Self-organization in the unit cell of a single crystal spinel \( \text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4 \) and self-distribution of magnetic ions of chromium \( \text{Cr}^{3+} \)

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Abstract. Self-organization of twelve structurally and magnetically non-equivalent sites and self-distribution of magnetic ions of chromium over these sites at the minima of the crystal field potential in a unit cell of single crystal lithium-gallium spinel \( \text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4 \) is considered. The form of the crystal field potential at the location of a magnetic ion is determined by the nearest neighbours. If the crystal symmetry is similar to the cubic one, structurally non-equivalent ion positions are formed. In this case, the compound contains the related number of magnetically non-equivalent positions of the magnetic ion that are found in the electron paramagnetic resonance spectra.

1. Introduction

Properties of materials are determined by orientation of the ion magnetic axes with respect to the crystallographic axes of the complexes, the number of available structurally non-equivalent positions of the ions in a unit cell, the symmetry of the crystal field at the location of the magnetic ion. The study of the location of a magnetic ion in the unit cell of the complex can be made by electron paramagnetic resonance (EPR). The present paper reports the results of testing of the EPR spectrum of the \( \text{Cr}^{3+} \) ion in single-crystal lithium-gallium spinel. The topicality of the research is determined by current active study of spinels determined by their wide scientific and technological applications [1-5]. Materials science deals with doped spinels, as a rule. That is why review [6] contains discussion of proper reliable description of the structure of chemical compounds.

2. Results

To study the complexes in single-crystal \( \text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4 \) doped by chromium ion, we use one of the most informative methods of testing of the electron structure of compounds with point defects, namely, EPR. EPR spectra of \( \text{Cr}^{3+} \) was studied in the temperature range of \( 4.2 \div 300 \text{K} \). Chromium concentration was about 0.1 weight %. Angular dependence of the positions of the \( \text{Cr}^{3+} \) EPR lines was registered in planes \{110\}, \{111\} etc. Fine structure of the EPR spectrum of the \( \text{Cr}^{3+} \) ion at one position is composed by three lines in accordance with the spin \( S=3/2 \). In the general case, a spectrum composed by 36 lines was observed. The analysis of the angular dependences allowed interpretation of the lines as the fine structure...
of the EPR spectrum of 12 magnetically non-equivalent positions of the \( \text{Cr}^{3+} \) ions in a unit cell of lithium-gallium spinel and description of every ion by a spin-Hamiltonian of rhombic symmetry:

\[
H = \beta (g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + D(S_x^2 - \frac{S_z^2}{2}) + E(S_y^2 - S_z^2),
\]

where \( \beta \) is Bohr magneton, \( g_x, g_y, g_z \) are the components of the spin operator; \( D, E \) are the parameters of the initial splitting. \( D \) characterizes the field of axial symmetry. \( H \) is magnetic field directed along the magnetic axes \( x, y, z \). At temperature \( T = 290 \text{ K} \): \( g_z = 1.9796 \pm 0.0005, g_x \approx g_y = 1.9803 \pm 0.0005, D(\text{GHz}) = 9.881 \pm 0.005, E(\text{GHz}) = 0.515 \pm 0.005. \)

The sign of \( D \) was found when comparing the intensities of the first line of the fine structure and the third one at \( H_0 \parallel z, T = 4.2 \) and 290 K. At \( T = 4.2 \text{ K} \), the intensity of the third line is double of the intensity of the first line, that is an evidence of positive \( D \).

In figure 1 the angular dependence of the EPR spectrum of the \( \text{Cr}^{3+} \) ion in \( \text{Li}_{0.5}\text{Ga}_{2.5}\text{O}_4 \) in \( \{z-y\} \) plane for one position at \( T = 290 \text{ K} \) is presented. The magnetic axes were selected as follows: \( z, x \) and \( y \) axis were located in the vicinity of \( \langle 111 \rangle, \langle 110 \rangle, \langle 112 \rangle \) crystallographic axes, respectively.

In figure 2, only [111] axis of four axes of (111) type is marked. It is shown that \( z \)-axes of three positions of \( \text{Cr}^{3+} \) are close to crystallographic axis \( \langle 111 \rangle \), being symmetrically deviated through an angle of \( \beta = 5 \pm 1^\circ \). Deviation of magnetic axes \( x \) and \( y \) from the nearest crystallographic axes \( \langle 110 \rangle \) and \( \langle 112 \rangle \) is found. All three magnetic axes are rotated through an angle of \( \alpha = 4 \pm 1^\circ \) in \{111\} plane. \( Y \)-axis is deviated from \{111\} plane through an angle of \( \beta = 5 \pm 1^\circ \).

In figure 3, the form of the crystal field potential at chromium ion locations in the vicinity of one crystallographic axis of (111) type is illustrated. The unit cell contains 12 available chromium positions (3 ions around one of four axis of (111) type). Only [111] axis is marked. The vertical axis presents the potential of the crystal field \( E \) in arbitrary units is presented. The horizontal axis presents the distance \( R \) between the \( \text{Cr}^{3+} \) ions in arbitrary units.
**Figure 3.** Form of the crystal field potential at the trivalent chromium sites in the vicinity of a crystallographic axis of [111] type.

**Figure 4.** The first neighbours and the second one for an ion located in a tetra-site of single-crystal Li$_{0.5}$Ga$_{2.5}$O$_4$. Small white and black circles mark Ga$^{3+}$ and Li$^+$, respectively; large white circles mark the oxygen ions. The scale of the cubes of the second neighbours is reduced.

The nearest neighborhood of a magnetic ion in the Li$_{0.5}$Ga$_{2.5}$O$_4$ spinel is composed by the first coordination sphere formed by oxygen (figure 4). This environment generates the field of cubic symmetry with axial distortion introduced by the Ga$^{3+}$ and Li$^+$ ions in the second coordination sphere.

The obtained results are unexpected because 4 magnetically non-equivalent positions of Cr$^{3+}$ in a spinel unit cell have been supposed with respect to four axes of (111) type. The fine structure of the $R$ spectrum of Cr$^{3+}$ for a site is composed by three lines according to spin $S = 3/2$. That is why we expected an EPR spectrum composed by 12 lines, not 36 ones. An additional spectrum is related to additional magnetically non-equivalent positions of Cr$^{3+}$ in a unit cell of lithium-gallium spinel (totally 12) because of the second coordination sphere (figure 4).

3. **Conclusion**

The self-organization in a unit cell of single-crystal spinel and self-distribution of doing ions of Cr$^{3+}$ over the non-equivalent positions is realized in the course of the crystal growth. The magnetic ions are positioned at 12 minima of the crystal field potential and distributed uniformly over the sample (figure 3).

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**References**

[1] Zheng W C, Mei Y, Yang Y G and Liu H G 2012 Philos. Mag. 92 760

[2] Raita O, Popa A, Toloman D, Badilita V, Piticescu R and Giurgiu L M 2015 J. Optoelectron. Adv. M. 17 1314

[3] Maigny L and Dupont M 2013 Spinels: Occurrences, Physical Properties, and Applications. (New York: Nova Science Publishers)

[4] Ganesh I 2013 Int. Mater. Rev. 58 63

[5] Zou Y, Gréaux S, Irifune T, Li B and Higo Y 2013 J. Phys. Chem. C 117 24518

[6] Li M, Li D, O’Keeffe M and Yaghi O M 2014 Chem. Rev. 114 1343

[7] Abragam A and Bleaney B 1970 Electron Paramagnetic Resonance of Transition Ions (Oxford: Clarendonpress)