} impurities were detected in several samples with different chromium concentrations. The parameters of the spin Hamiltonians Cr^{3+} , Gd^{3+} , V^{2+} are determined. Near the signals of Cr^{3+} centers, weak satellites were observed, attributed to transitions of interacting pairs of chromium ions.

Keywords: LiCaAlF_6 , uncontrolled impurities, paramagnetic resonance.

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1. Introduction

Isostructural crystals LiMAlF_6 (M — Ca, Sr, Ba) of type colquiriite, having high transparency, large band gap [1] and not suffering from hygroscopicity [2], allow their activation by both ions of iron group and by rare-earth. Compounds LiCaAlF_6 (LiCAF) and LiSrAlF_6 (LiSAF), doped with chromium, demonstrate combination of laser and optical properties making them unique tunable media in the near infrared range [3,4]. Their another feature is presence in compounds of light isotope of lithium ${}^6\text{Li}$, able to absorb neutrons, this provides the possibility of these materials use as neutron detector, their doping (for example, by europium) allows optimize of their parameters [2].

The paramagnetic resonance (EPR) of ions Cr^{3+} ($3d^3$, electronic spin $S = 3/2$) in LiCAF and LiSAF was studied by authors [3,5], the observed in LiCAF centers Cr^{3+} were described by trigonal spin hamiltonian [3]. In paper [6] parameters of centers Cr^{3+} (g and D) were obtained by method of full diagonalization of the energy matrix based on the model of two spin-orbit parameters. The calculation results show that the observed positions of optical bands and three parameter of spin-hamiltonian (two g -factors and splitting in zero field D) can only be explained rationally with the help of four adjustable parameters [6]. Authors [3,5,6] conclude that ions Cr^{3+} replace the positions of aluminium.

This work presents study by method of EPR of paramagnetic centers implemented in $\text{LiCaAlF}_6 : \text{Cr}^{3+}$.

2. Samples and experimental procedure

We studied three single-crystals LiCaAlF_6 , doped by chromium and grown by Bridgman–Stockbarger method in laboratory of magnetic radiospectroscopy of Kazan State University. The growth was carried out in a resistance

furnace (in a new graphite crucible and in an atmosphere of ultra-pure argon) [7].

First studied sample („first“) with chromium concentration about 1 at.% has form of a parallelepiped $6 \times 2 \times 2$ mm with axis C_3 along long dimension. Chromium concentration in two other, formless samples („second“ and „third“) was estimated by value of integral intensities of EPR of low field transition of centers Cr^{3+} (45 : 100 : 1) respectively.

Spatial group of crystals LiCaAlF_6 and LiSrAlF_6 according to papers [8,9] — (N^b 163) $P\bar{3}1c(D_{3d}^2)$, $a = b = 0.5007$ nm, $c = 0.9641$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The octahedral positions of lithium and aluminium have symmetry $32(D_3)$, point symmetry group of octahedral positions of calcium or strontium — $\bar{3}(C_{3i})$, symmetry of position of fluorine ions — $1(C_1)$ [8,9].

The orientation behavior of position of EPR-transitions of centers Cr^{3+} was measured at the magnetic field rotation in plane comprising axis $C_3 \parallel \mathbf{z}$ (polar dependence) on spectrometer of X-band EMX Plus Bruker at room temperature in magnetic fields up to 1.4 T. The sample in a spectrometer resonant cavity was attached to a holder that is secured on the rod of the standard automatic goniometer and designed to rotate around the axis perpendicular to the rod.

3. Results and discussion

EPR spectrum of „first“ sample $\text{LiCaAlF}_6 : \text{Cr}^{3+}$ at $\mathbf{B} \parallel \mathbf{z} \parallel C_3$ is given in Figure 1. Three intensive signals belong to allowed ($\Delta M = \pm 1$, M — projection of electron spin) transitions of trigonal isolated centers Cr^{3+} . In arbitrary orientations of the magnetic field ($\theta \neq 0^\circ$, 90°) additional three prohibited transitions ($\Delta M \neq \pm 1$) are observed, having intensities comparable with that of the allowed transitions. The transition $2 \leftrightarrow 3$ at $\theta \approx 0^\circ$ ($\mathbf{z} \parallel C_3$) demonstrates superhyperfine structure (SHFS) with components spacing 0.6 mT (Figure 2, a), caused by interaction with six equivalent nuclear spins ($I = 1/2$) of fluorine.

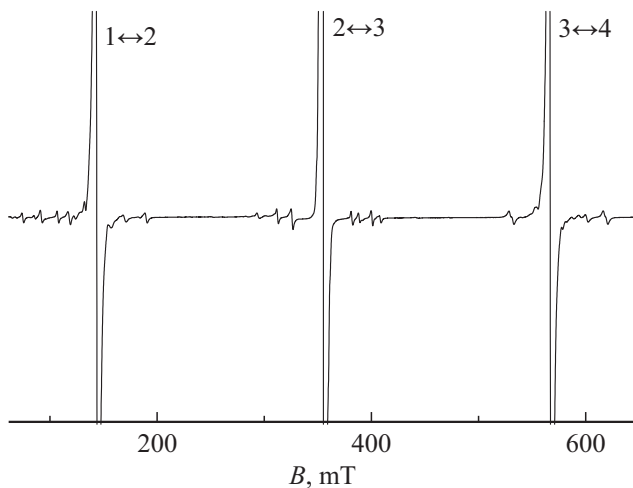


Figure 1. EPR spectrum (derivative of absorption signals) of „first“ sample $\text{LiCaAlF}_6:\text{Cr}^{3+}$ at $\mathbf{B} \parallel C_3$ (\mathbf{B} — magnetic field induction) at frequency 9810 MHz. The shown in Figure numbers of energy levels for $S = 3/2$, between which appropriate transitions occur, are enumerated upwards.

Experimental and calculated parameters of SH of trigonal center Cr^{3+} in LiCAF at room temperature. F — RMS deviation by N used experiment points

Parameters	Experiment	Experiment [3]	Calculation [6]
g_{\parallel}	1.973(1)	1.974(1)	1.976
g_{\perp}	1.975(1)	1.974(2)	1.977
$b_{20} = D$, MHz	-2920(10)	-3028(15)	-3058
$F(N)$, MHz	5.2(527)	—	—

Note. Sign of D was determined in paper [3].

To describe the orientation behavior of positions of six transitions Cr^{3+} the spin Hamiltonian (SH) of trigonal symmetry was used [10] without two last terms

$$H_{\text{sp}} = \beta(\mathbf{BgS}) + \frac{1}{3} \cdot b_{20}O_{20} + \frac{1}{60} \cdot (b_{40}O_{40} + b_{43}O_{43}) + 1/1260 \cdot (b_{60}O_{60} + b_{63}O_{63} + b_{66}O_{66}), \quad (1)$$

where \mathbf{g} — \mathbf{g} -tensor β — Bohr magneton, O_{nm} — Stevens spin operators, b_{nm} — fine structure parameters. Fitting of the parameters of SH centers Cr^{3+} was carried out by minimizing the RMS deviation of the calculated and measured transition frequencies at the resonant fields. The fitting results are given in Table, quality of experiment description is demonstrated by Figure 3.

Measurements at frequency 37.3 GHz provide observations in region 700 mT of polar dependence of transitions $1 \leftrightarrow 3$ and $2 \leftrightarrow 4$, their positions are well described by Table parameters.

Besides transition of trigonal centers Cr^{3+} , spectrum in Figure 1 shown multiple weak signals (satellites), surrounding transitions of the isolated centers. Peak intensities

of first derivative lines of isolated centers are by about one hundred times higher than these signals. Most likely, these signals are due to ions Cr^{3+} , localized in aluminium positions, but having defect in the environment, that slightly changes values of parameters of the fine structure, but resulting in symmetry decreasing. The defects indicated may be vacancies, host atoms in interstices, impurity atoms in sites or interstices, and also rearrangement defects (so-called antisite-defects). [11,12]. Orientation behavior of spectrum of said satellites is shown in Figure 3.

As the ions Cr^{3+} replaces the aluminium position isovalently, the formation of charges that compensate for defects does not occur, i.e. the association of chromium ions is possible only with the crystal's own defects. Due to different charge states of cations the formation of antisites in LiCaAlF_6 is also unlikely. On other hand, rather high concentration in chromium crystal makes it possible to form pairs of ions Cr^{3+} associated with magnetic dipole and exchange interactions.

EPR spectrum of „second“ sample is similar to the „first“ sample, but with larger intensities and width of signals. As for the rest the spectra of „first“ and „second“ samples demonstrate equal set of centers and signals.

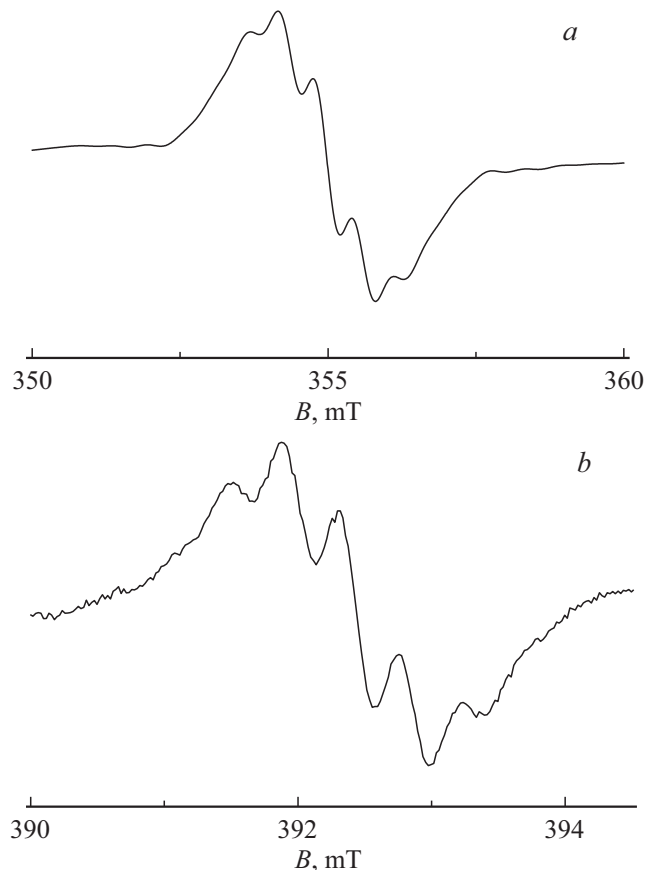


Figure 2. Superhyperfine structure *a*) of transition $2 \leftrightarrow 3$ of centers Cr^{3+} of „first“ sample and *b*) high field (~ 400 mT) superhyperfine component of transition $1 \leftrightarrow 3$ (see Figure 7) of centers V^{2+} of „third“ sample $\text{LiCaAlF}_6:\text{Cr}^{3+}$ at $\mathbf{B} \parallel C_3$.

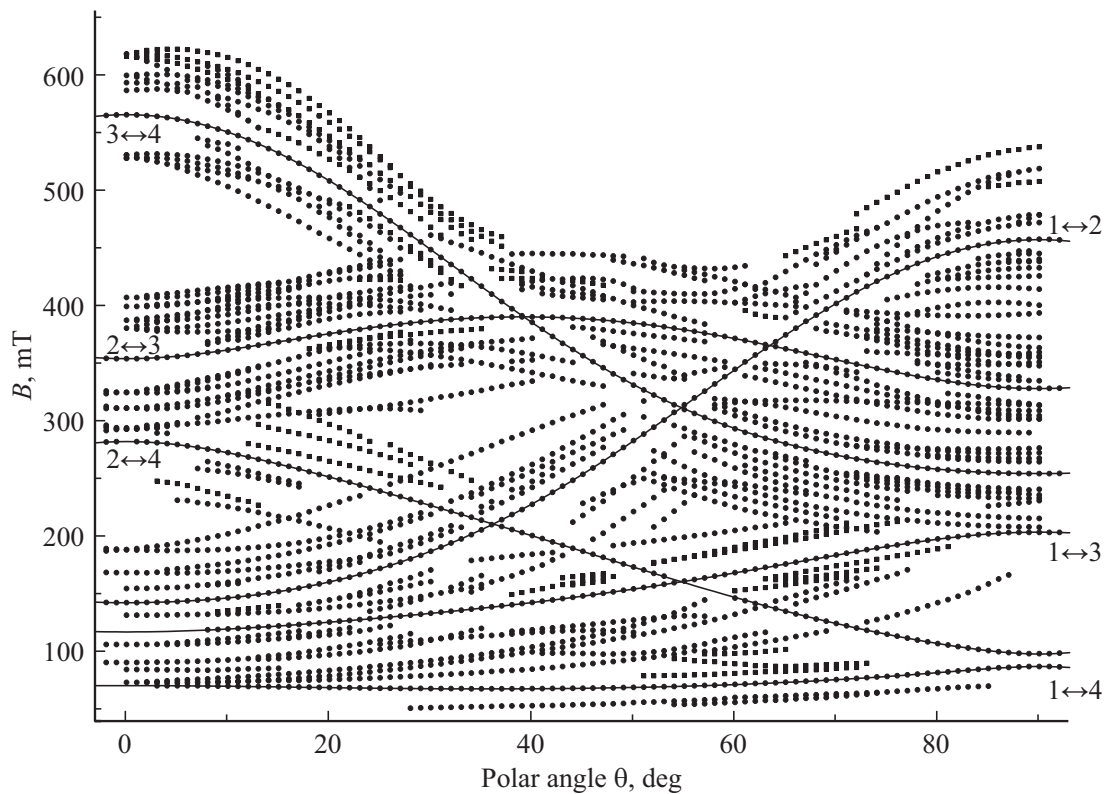


Figure 3. Polar dependence of positions of transitions of trigonal centers Cr^{3+} and their satellites in „first“ sample LiCAF. The dots — the experiment, the curves — calculation with the Table parameters.

In EPR spectrum of „third“ sample LiCAF besides the isolated centers Cr^{3+} the intense signals of ions Mn^{2+} ($3d^5$, ${}^6\text{S}_{5/2}$, $S = 5/2$, $I = 5/2$ are observed with natural spreading 100%), as well as centers Gd^{3+} ($4f^7$, ${}^8\text{S}_{7/2}$, $S = 7/2$) and hyperfine octet of signals V^{2+} ($3d^3$, ${}^4\text{F}$, $S = 3/2$, $I = 7/2$, 99.7%) are detected (see Figures 4 and 5). Considering the charge states of the observed impurity centers, we can logically suppose that ions Gd^{3+} , like Cr^{3+} , are localized in aluminum positions, and ions Mn^{2+} and V^{2+} occupy positions of two-charge calcium cation. As width of fine structure of centers Mn^{2+} is same as width of hyperfine structure, all components of which are perturbed by interaction with the nuclear spins of the fluorine environment (step along the field 1.5 mT), the very complex spectrum is observed.

For six transitions of centers Gd^{3+} (the central one is overlapped by intense signals Mn^{2+}) the polar angular dependence is measured at unknown azimuthal angle φ . In arbitrary orientation of magnetic field centers of gadolinium have doublet splitting of signals, but transitions of axial center Cr^{3+} do not demonstrate such splitting. Most likely, said splitting is due to presence in sample of blocks turned around the axis C_3 , which is detected in the spectrum of only high-spin Gd^{3+} . The superhyperfine structure on signals Gd^{3+} was not detected. The orientation behavior of positions (upon doublet splitting presence the average field value was used) is well described by spin Hamiltonian (1)

with parameters obtained in fitting procedure

$$g = 1.991(1), \quad b_{20} = 856(3), \quad b_{40} = 12(3),$$

$$b_{43} = -20, \quad b_{60} = -4(2) \quad (b_{nm} \text{ in MHz}) \quad (2)$$

at RMS deviation $F = 7.1$ MHz and considering 226 experiment resonances. Absence of information on azimuthal dependence of spectrum excludes correct determination of b_{43} .

To refine value of trigonal parameter b_{43} the amplitude of azimuthal dependence of positions of transitions $1 \leftrightarrow 2$ and $2 \leftrightarrow 3$ of centers Gd^{3+} was measured at $\theta = 63.5^\circ$, at that permanent polar angle is ensured by monitoring of overlap of transitions $1 \leftrightarrow 2$ and $2 \leftrightarrow 3$ of axial center Cr^{3+} . Parameter b_{43} evaluation from these data provides value 130 MHz. Then polar dependence of positions of signals Gd^{3+} at $\varphi = 0^\circ$ was measured, i.e. when in azimuthal dependence the extremums of transition positions are implemented. This polar dependence is described by the following set of SH parameters (1):

$$g = 1.992(2), \quad b_{20} = 857(4), \quad b_{40} = 12(2),$$

$$b_{43} = 120(32), \quad b_{60} = -4(2), \quad b_{63} = -25(30),$$

$$b_{66} = -25(25) \quad (b_{nm} \text{ in MHz}). \quad (3)$$

$F = 6.7$ MHz considering 127 experimental resonances. As we see the obtained values b_{43} and b_{63} are in good

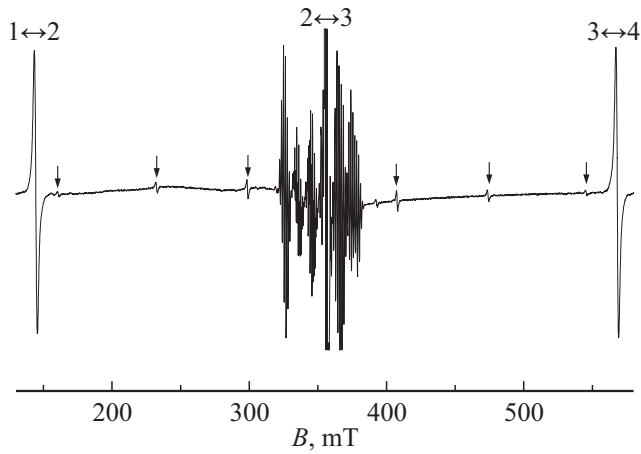


Figure 4. EPR spectrum of „third“ sample $\text{LiCaAlF}_6 : \text{Cr}^{3+}$ at $\mathbf{B} \parallel C_3$. The intense signals in center — five hyperfine sextets of fine structure Mn^{2+} with fluorine structure, arrows show transitions of centers Gd^{3+} .

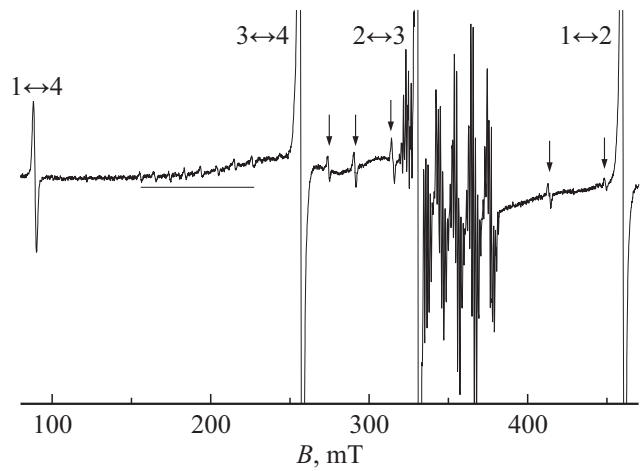


Figure 5. EPR spectrum of „third“ sample $\text{LiCaAlF}_6 : \text{Cr}^{3+}$ at $\mathbf{B} \perp C_3$, horizontal line marks eight components of hyperfine structure V^{2+} (transition $1 \leftrightarrow 2$), arrows show transitions of centers Gd^{3+} .

agreement with evaluations from measurements of the azimuthal dependence.

Figure 5 shows that components of SHFS of ions V^{2+} have low intensity as compared to signals of other centers detected in LiCAF. When going from orientations $\theta = 0^\circ, 90^\circ$ the observed SHFS becomes very complicated due to occurrence of prohibited hyperfine components, i.e. literally by several degrees converts in set of large number of components with close intensities (Figure 6). At that on transition ($1 \leftrightarrow 2$) we can track the change in resonance positions of eight initial components in rather large range of angles (Figure 7).

As EPR spectra were measured at room temperature only, the sign of parameter of zero field splitting for centers V^{2+} , like for centers Gd^{3+} , was not determined. So, when determining SH parameters for V^{2+} two options were

considered: parameters of zero field splitting and hyperfine interaction of same and different signs. Values of resonance magnetic fields of hyperfine components, not overlapped by more intense signals of other centers, were taken from polar dependence shown in Figure 7. Only those electron transitions and angles were used where the resonance positions of the components arising from 8 initial ones (corresponding to the allowed electron-nuclear transitions) were measured at $\theta = 0^\circ, 90^\circ$. Signals of transitions $1 \leftrightarrow 3, 2 \leftrightarrow 3$ are very weak and were detected with confidence only using accumulation.

Calculation of signal positions during parameters fitting of two first members of spin Hamiltonian (1) with terms (SAI) and $g_N \beta_N (\mathbf{BI})$, but without weak nuclear quadrupole interaction [13], is performed by diagonalization of the complex energy matrix of 32-nd order $\{(2S + 1) \cdot (2I + 1)\}$. The following results were obtained:

$$g_{\parallel} = 1.9572, \quad g_{\perp} = 1.9552, \quad b_{20} = \pm 8622.7,$$

$$A_{\parallel} = \mp 275.4, \quad A_{\perp} = \mp 274.8, \quad F = 4 \quad (4)$$

(b_{20} , parameters of hyperfine interaction — A_{\parallel}, A_{\perp} and F — in MHz, number of used positions of signals 294). Note that said value F is implemented only at specified ratio of signs b_{20} and A , supposing their same signs the

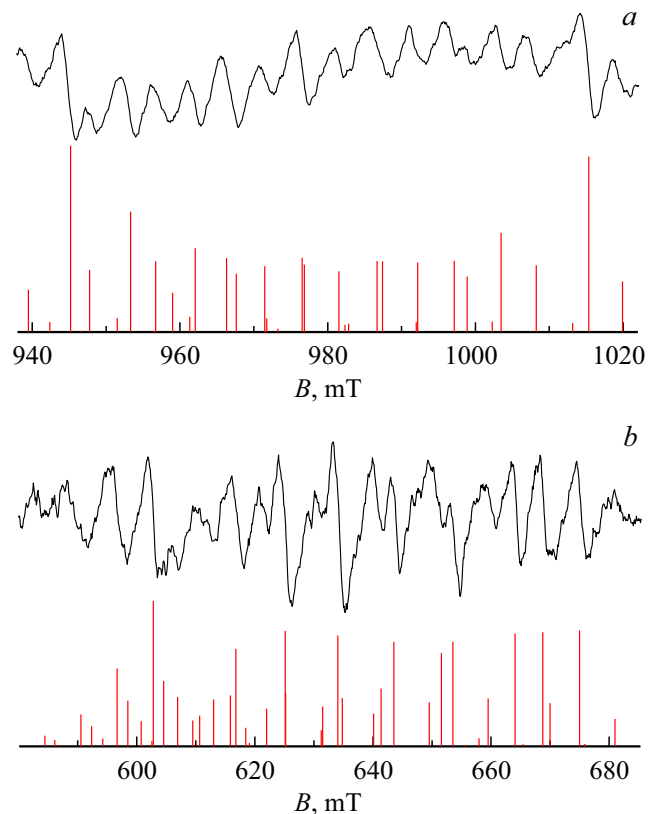


Figure 6. SHFS of centers V^{2+} at LiCAF: a) transition $1 \leftrightarrow 2$ at $\theta = 3^\circ$, b) transition $3 \leftrightarrow 4$ at $\theta = 86^\circ$. Vertical sections — calculated positions and intensities of components obtained with SH parameters (4).

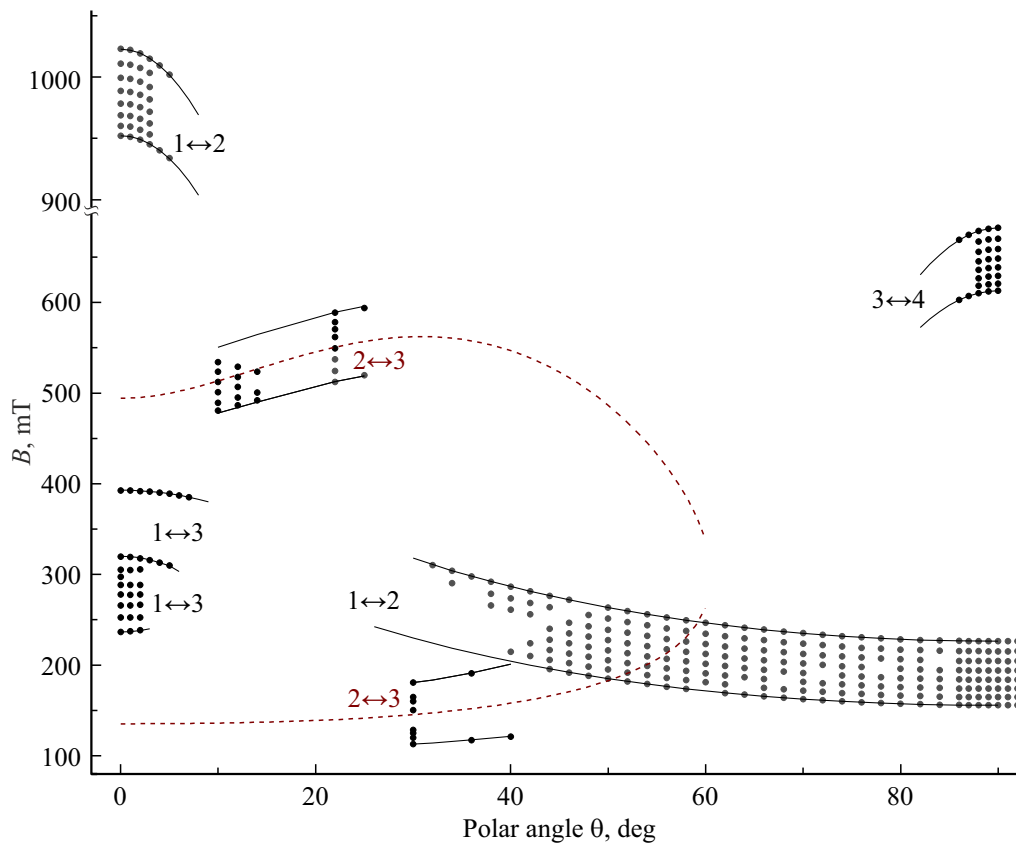


Figure 7. Orientation behavior of orientation positions of components of SHFS of centers V^{2+} : dots — experiment, curves — calculation with parameters (4). Solid curves — positions of extreme hyperfine components, dashed — behavior of transition $2 \leftrightarrow 3$ not considering hyperfine interaction. Electron levels are enumerated upward.

value F increases by more than two times. Qualitative description of SHFS V^{2+} by parameters (4), determined from resonance position of 8 allowed hyperfine components at different transitions, is demonstrated by calculated curves in Figure 7, and by calculated multicomponent SHFS in arbitrary orientations (Figure 6).

Same result (i.e. different signs of parameters) is obtained by authors [13] for centers V^{2+} in crystals CsMgX_3 ($X = \text{Cl}, \text{Br}, \text{I}$). Negative sign of parameter of hyperfine interaction V^{2+} in said compounds is predicted in [14], and in crystals MCl ($M = \text{Na}, \text{K}, \text{Rb}$), MO ($M = \text{Mg}, \text{Ca}$) and CsCdCl_3 in [15], [16] and [17], respectively. EPR spectra of centers V^{2+} were also studied in ZnO [18] and $\text{Y}_3\text{Al}_5\text{O}_{12}$ [19], but signs of parameters in them were not determined.

Figure 7 shows that orientation behavior of resonance positions of SHFS components of some electronic transitions of centers V^{2+} has features that are mainly determined by crossing in region of observed transitions of electronic levels with $|\Delta M| = 2$. Energy levels of ions V^{2+} at $\theta = 0$, calculated with parameters (4), explaining observed SHFS of transition $1 \leftrightarrow 3$ (Figure 7), are shown in Figure 8. Absence of average components in top in field eight of SHFS and of high field component in bottom (Figure 7) is due to their overlapping by intense signals of centers Mn^{2+} .

Figure 8 shows that in region of crossing the electronic states $1/2$ and $-3/2$ the hyperfine sub-levels of these states behave differently, namely: major of them pass the crossing region with repulsing (anticrossing), and some remain linear.

It is obvious that if we have possibility to study by experiments the frequency-field dependence of resonance positions of hyperfine components in the crossing region (Figure 8), then part of components will have linear dependence, and another one — non-linear dependence and with strong dependence of intensity. Such dependences were obtained in paper [20] for centers Mn^{2+} in $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ near crossing of levels $+1/2$ and $-3/2$, namely for transition $-1/2 \leftrightarrow 3/2$ in converging electronic levels (for transition $-1/2 \leftrightarrow +1/2$ — in diverging electronic levels) the linear frequency-field dependence was implemented for two lower (top) over magnetic field components of SHFS, see Figure 8.

Of course, the above-described method of determining the relative signs of parameters is for ions V^{2+} in LiCAF purely hypothetical, since no experimental study of the type of frequency-field dependence was carried out due to the impossibility of changing the resonance frequency in the range necessary to observe the effect.

Confirmation of relative signs of parameters b_{20} and A in (4) was obtained when describing complex multicom-

ponent SHFS of transitions of centers V^{2+} in orientations of magnetic field $\theta \neq 0^\circ, 90^\circ$. For example in Figure 9 shows SHFS of transition in levels 1–2 (Figure 7) at $\theta = 2^\circ$. We see that number of observed components in intervals between 8 intensive (initial) is different. Besides, shown in Figure 9 results of SHFS calculation with different signs of SH parameters clearly indicate that the experimental SHFS considering width of components is described by parameters of the zero field splitting b_{20} and hyperfine interaction A of different signs.

In spectrum of „third“ sample satellites practically disappear in vicinity of transition $2 \leftrightarrow 3$ of isolated Cr^{3+} , well observed in spectra of „first“ and „second“ samples (Figure 1). This fact is not surprising, as chromium concentration in this sample, according to the integral intensity Cr^{3+} , is lower than in „first“ sample, by about 45 times (see Sec. 2). Measurement and analysis of EPR-spectrum of „second“ sample $LiCaAlF_6 : Cr^{3+}$ showed that increase in chromium concentration by about two times (see Sec. 2) resulted in doubling of ratio of integral dependences of satellites and isolated centers of chromium. So, ratio of integral intensities of satellites and signals of individual chromium ions increases with concentration almost linearly, this is sign of dimeric nature of satellites.

In structure $LiCaAlF_6$ the closest positions Al^{3+} , which can replace pairs of chromium ions, have the following parameters:

$$R_1 = 0.5 \text{ nm}, \quad \theta_1 = 90^\circ, \quad C_1, \quad \alpha_1 \approx 400 \text{ MHz};$$

$$R_2 = 0.562 \text{ nm}, \quad \theta_2 = 30.9^\circ, \quad C_1, \quad \alpha_2 \approx 300 \text{ MHz};$$

$$R_3 = 0.964 \text{ nm}, \quad \theta_3 = 0^\circ, \quad \text{symmetry } C_3,$$

$$\alpha_3 = g^2 \beta^2 / r^3 \approx 60 \text{ MHz}.$$

Dimers of chromium ions with point symmetry group C_1 reproduce by operation C_3 of crystal to three, this is observed in Figure 3 in arbitrary orientation of magnetic field, signals of third pair during going from $\mathbf{B} \parallel C_3$ shall not be split.

In order to determine the parameters of the spin Hamiltonians of the observed pair complexes, the polar angular dependence was measured (see Figure 3). For calculations the spin Hamiltonian of pair of ions Cr^{3+} of the following view was used:

$$H = H_1 + H_2 + \alpha(\mathbf{S}_1 \cdot \mathbf{S}_2 - 3S_{1z}S_{2z}) + J(\mathbf{S}_1 \cdot \mathbf{S}_2),$$

where H_i — Hamiltonian of individual ion, α — parameter of dipole interaction, J — exchange integral. Making the complex matrix of 16-th order, its diagonalization, determination of positions and intensities of transitions of dimers $Cr^{3+}-Cr^{3+}$ showed that signals of the third pair are located mainly on wings of lines of isolated ions, greatly broadened by interaction with fluorine environment, and, more likely, and therefore are not detected.

Calculation results of transitions of first and second pairs of ions $Cr^{3+}-Cr^{3+}$ with parameters $\alpha_1 \approx 400, J_1 = -400$

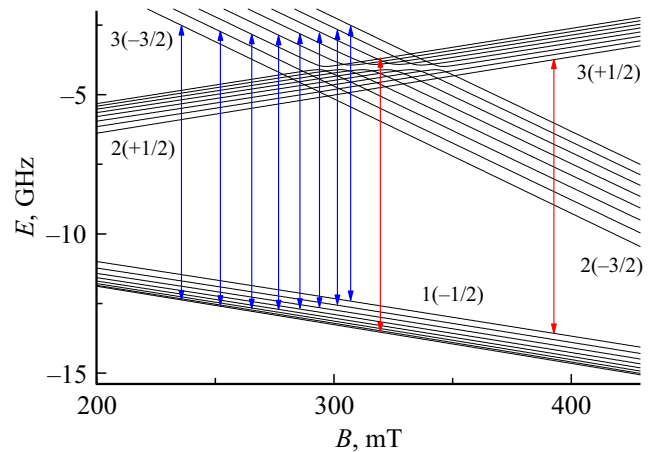


Figure 8. Calculated energy levels and components of SHFS of centers V^{2+} in LiCAF at $\theta = 0^\circ$. In range of fields 320–380 mT in „third“ sample the intensive signals of ions Mn^{2+} are observed (see Figure 4).

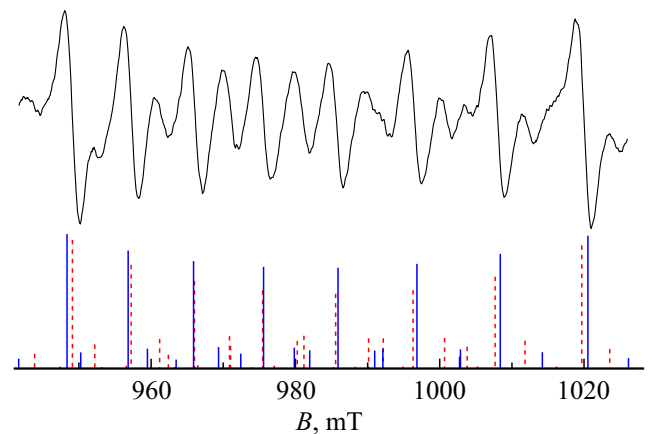


Figure 9. SHFS of transition between levels $1 \leftrightarrow 2$ at $\theta = 2^\circ$. Vertical sections — positions and intensities of components calculated with parameters $b_{20} > 0, A > 0$ (solid blue) and $b_{20} > 0, A < 0$ (dashed red).

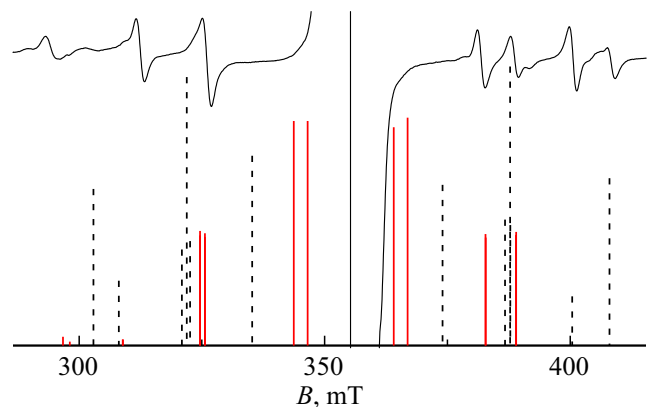


Figure 10. Experimental spectrum, as well as calculated positions and intensities of signals of second (black dashed segments) and first (red solid) pairs of ions $Cr^{3+}-Cr^{3+}$ in the vicinity of transition $2 \leftrightarrow 3$ of isolated ion at $\mathbf{B} \parallel C_3$.

and $a_2 \approx 300$, $J_2 = -200$ MHz respectively, are given in Figure 10 near transition $2 \leftrightarrow 3$. It is shown that calculated positions of transitions of pairs approximately enter the range of observed signals-satellites. This fact is important argument of these signals referring to the transitions of pair complexes of chromium. Unfortunately, we were unable to identify the detected signals with transitions of specific pair and, therefore, determine SH parameters. Only considering the concentration dependence of intensity of signals-satellites, we state that said resonances near transition $2 \leftrightarrow 3$ are determined by pair complexes Cr^{3+} .

Near transitions of isolated ions Cr^{3+} $1 \leftrightarrow 2$, $3 \leftrightarrow 4$ „third“ sample demonstrates signals similar to resonances of „first“ sample, due to this they can not be referred to the transitions of pair complexes Cr^{3+} . Most likely, these signals belong to transitions of isolated ions associated with crystal defects and having triclinic symmetry. Unfortunately, the impossibility of tracking the orientation behavior of these signals in sufficient range of angles does not allow us to determine their SH parameters.

4. Conclusion

EPR-spectrum of three samples LiCaAlF_6 containing different concentration of chromium ions is studied. In samples with mean and large concentration of chromium additionally to spectrum of isolated ions Cr^{3+} , which fine structure parameters were determined by us, weak signals-satellites were observed. As a result of spectrum calculation of pairs of ions linked by magnetic dipole interaction, and analysis of concentration dependence of intensity the specified satellites are referred to pair complexes Cr^{3+} .

In low doped with chromium sample LiCaAlF_6 , besides the intense signals Cr^{3+} and Mn^{2+} , weak spectra of trigonal centers Gd^{3+} and V^{2+} are detected, for them parameters of spin Hamiltonians are determined. The comparable widths of fine, hyperfine and superhyperfine structures of ions Mn^{2+} resulted in spectrum very complex for analysis. Considerations on localization of observed paramagnetic centers are provided.

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Conflict of interest

The authors declare that they have no conflict of interest.

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