
**ELECTRICAL AND MAGNETIC
PROPERTIES**

Distribution of Cobalt Co^{2+} Ions in Single Crystals of Spinel $\text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4$

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Abstract—The distribution of Co^{2+} ions over sublattices and structurally nonequivalent positions in the unit cell of the crystal lattice of a single crystal of lithium gallium spinel $\text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4$ is shown. This distribution determines the properties of both mono- and nanocrystalline substances. The distribution is obtained by a special technology and is manifested in the electron paramagnetic resonance (EPR) spectra. The distribution of Co^{2+} ions depends on the structural and magnetic nonequivalence. The structural and magnetic nonequivalence causes a multimimum behavior of the crystal field potential in the unit cells of single crystals at the locations of Co^{2+} ions. The Co^{2+} ions are found in complexes with tetrahedral and octahedral oxygen ions. Three types of EPR spectra of Co^{2+} ions have been found and investigated. The $\text{Co}_{\text{tet}}^{2+}$ spectrum is attributed to the Co^{2+} ion, which replaces the Ga^{3+} ion located in a tetrahedral oxygen environment. The spectrum of the $\text{Co}_{\text{oct}}^{2+}$ ion located in the crystal field with axial symmetry belongs to the Co^{2+} ion replacing the Li^+ ion located in an octahedral oxygen environment. The spectrum of the $\text{Co}_{\text{oct}}^{2+}$ ion located in a low symmetry crystal field belongs to the Co^{2+} ion replacing the Ga^{3+} ion located in an octahedral oxygen environment. The nearest cationic environment of the ion creates rhombic distortions due to the different valence numbers of Li^+ and Ga^{3+} . The results of studying the angular dependences of the spectra show the presence of four and twelve magnetically nonequivalent positions in the unit cells.

Keywords: electron paramagnetic resonance, spinel single crystal, unit cell, crystal lattice, structurally nonequivalent positions of ions

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INTRODUCTION

Spinel is currently being actively studied due to their wide scientific and technological applications [1–4]. As a rule, spinels with certain impurities are used in materials science. Such impurities are located in octahedral and tetrahedral complexes of unit cells of spinel crystal lattices. In the complexes, magnetic Co^{2+} ions are in an oxygen environment. The distribution of cobalt Co^{2+} ions depends on the structural and magnetic nonequivalence of the ions and on the multimimum potential of the crystal field in the unit cells of single crystals. The properties of materials used in devices and medicaments depend on the distribution of ions. However, the technology for analyzing a separate complex in a material has not yet been developed. Therefore, it is relevant to study the magnetic ion in the unit cell of a single crystal, which is possible when using the method of electron paramagnetic resonance (EPR) in a single crystal for studying the angu-

lar and temperature dependences of the EPR spectra of magnetic ions. In [5–13], $\text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4$ nanocrystals doped with cobalt were studied in detail.

Currently, there is an increased interest in compounds with a spinel structure due to the possibility of synthesis of nanocrystalline samples [7]. However, difficulties arise when studying nanocrystalline samples, which do not exist in single crystals. The most characteristic property of a single crystal is anisotropy i.e., the dependence of most physical properties on spatial direction. There is no such dependence in nanocrystalline materials, since the anisotropy of properties in a real compound is averaged. Interpretation of the properties of nanocrystalline and single crystal materials with the same composition is an urgent problem [8–17]. However, the above studies did not take into account the properties of an individual complex with a magnetic $3d^n$ ion in the used composite materials (single crystals, nanocrystals, poly-

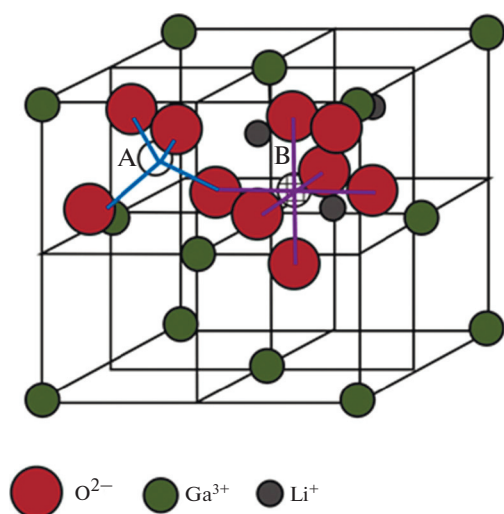


Fig. 1. Unit cell of a single crystal of lithium–gallium spinel $\text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4$. The closest environment of cobalt Co^{2+} ions (positions A and B) are oxygen tetrahedrons and octahedrons.

mers, etc.). In the nanocomplex, the metal ion under study is in a ligand environment. Such a nanocomplex is part of the unit cell of the material. In each nanocomplex, the environment of the ion has the same crystallographic symmetry as in a single crystal. As a rule, the magnetic axes of $3d^n$ ions are located along the crystallographic axes of the complex. Studies [8–17] do not take into account the existence of structural nonequivalence of the magnetic ions incorporated into the unit cell of the crystal lattice. Therefore, it is difficult to get objective information about the compounds under study. There are still a number of problems in obtaining reliable characteristics, namely, in determining the location of the ion, its immediate environment, the parameters of the electric field at the location of the ion, etc. The structure of the complex with a metal ion in composite materials [8–18] was analyzed without studying the electric crystal field parameters at the location of the metal ion, which is possible to perform with use of the EPR method.

To study complexes in a $\text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4$ single crystal with a cobalt ion, we used the EPR method, which is among the most informative methods for studying the electronic structure of compounds with point impurities [19]. In this study, experiments were carried out to record and study the EPR spectra of Co^{2+} ions in single crystals of lithium–gallium spinel $\text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4$ in the temperature range from liquid helium to room temperatures.

The unit cell of a single crystal of lithium–gallium spinel $\text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4$ is shown in Fig. 1. The unit cell contains oxygen octahedrons and tetrahedrons, inside of which there are magnetic probes, i.e., cobalt Co^{2+}

ions that occupy the A (tetrahedral) and B (octahedral) positions.

EXPERIMENTAL

The experimental procedure and measurement techniques are determined by a physical problem, for the successful solution of which it is necessary to fulfill a number of requirements for the experimental setup. The above facts provided the basis for choosing the radio spectrometer operating frequency equal to $\nu = 37.5$ GHz ($\lambda = 8$ mm). To satisfy the conditions for $g = 2$, magnetic fields must be stronger than 13.5 kG.

To accomplish the imposed objective, a superheterodyne spectrometer with a reflection resonator was chosen, which can achieve extremely high sensitivity and is well suited for operation at low temperatures. A low temperature rectangular resonator of the reflective type is one of the main components of the radio spectrometer. The resonator frequency is adjusted over the klystron range using a noncontact plunger. To align the magnetic axes, the resonator is equipped with a device for rotating the samples with an extended limb for measuring angles. The crystal is glued onto a turntable mounted on the narrow side wall of the resonator at the antinode of microwave magnetic field H_1 aligned in a vertical direction. Since the constant field has a horizontal direction when the magnet rotates, condition $H_1 \perp H_0$ is always satisfied.

To solve the posed physical problem, it was necessary to vary the operating temperature of the crystal under study within wide ranges. Therefore, the resonator was placed in a four-wall Dewar flask with helium, which ends with a three-wall appendix in the form of a finger placed between the tips of the magnet. Liquid helium has a dielectric constant of $\epsilon \approx 1$ and, consequently, does not substantially change the frequency when it gets into the resonator. However, liquid helium boils in the resonator because of the heat supply, which leads to substantial interference when measuring EPR spectra. Therefore, the resonator was isolated from the helium bath with a thin-walled stainless steel vessel. A heating furnace made of constantan wire with $R = 200 \Omega$, which was wound around the body of the resonator, was used to change the temperature from 4.2 K to liquid nitrogen temperature $T = 77$ K. The furnace was powered from a DC source. To reduce heat removal from the resonator, a stainless steel waveguide bridge was used, and the resonator was evacuated. Similarly, the temperature was increased from $T = 77$ K to room temperature when liquid nitrogen was poured into the Dewar flask. Temperature sensors in the temperature ranges of 4.2–77 K and 55–300 K were carbon and copper resistors placed on the outer wall of the resonator in close proximity to the sample. The temperature sensors were calibrated by the method described in [20].

RESULTS

The electron configuration of divalent cobalt is $3d^7$, $L = 3$, and $S = 3/2$. According to Hund rule, the ${}^4F_{9/2}$ term is the main term of Co²⁺ in a free state. Consequently, the ${}^4F_{9/2}$ ground spectroscopic state is sevenfold degenerate in the orbital quantum number ($2L + 1$) and fourfold degenerate in the spin ($2S + 1$). In a purely cubic crystal field of octahedral symmetry, the degeneracy is partially removed; the lower level is an orbital triplet, each level of which is fourfold degenerate in spin. When exposed to crystal fields with symmetry features below the cubic symmetry and with spin-orbit coupling, the Γ_4 triplet splits into six Kramers doublets, the distance between which is about a few hundreds of inverse centimeters. Therefore, the EPR spectrum of Co²⁺ in an octahedral environment can only be observed at low temperatures on the lower doublet with effective spin $S' = 1/2$ (true spin $S = 3/2$) because of the strong spin-orbit coupling. The EPR spectrum has strong anisotropy and a substantial deviation of the g -factor from the g -factor for a pure spin state.

Single crystals with the structure of spinel Li_{0.5}Ga_{2.5}O₄ were grown by spontaneous crystallization from a solution of metal oxides in molten salts. The technology for producing single crystals of Li_{0.5}Ga_{2.5}O₄ is similar to the technology used for growing the corresponding ferrites [21]. During crystallization, the following temperature regime was maintained: heating to 1150°C and exposure to this temperature for 10 h; cooling from 1150 to 1000°C with a programmed rate of 6 °C/h; exposure to 1000°C for 30 h; cooling to 600°C with a programmed rate of 2°C/h and then from 600 to 400°C with a rate of 6°C/h; the oven was turned off at 400°C. This temperature regime ensures the growth of crystals in an ordered state. The grown single crystals of lithium-gallium spinel had the shape of octahedrons with a face size of up to 4 mm. The content of introduced paramagnetic ions was varied within the range of 0.01–0.5 wt %. The distribution of Co²⁺ occurs during the growth of a single crystal and is ensured by setting the adjusted growth parameters of the single crystal.

The EPR spectrum of Co²⁺ ions was studied at a frequency of 37 GHz in the temperature range of 4.2–77 K. A study of the EPR spectrum of Co²⁺ in Li_{0.5}Ga_{2.5}O₄ at $T = 4.2$ K in the {110} and {111} planes showed the presence of three types of EPR spectra, which correspond to crystal fields with axial and rhombic symmetry and the Co²⁺_{tetra} spectrum in the field with axial symmetry.

The EPR spectrum of Co²⁺_{rhomb} was measured at $T = 4.2$ K. No signals were observed at $T = 77$ K. The EPR spectrum consists of resolved hyperfine structure (HFS) along the z and x axes and is unresolved for $H_0 \parallel y$. A study of the angular dependence of the spec-

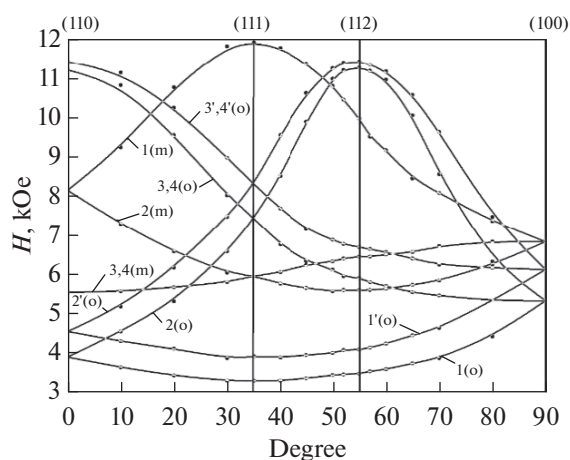


Fig. 2. Angular dependence of the positions of the EPR spectrum lines for Co²⁺ ions with axial symmetry in the {110} plane at $T = 4.2$ K [22]. Letters o and t next to the number at the line indicate the octahedral and tetrahedral positions of Co²⁺, respectively.

trum showed the presence of twelve magnetically nonequivalent Co²⁺_{rhomb} positions in the unit cell. Such low symmetry of the crystal field leads to the existence of three values of g -factors in three main orientations, as well as three values of the A_{ij} constants in the hyperfine interaction tensor. Each position of Co²⁺ is described by a spin Hamiltonian

$$H = g_x \beta H S_x + g_y \beta H S_y + g_z \beta H S_z + A S_z I_z + B S_x I_x + C S_y I_y \quad (1)$$

with effective spin $S' = 1/2$ and nuclear spin $I = 7/2$.

The z axis of the crystal field is tilted at an angle of 14° from the $\langle 111 \rangle$ axis, and the x axis is coaligned with the $\langle 110 \rangle$ direction. Experimental values of the spin Hamiltonian constants in three main orientations are as follows:

$$g_z = 6.927 \pm 0.005, A = (229.6 \pm 3) \times 10^{-4} \text{ cm}^{-1}, \\ g_x = 1.972 \pm 0.002, B = (30.4 \pm 1) \times 10^{-4} \text{ cm}^{-1}, \\ g_y = 2.855 \pm 0.005, C = 0. \quad (2)$$

The EPR line splits into 8 HFS components.

Measurements of the axial spectrum of Co²⁺_{oct} in the oxygen octahedron were carried out at $T = 4.2$ K. The EPR spectrum is not observed at 77 K. An analysis of the angular dependence of the spectrum (Fig. 2) reveals the presence of four magnetically nonequivalent positions of Co²⁺_{oct} ions in the unit cell. The EPR spectrum in parallel orientation consists of a well resolved hyperfine structure composed of eight lines due to nuclear spin $I = 7/2$. In perpendicular orientation, the HFS is not resolved. The spectrum is resolved when the magnetic field deviates from the perpendicular orientation in the {110} plane by an

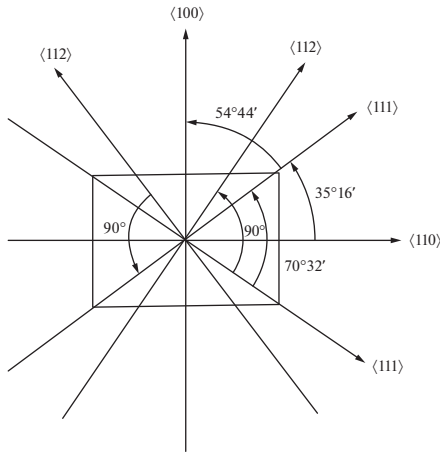


Fig. 3. Plane $\{110\}$ of a regular octahedron.

angle of 6° . The parallel orientation of the crystal field coincides with the $\langle 111 \rangle$ axis. To check the axial symmetry of the spectrum, its angular dependence was measured in the $\{111\}$ plane corresponding to the face of the octahedron. Figure 2 shows the angular dependence of the EPR spectrum for Co^{2+} ions located in an electric crystalline field with axial symmetry in the $\{110\}$ plane at a temperature $T = 4.2$ K. The lines indicated by numbers without a prime symbol correspond to the first line of the HFS, and those indicated with a prime symbol correspond to the eighth HFS line. Curves 1 and 2 show the angular dependences of EPR signals for ions with parallel orientations coaligned with the $\langle 111 \rangle$ directions of the $\{110\}$ plane under study (Fig. 3). Curves 3 and 4, and 3' and 4' show the EPR spectra from two magnetically nonequivalent ions with parallel orientations that are in a plane perpendicular to the $\{110\}$ plane under study.

The spectrum of each Co^{2+} ion is described by spin Hamiltonian

$$H = g_{\parallel} \beta H_z S_z + g \beta (H_x S_x + H_y S_y) + A S_z I_z + B (S_x I_x + S_y I_y) \quad (3)$$

with effective spin $S = 1/2$ and nuclear spin $I = 7/2$.

The following experimental values of the spin Hamiltonian constants were obtained:

$$g_{\parallel} = 7.295 \pm 0.005, \quad A = (283 \pm 2) \times 10^{-4} \text{ cm}^{-1}; \quad (4)$$

$$g_{\perp} = 2.311 \pm 0.002, \quad B = 0.$$

A study of the angular dependences of positions of the EPR spectrum lines at 4.2 K in the $\{110\}$ and $\{111\}$ planes showed the presence of $\text{Co}_{\text{tetra}}^{2+}$ ions in the field with axial symmetry.

Tetrahedral Co^{2+}

The main spectroscopic state of Co^{2+} corresponds to the ${}^4F_{9/2}$ term. The lowest energy level in a cubic

field of tetrahedral symmetry is an orbital singlet, which is separated from the nearest orbital triplet at a distance of about 10^4 cm^{-1} and is fourfold degenerate in spin. The lower orbital singlet splits into two spin doublets, the lower of which corresponds to the level with $S_z = 1/2$. The spectrum is clearly resolved at both helium and nitrogen temperatures, and the intensity of the spectrum at helium temperatures is much higher.

The EPR spectrum recorded at $T = 4.2$ K was studied in the $\{110\}$ plane (Fig. 3). The parallel orientation coincides with the $\langle 111 \rangle$ direction; the hyperfine EPR structure in this orientation is well resolved. The HFS consisting of eight components according to $I = 7/2$ disappears with deviation from the parallel orientation by an angle of 4° . The HFS at $T = 77$ K is not resolved. A study of the angular dependence of the position of the EPR spectrum lines showed the presence of four magnetically nonequivalent positions of ions in the unit cell. The spectrum of each ion is described by the Hamiltonian with axial symmetry. The effective spin equals $S = 1/2$, since we observed the transition only at the lower level with $S_z = \pm 1/2$. Hamiltonian constants at $T = 4.2$ K are as follows:

$$g_{\parallel} = 2.203 \pm 0.002, \quad A = (30 \pm 1) \times 10^{-4} \text{ cm}^{-1}, \quad (5)$$

$$g_{\perp} = 4.621 \pm 0.005, \quad B = 0.$$

DISCUSSION

Next, we discuss experimental results of studying the EPR spectra of Co^{2+} ions in a single crystal of $\text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4$. Two octahedral Co^{2+} sites were discovered and studied, which correspond to spectra with axial and orthorhombic symmetry. The intensity ratio of signals of octahedral Co^{2+} ions is $\text{Co}_{\text{ax}}^{2+} : \text{Co}_{\text{rhomb}}^{2+} = 2 : 1$ at $T = 4.2$ K. The different intensities of the spectra made it possible to clearly separate them.

The third type of spectra is attributed to the Co^{2+} ion located in a tetrahedral environment. This assumption is based on the following facts.

(1) The EPR spectrum of $\text{Co}_{\text{tetra}}^{2+}$ ions was observed not only at liquid helium temperatures, but also at $T = 77$ K, which is ruled out for $\text{Co}_{\text{oct}}^{2+}$ ions.

(2) The angular dependence of the EPR spectrum (Fig. 2) shows that the spectrum of $\text{Co}_{\text{tetra}}^{2+}$ ions is as if being the inverse version of the spectrum of $\text{Co}_{\text{oct}}^{2+}$ ions, which agrees with the signs of the potential functions for the considered cases.

(3) The HFS constant for the $\text{Co}_{\text{tetra}}^{2+}$ spectrum is several times smaller than that for the $\text{Co}_{\text{oct}}^{2+}$ spectrum, since the orbital momentum for the ground state in the field with octahedral symmetry is not frozen and makes a first-order contribution to the A value.

The three types of the observed and studied EPR spectra allowed us to draw the following conclusions.

(1) With introduction of a cobalt impurity into the matrix of an ordered lithium–gallium spinel, the former replaces Ga^{3+} ions in both the *A* and *B* positions, as well as Li^+ ions located in the *B* position.

(2) The $\text{Co}_{\text{tetra}}^{2+}$ spectrum is attributed to the Co^{2+} ion replacing the Ga^{3+} ion located in a tetrahedral oxygen environment (position *A*).

(3) The spectrum of the paramagnetic center located in the crystal field with axial symmetry belongs to the Co^{2+} ion replacing the Li^+ ion in the octahedral oxygen environment (position *B*). The nearest cationic environment of the ion under study creates only axial distortions along the $\langle 111 \rangle$ axes.

(4) The spectrum of octahedral Co^{2+} ions located in a low symmetry crystal field belongs to the Co^{2+} ion replacing the Ga^{3+} ion in the *B* position. The nearest cationic environment of the ion creates orthorhombic distortions due to the different valence numbers of Li^+ and Ga^{3+} .

(5) The intensity ratio equal to $\text{Co}_{\text{ax}}^{2+} : \text{Co}_{\text{rhomb}}^{2+} = 2 : 1$ for octahedral Co^{2+} ions suggests that Co^{2+} ions in the oxygen octahedral environment of lithium–gallium spinel more preferably replace Li^+ ions rather than Ga^{3+} ions. This preference can be explained by the fact that the characteristic anion–cation distances for Li^+ , Ga^{3+} , and Co^{2+} ions with coordination number 6 are 2.135, 1.993, and 2.126, respectively. That is, it is more energetically preferable for Co^{2+} ions to replace Li^+ ions rather than Ga^{3+} ions.

(6) The results of comparing the spin Hamiltonian constants for octahedral Co^{2+} suggests that the degree of covalence is higher in the case of substitution of octahedral Ga^{3+} ions with Co^{2+} ions, since the orbital contributions to the *g*-factor and to HFS constant *A* in this case are smaller than in the case of substitution of octahedral Li^+ ions. This fact is also confirmed by the corresponding characteristic anion–cation distances.

A schematic explanation of the distribution of Co^{2+} in $\text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4$ single crystals is given in Fig. 4. The dependence of crystal field potential *E* on distance *R* in relative units is shown. Distance *R* is given in relative units, since the concentration of Co^{2+} ions is low and the distances between the ions in the unit cells are different.

The study of the angular dependences of the EPR spectra made it possible to determine the shape of the crystal field potential at the location of the Co^{2+} ions.

The shape of the multimimum potential along crystallographic directions of the $[111]$ type has equivalent minima separated by potential barriers. The arrows in Fig. 4 indicate the $\langle 111 \rangle$ directions. These

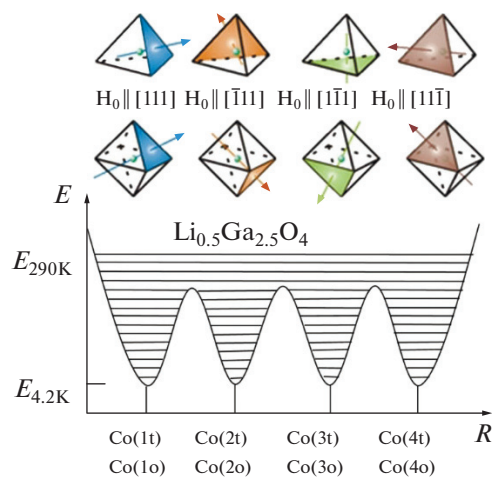


Fig. 4. Dependence of crystal field potential *E* on distance *R*. The minima are located along axes of the $[111]$ type. Tetrahedral (t) and octahedral (o) sites with Co^{2+} ions in the unit cell are shown.

directions are perpendicular to the (111) planes of octahedrons and tetrahedrons. Four minima are given. Magnetic field H_0 is parallel to main magnetic axis *z* of the Co^{2+} ion, the direction of which is shown by the arrow. The unit cell contains magnetically nonequivalent positions of Co^{2+} ions located in tetrahedral and octahedral oxygen environments. Such complexes are shown as octahedrons and tetrahedrons. The positions of Co^{2+} ions are indicated by letters o and t. The $\text{Co}(1t)$, $\text{Co}(2t)$, $\text{Co}(3t)$, and $\text{Co}(4t)$ tetrahedral sites and the $\text{Co}(1o)$, $\text{Co}(2o)$, $\text{Co}(3o)$, and $\text{Co}(4o)$ octahedral sites of nonequivalent positions of cobalt ions are shown.

CONCLUSIONS

In the unit cell of a single crystal of $\text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4$, doped cobalt Co^{2+} ions unleash different preferential distribution possibilities in four tetrahedral sites when replacing Ga^{3+} ions, four axial octahedral sites when replacing Li^+ ions, and twelve low symmetry octahedral sites when replacing Ga^{3+} ions. These distributions of cobalt ions determine both monocrystalline and nanocrystalline properties of substances. Hence, it is possible to obtain at least twenty types of materials from lithium–gallium spinel $\text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4$ doped with Co^{2+} ions with desired properties. Such a result can be achieved using a certain manufacturing technology for both single crystal and nanocrystalline materials. In the case of a mixed distribution of Co^{2+} ions, it is possible to obtain a much larger number of new types of materials.

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CONFLICT OF INTEREST

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

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