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ANGULAR DEPENDENCE OF EPR LINE INTENSITIES OBSERVED IN NICKEL-DOPED $GaBO_3$

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In experimental EPR studies of single crystals, the question of intensities of different resonance lines is usually considered as secondary. Meanwhile, in studying the EPR of Ni-doped $GaBO_3$ we have observed a drastic change in intensity of several lines when the microwave magnetic field was rotated with respect of the crystal axes. A theoretical consideration of the corresponding perturbation operator allows to adequately account for this phenomenon.

Keywords: EPR transition intensity, gallium borate.

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INTRODUCTION

The electron paramagnetic resonance (EPR) is observed in the conditions where the ground state of a paramagnetic ion is split by an applied magnetizing field $\boldsymbol{B}$, and the energy difference between different split levels is matched by energy quanta of the microwave field $\boldsymbol{B}_1$. Usually, $\boldsymbol{B}$ is much stronger than $\boldsymbol{B}_1$, therefore the latter does not affect the positions of different spectral lines but it is directly responsible for their intensities. Meanwhile, in the analysis of single crystal EPR spectra, the issue of relative intensities of different features is usually considered as secondary in comparison with that of the resonance fields.

Recently, we have studied the EPR of $GaBO_3$ single crystals doped with iron and nickel [1]. In the latter case, we have found a striking dependence in intensity of certain lines; almost disappearing at some orientations. Is has seemed interesting to provide a theoretical analysis of this dependence and compare it with the experimental findings.

THEORY

Electronic transitions between the energy levels corresponding to different projections of the effective electron spin $\boldsymbol{S}$ are induced by the magnetic component of the electromagnetic wave interacting with the electron magnetic moment whose components are:

$$\left(\beta g S\right)_i = \beta \sum_i g_i S_i, \quad i = x, y, z \tag{1}$$

where x, y and z are local symmetry axes (coinciding in our case with main crystallographic directions $x_\mathrm{c}, y_\mathrm{c}, z_\mathrm{c}$), β is the Bohr magneton and g_i are components of the electron g tensor $\boldsymbol{g}$ supposed to be diagonal. The transition intensity W_{pq} between a couple of levels p and q is proportional to the square of modulus of the matrix element [2]

$$\mu_{pq} = \beta \langle p | \boldsymbol{B}_1 \cdot \boldsymbol{g} \cdot \boldsymbol{S} | q \rangle . \tag{2}$$

Usually, in EPR conditions $\boldsymbol{B}_1 \perp \boldsymbol{B}$, so, we choose $\boldsymbol{B}$ and $\boldsymbol{B}_1$ respective directions along z_l and y_l axes of the laboratory frame x_l, y_l, z_l. The relation between the laboratory and the crystallographic frame is described by the following rotation matrix [3]:

$$\boldsymbol{A}_{\mathrm{c}l} = \begin{pmatrix} -\cos\psi\cos\vartheta\cos\varphi - \sin\psi\sin\varphi & -\sin\psi\cos\vartheta\cos\varphi + \cos\psi\sin\varphi & \sin\vartheta\cos\varphi \\ -\cos\psi\cos\vartheta\sin\varphi + \sin\psi\cos\varphi & -\sin\psi\cos\vartheta\sin\varphi - \cos\psi\cos\varphi & \sin\vartheta\sin\varphi \\ \cos\psi\sin\vartheta & \sin\psi\sin\vartheta & \cos\vartheta \end{pmatrix} \tag{3}$$

Where $\vartheta, \varphi, \pi - \psi$ are Euler angles, see Fig. 1. One can see that in the $x_\mathrm{c}, y_\mathrm{c}, z_\mathrm{c}$ frame ϑ and φ are spherical angles of $\boldsymbol{B}$, and ψ describes the orientation of $\boldsymbol{B}_1$ in the plane perpendicular to $\boldsymbol{B}$.

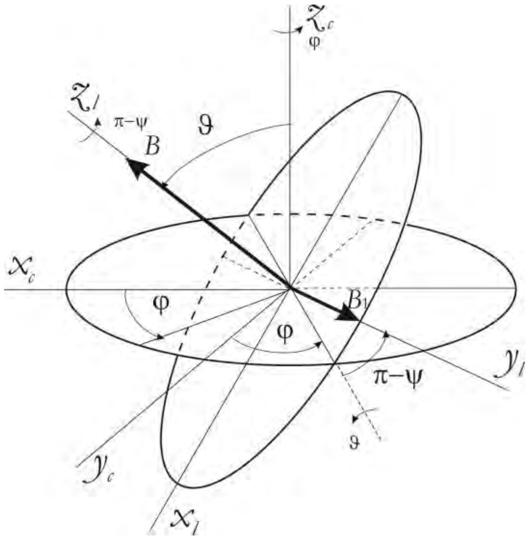

Fig. 1. Definition of Euler angles between the crystallographic frame and the laboratory frame.

The unit vectors of $\boldsymbol{B}$ and $\boldsymbol{B}_1$ in the crystallographic frame are given, respectively, by the third and the second columns of the $\boldsymbol{A}_{cl}$ matrix, viz.:

$$\boldsymbol{l} = \begin{pmatrix} \sin\vartheta\cos\varphi \\ \sin\vartheta\sin\varphi \\ \cos\vartheta \end{pmatrix} \quad \text{and} \quad \boldsymbol{l}_1 = \begin{pmatrix} -\sin\psi\cos\vartheta\cos\varphi + \cos\psi\sin\varphi \\ -\sin\psi\cos\vartheta\sin\varphi - \cos\psi\cos\varphi \\ \sin\psi\sin\vartheta \end{pmatrix}. \tag{4}$$

Thus, the matrix element (2) can be expressed as follows:

$$\mu_{pq} = \beta B_1 \langle p | \boldsymbol{l}_1(\vartheta,\varphi,\psi)\cdot\boldsymbol{g}\cdot\boldsymbol{S} | q \rangle . \tag{5}$$

with $\boldsymbol{l}_1$ defined in Eq. (4).

EXPERIMENTS AND DISCUSSION

Nickel-doped $GaBO_3$ crystals were prepared in the Crystal Growth Laboratory of the Taurida National University (Simferopol) [4]. They have rhombohedral calcite structure with the space group $\mathrm{D}_{3\mathrm{d}}^{6}$ [5]. The crystals having the shape of thin hexagonal plates, have been studied by EPR with an X-band spectrometer in the Institut de Chimie de la Matière Condensée de Bordeaux (Pessac, France). The spectra have been measured in two different configurations (i) and (ii), see Fig. 2. In both configurations, $\boldsymbol{B}$ was in the basal plane ($\vartheta = 90°$) and $\boldsymbol{B}_1$ was either parallel (i), $\psi = 0°$ or perpendicular (ii), $\psi = 90°$ to this plane.

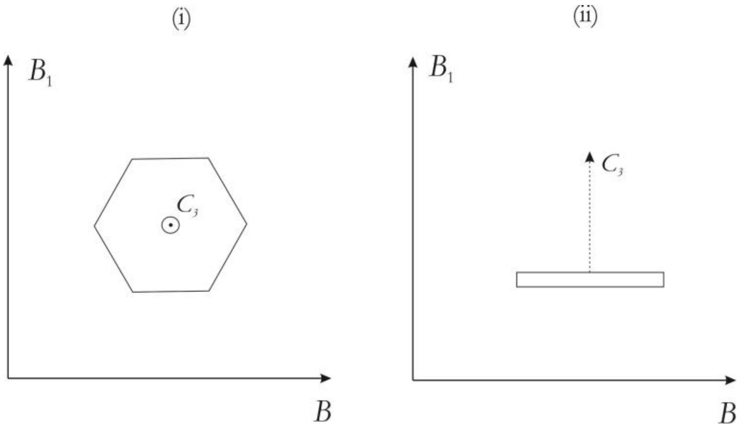

Fig. 2. Two different orientations of the crystals: (i) $\boldsymbol{B}_1 \perp \mathrm{C}_3$ and (ii) $\boldsymbol{B}_1 \parallel \mathrm{C}_3$. In both cases, $\boldsymbol{B} \perp \boldsymbol{B}_1$ and $\boldsymbol{B} \perp \mathrm{C}_3$.

Fig. 3 compares the EPR spectra for both configurations. In the context of the present study, most interesting are two features – closely spaced doublets – at ca. 0.04 and 0.23 T.

One can see that the intensities of these features in the cases (i) and (ii) are strikingly different.

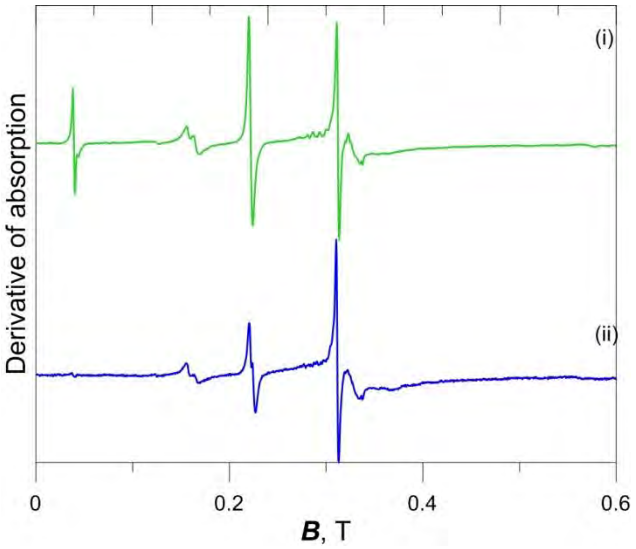

Fig. 3. EPR spectra for $\boldsymbol{B}_1$ parallel, $\psi = 0^\circ$ (i) and perpendicular, $\psi = 90^\circ$ (ii) to the basal plane of the crystal.

The exact values of the resonance fields for these features, respectively, 0.0396 and 0.0406 T for the low-field one and 0.2259 and 0.2286 T for the medium-field one, have been determined by diagonalizing the general spin Hamiltonian matrix for trigonal symmetry [6, 7]. The corresponding resonance intensities have been calculated as follows [8]:

$$W_{pq} \propto \nu^2 \beta^2 B_1^2 \left| \langle p | l_{1x} (\boldsymbol{g} \cdot \boldsymbol{S})_x + l_{1y} (\boldsymbol{g} \cdot \boldsymbol{S})_y + l_{1z} (\boldsymbol{g} \cdot \boldsymbol{S})_z | q \rangle \right|^2 , \tag{6}$$

where ν is the frequency of microwave field and l_{1x},, l_{1y} and l_{1z} are direction cosines of $\boldsymbol{B}_1$, see expression (4).

Fig. 4 shows calculated relative intensities of the resonance features in question. The transitions (a) and (b) occur between non-adjacent levels 1↔3 and 1↔4, respectively, and one can see that their intensities are much weaker that the intensities of transitions (c) and (d) between adjacent levels, 1↔2 and 2↔3, respectively. The intensities of (a) and (b) transitions become particularly low in the vicinity of $\psi = 90^\circ$, resulting in “disappearance” of these features, in good accordance with the experimental results shown in Fig. 3.

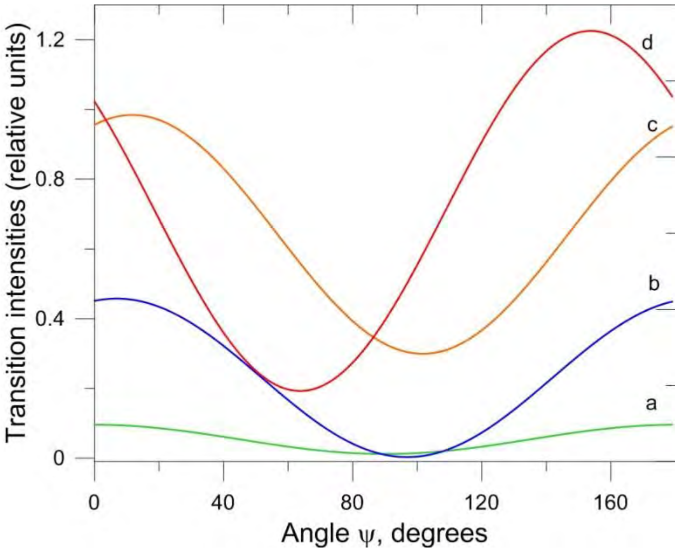

Fig. 4. Transition intensities for low-field, 0.0406 (a) and 0.0396 T (b), and medium-field, 0.2286 (c) and 0.2259 T (d) resonance features vs. the angle ψ .

CONCLUSIONS

We have observed an unusually pronounced dependence on the orientation of the microwave field $\boldsymbol{B}_1$, of intensities of certain EPR lines of Ni^{3+} in gallium borate single crystals. The results of the theoretical analysis of this dependence are in good agreement with the experimental observations and clearly show the importance of using correct expressions of intensities of the resonance transitions interpreting the experimental EPR spectra.

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Селезньова К. Кутова залежність інтенсивностей ліній ЕПР в GaBO$_3$, легованому нікелем / К. Селезньова, М. Стругацький, С. Ягупов, Я. Клява // Вчені записки Таврійського національного університету імені В. І. Вернадського. Серія : Фізико-математичні науки. – 2014. – Т. 27 (66), № 2. – С. 86-91.

В експериментальних дослідженнях ЕПР монокристалів питання про інтенсивності різних резонансних ліній, як правило, вважається вторинним. Проте, при ЕПР-дослідженнях GaBO$_3$, легованого Ni, ми спостерігали різку зміну інтенсивності ряду ліній при обертанні мікрохвильового магнітного поля відносно кристалічних осей. Теоретичний розгляд відповідного оператора збурення дозволяє адекватно пояснити це явище.

Ключові слова: інтенсивність ліній ЕПР, борат галію.

Селезнева К. Угловая зависимость интенсивностей линий ЭПР в GaBO3, легированном никелем / К. Селезнева, М. Стругацкий, С. Ягупов, Я. Клява // Ученые записки Таврического национального университета имени В. И. Вернадского. Серия : Физико-математические науки. – 2014. – Т. 27 (66), № 2. – С. 86-91.

В экспериментальных исследованиях ЭПР монокристаллов вопрос об интенсивностях различных резонансных линий, как правило, считается вторичным. Тем не менее, при ЭПР-исследованиях GaBO3, легированного Ni, мы наблюдали резкое изменение интенсивности ряда линий при вращении микроволнового магнитного поля относительно кристаллических осей. Теоретическое рассмотрение соответствующего оператора возмущения позволяет адекватно объяснить это явление.

***Ключевые слова*:** интенсивность линий ЭПР, борат галлия.

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