

EPR OF LITHIUM-SODIUM TETRAGERMANATE SINGLE CRYSTAL DOPED WITH COPPER IONS

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For the first time electron paramagnetic resonance (EPR) spectra are studied in lithium-sodium tetragermanate ($\text{LiNaGe}_4\text{O}_9$) single crystal doped with copper impurity. The hyperfine quadruplets of two-valent Cu^{2+} ions ($3d^9$, $S = 1/2$, $I = 3/2$) are detected. The angular variations of the EPR spectra are studied in crystal planes at 295 K. The components of g -factor and hyperfine interaction tensor A are calculated. The EPR spectra anisotropy testifies the triclinic symmetry of the Cu^{2+} ions position in the lattice. The symmetry of the impurity site as well as the ratio of the ionic charges and radii give evidence that Cu^{2+} centers are substituted for Li^+ ions in the $\text{LiNaGe}_4\text{O}_9$ crystal lattice. The charge imbalance of the dopant is presumably compensated by non-stoichiometric lithium ions vacancies.

Keywords: lithium-sodium tetragermanate crystal, Cu^{2+} doping ion, electron paramagnetic resonance.

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1. Introduction

The crystal of lithium-sodium tetragermanate ($\text{LiNaGe}_4\text{O}_9$) represents the family of lithium-germanium oxides ($\text{Li}_2\text{O-GeO}_2$) [1] with high ion mobility [2]. At room temperature, the crystal structure of $\text{LiNaGe}_4\text{O}_9$ is orthorhombic with space symmetry group D_{2h}^8 [3, 4]. Its basic structural unit incorporates GeO_6 octahedron linked via common vertices with two GeO_4 tetrahedra and includes also one Li^+ and one Na^+ ion. The alkali metals ions occupy the sites within structural cavities and are weakly bound to Ge-O framework.

Aliovalent doping is an efficient tool to control ionic conductivity in crystalline solids. The doping effect on ionic conductivity in the crystalline and glassy lithium-germanium oxides ($\text{Li}_2\text{O-GeO}_2$) is explored in [5-7]. The dopants' influence is demonstrated to depend on the compensation mechanism of the charge imbalance introduced by the impurity. Negative charge imbalance is compensated by non-stoichiometric interstitial lithium ions (A_{Li}). Then doping increases conductivity. Conversely, if the impurity introduces excess positive charge, its compensation is provided by lithium vacancies (V_{Li}) which lower ionic transport.

Thus, knowing the position of the impurity ion in the lattice and understanding the charge compensation mechanism become of key importance. For magnetically active impurities, such information can be obtained using radiospectroscopic methods. In the previous works [8, 9] we studied EPR and optical spectra in $\text{LiNaGe}_4\text{O}_9\text{:Mn}^{4+}$ crystal and proposed the model for impurity in the lattice. In this paper we report the data on EPR spectra studies in $\text{LiNaGe}_4\text{O}_9\text{:Cu}$ and discuss the dopant localization in the lattice and the mechanism of charge compensation. To our knowledge, such results are published for the first time.

2. Crystal growth and experimental technique

The $\text{LiNaGe}_4\text{O}_9\text{:Cu}$ single crystals were grown by the Czochralski method. The dopant CuO (0.07 wt %) was added to the starting chemicals (Li_2CO_3 , Na_2CO_3 , GeO_2), the resulting mixture was milled and subjected to solid-state synthesis. The composition of the synthesized batch was controlled by XRD phase analysis. Doping with Cu resulted in slightly green coloration of the crystals grown as compared to the colorless undoped crystals.

The samples were cut off as parallelepipeds with the edges about 3 mm long oriented along the crystal axes. The spectra were recorded at room temperature in X frequency band ($f = 8592$ MHz) using the conventional EPR spectrometer.

3. Experimental results

The EPR spectrum of Cu^{2+} ions in the ground state $^2D_{5/2}$ (electron and nuclear spins $S = 1/2$ and $I = 3/2$) was detected in $\text{LiNaGe}_4\text{O}_9$ crystal. Fig. 1 shows the typical hyperfine (HF) quartet, recorded at the orientation of static magnetic field $\mathbf{B} \parallel c$ at room temperature ($T = 295$ K). Presence of the copper isotopes ^{63}Cu ($I=3/2$) and ^{65}Cu ($I=3/2$) [10] causes doubling of each component of the hyperfine (HF) quartet.

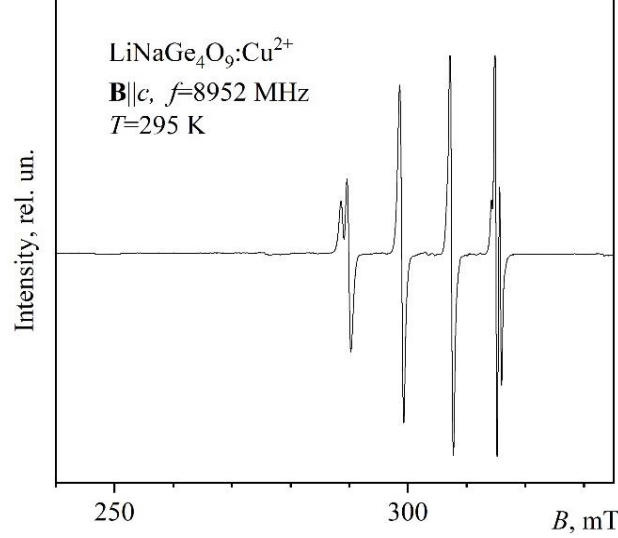


Fig. 1. The EPR spectrum of $\text{LiNaGe}_4\text{O}_9:\text{Cu}^{2+}$ single crystal at $\mathbf{B} \parallel c$, $T = 295$ K.

The orientational dependences of the Cu^{2+} EPR spectra were measured by rotating the static field \mathbf{B} in crystallographic planes. Angular variations of the EPR line positions were described using the spin Hamiltonian (SH), including electron Zeeman and electron-nuclear HF interactions [10]:

$$\mathcal{H} = \beta \mathbf{B} \mathbf{g} \mathbf{S} + \mathbf{S} \mathbf{A} \mathbf{I} \quad (1)$$

where β is Bohr magneton, \mathbf{g} and \mathbf{A} represent the tensors of spectroscopic splitting and HF interaction, correspondingly, \mathbf{S} and \mathbf{I} represent operators of electron and nuclear spins.

Fig. 2 shows the angular dependences of the squared effective factor (g_{eff}) and HF splitting ($A/g\beta$) for field \mathbf{B} rotated in crystallographic planes. Two conjugate Cu^{2+} spectra are observed for each plane. These spectra correspond to the centers occupying structurally equivalent positions, which transform into each other by the point symmetry operations. Correspondingly, these spectra exhibit the same angular variations connected by the point symmetry elements (Fig.2). At arbitrary \mathbf{B} orientations with respect to the crystallographic axes (abc), four ($k_m = 4$) conjugate Cu^{2+} spectra can be observed.

The data in Fig. 2 show that the EPR lines positions and the HF splitting reach extreme values at the same angles. Therefore, within an experimental error, the principal axes of \mathbf{g} -factor and \mathbf{A} tensor coincide. The symmetry of \mathbf{g} -factor and \mathbf{A} tensor is close to axial ($g_z > g_x \approx g_y$, $A_z > A_x \approx A_y$). Thus, the orientation of magnetic axis \mathbf{Z} is determined with higher accuracy, whereas the directions of axes \mathbf{X} , \mathbf{Y} are close to degeneracy and are determined more roughly.

The principal values of \mathbf{g} -factor and HF tensor \mathbf{A} (in 10^{-4} cm^{-1}), as well as the direction cosines of the magnetic axes (\mathbf{XYZ}) with respect to the crystal axes (abc) are given below:

$$\begin{aligned} g_X &= 2.058(1); & A_X &= 30(1); \\ g_Y &= 2.072(1); & A_Y &= 50(1); \\ g_Z &= 2.305(1); & A_Z &= 162(1). \end{aligned}$$

	<i>a</i>	<i>b</i>	<i>c</i>
X	-0.86203	0.100591	0.458668
Y	0.215702	-0.814121	0.571917
Z	0.444705	0.573495	0.680099

(2)

The experimental dependences of the effective g -factor and HF splitting ($A/g\beta$) are described by SH (1) with the parameters (2) with good accuracy (Fig. 2a, b).

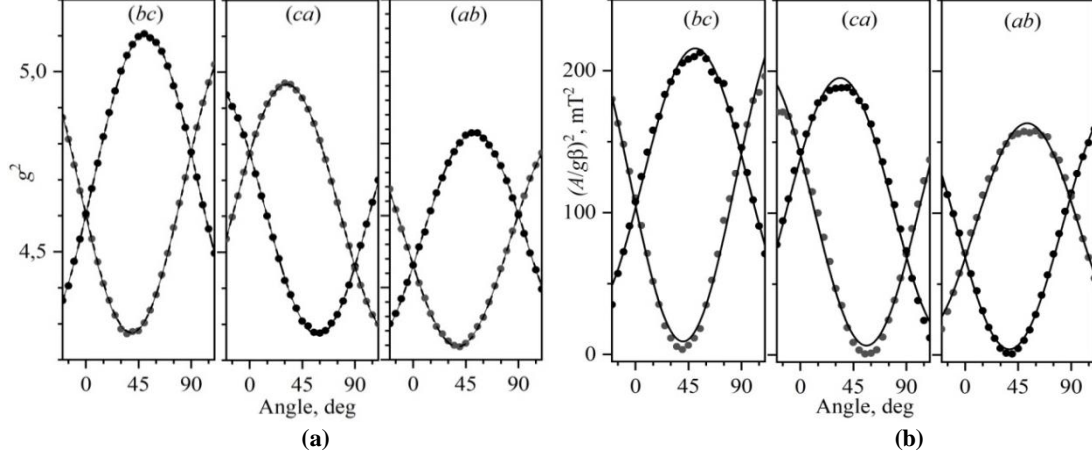


Fig. 2 Angular dependences of the squared g -factor (a) and HF splitting ($A/g\beta$) (b) in crystallographic planes of $\text{LiNaGe}_4\text{O}_9:\text{Cu}^{2+}$ ($T = 295 \text{ K}$). Circles show experimental data for more intense spectrum of ^{63}Cu isotope; solid lines are calculated with the help of (1,2).

4. Discussion

Ratio of the ionic charges and radiuses of the impurity and the cations in the $\text{LiNaGe}_4\text{O}_9$ formula unit testifies that most likely Cu^{2+} centers are substituted for alkali metal ions Li^+ or Na^+ ($r_{\text{Cu}^{2+}} = 0.73 \text{ \AA}$, $r_{\text{Ge}^{4+}} = 0.53 \text{ \AA}$, $r_{\text{Li}^+} = 0.76 \text{ \AA}$, $r_{\text{Na}^+} = 1.02 \text{ \AA}$, all values are given for coordination number $\text{CN} = 6$) [11].

The experimental data (Figs. 1, 2) show that Cu^{2+} centers in the lattice (space group D_{2h}^8) occupy the sites with magnetic multiplicity $k_m = 4$ and triclinic positional symmetry (C_i or C_1 group). Alkali metals ions are coordinated with six oxygen ions, and the surrounding complexes can be considered as distorted octahedra. Li^+ ions occupy the sites of general type ($8(f)$, C_1 group), whereas Na^+ ions occupy the positions of monoclinic symmetry ($4(e)$ type, C_2 group) [3, 4]. Since EPR spectra are centrosymmetric, the magnetic multiplicity of Li^+ sites is $k_m = 4$, while for Na^+ sites the multiplicity is degenerated to $k_m = 2$.

Thus, the anisotropy of Cu^{2+} EPR spectra corresponds to the local symmetry of the Li^+ sites (C_1 group). This suggests that the paramagnetic centers are substituted for lithium ions: $\text{Cu}^{2+} \rightarrow \text{Li}^+$. Lithium-ion vacancies (V_{Li}) can be supposed as a charge-compensating defects. Since the anisotropy of the EPR spectrum reflects the symmetry of the regular lattice site, the charge-compensating vacancy V_{Li} is located at a significant distance from impurity ion $\text{Cu}^{2+}_{\text{Li}^{+}}$. As it was demonstrated in [5-7], this supposition can be confirmed by measuring electrical conductivity in $\text{LiNaGe}_4\text{O}_9:\text{Cu}^{2+}$ crystal. As anticipated, appearance of excess charge-compensating V_{Li} should decrease the concentration of lithium-ion interstitials (A_{Li}) and suppress ionic transport.

5. Conclusions

The EPR spectra of Cu^{2+} ions are detected in the lithium-sodium tetragermanate ($\text{LiNaGe}_4\text{O}_9$) single crystal. The components of g -factor and hyperfine interaction tensor \mathbf{A} are calculated based on the orientational dependences of the EPR spectra. The anisotropy of the EPR spectra evidence that Cu^{2+} ions occupy the sites of triclinic symmetry (C_i or C_1 point symmetry group). Comparing the ionic charges and radiuses, as well as the symmetry of the impurity position, testifies that doping Cu^{2+} ions are substituted for Li^+ hosts (C_1 positional symmetry group) in the regular lattice sites. It is assumed that the charge imbalance is compensated by the appearance of non-stoichiometric lithium vacancies (V_{Li}).

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