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SPIN-HAMILTONIAN PARAMETERS OF Cr^{3+} IONS IN $CdIn_2S_4$ CRYSTAL

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Abstract
The spin-hamiltonian parameters (zero – field splitting D, g – factors $g_{\|}$, $g_{\perp}$) for trigonal Cr^{3+} doped in $CdIn_2S_4$ crystal are calculated from the higher – order perturbation formulas , based on the cluster approach. The method is based on the single spin-orbit coupling parameter model. The comparision with experimental data gives a satisfactory agreement.
Key words: EPR, spin Hamiltonian parameters, crystal field.

1. Introduction

$CdIn_2S_4$ is a ternary compound of the $A^{II}B^{III}C^{VI}$ family to which great attention has been devoted in the last few years [1]. Chromium – doped $CdIn_2S_4$ have been studied by many investigators to provide some insights on the electronic structure of the ferromagnetic spinels. $CdIn_2S_4$ crystallizes in the cubic spinel structure [2] (space group O_h^7 – Fd3m) and its cubic unit cell has lattice constants a = b = c = 10.845Å [3].

In the spinel structure one third of the cations are on tetrahedrally coordinated A- sites with local symmetry Td. Two thirds of the cations are on octahedrally coordinated B- site with local symmetry D_{3d}. The chromium ions in the trivalent state Cr^{3+} replace indium and form an octahedral cluster $[C_rS_4]^{-5}$. The aim of the present study is to calculate the spin – hamiltonian parameters (zero – field splitting D, g factors g_{II} and $g_{\perp}$) for trigonal Cr^{3+} doped in $CdIn_2S_4$ crystal, from the perturbation formulas based on the single spin-orbit coupling parameter model. The spectroscopic parameters for $CdIn_2S_4$: Cr^{3+} are B = 310 cm^{-1}, C = 3500 cm^{-1} and Dq = 1490 cm^{-1} [4].

2. Calculations

Effective spin-Hamiltonian (SH) for 3d ions in a trigonal crystal field is express by the following relation [5]:

$$H = g_{\|}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + D[S_z^2 - \frac{1}{3}S(S+1)] \qquad (1)$$

where: β is the Bohr magneton, the first two terms are referred to Zeeman interaction, whereas the last term is known as the zero-field splitting (ZFS) term. D is the zero-field splitting parameter and $g_{\|}, g_{\perp}$ stand for the electronic paramagnetic resonance (EPR) g-factors.

Using Macfarlane's equations [6, 7], which has considered a d^3-ion in a trigonal octahedral center based on the high-order perturbation approach, we calculate the EPR parameters D, $g_{\|}, \Delta g = g_{\|} - g_{\perp}$:

$$D = \frac{2}{9}\xi^2 \nu \left(\frac{1}{D_1^2} - \frac{1}{D_3^2} \right) - \sqrt{2}\xi^2 \nu' \left(\frac{2}{3D_1 D_4} + \frac{1}{D_2 D_3} + \frac{1}{3D_3 D_4} + \frac{1}{D_2 D_4} + \frac{4\sqrt{2}B}{D_1 D_4 D_5} + \frac{4B}{D_3 D_4 D_5} + \frac{9B}{2D_2^2 D_3} \right) \quad (2)$$

$$g_{\|} = g_s - \frac{8\xi k}{3D_1} - \frac{2\xi^2}{3D_2^2}(k + g_s) + \frac{4\xi^2}{9D_3^2}(k - 2g_s) + \frac{8\xi^2}{9D_1^2}(k - 2g_s) - \frac{4\xi^2 k}{3D_1 D_2} + \\ + \frac{4\xi^2 k}{9D_1 D_3} + \frac{4\xi^2 k}{3D_2 D_3} + \frac{8\xi k}{9D_1^2}\nu - \frac{8\sqrt{2}\xi k}{3D_1 D_4}\nu' \quad (3)$$

$$\Delta g = g_{\|} - g_{\perp} = \frac{4\xi k}{3D_1^2}\nu - \frac{4\sqrt{2}\xi k}{D_1 D_4}\nu' \quad (4)$$

in which: g_s=2.003, $\xi = k\xi_0$ is the spin-orbit constant in a crystal, $k \approx \left(\sqrt{B/B_0} + \sqrt{C/C_0}\right)/2$ [8] is the orbital reduction factor with B_0 and C_0 being the Racah parameters for a free ion and B and C the Racah parameters in a crystal [9]. For Cr^{3+} free ion we take [8] B_0 = 1030 cm^{-1}, C_0 = 3850 cm^{-1} and $\xi_0 = 273$ cm^{-1}.

The zeroth-order energy denominations D_i are defined in tems of Racah parameters and crystal field strength Dq as follows:

$$D_1 = \Delta = 10Dq, \qquad D_2 = 15B + 4C,$$
$$D_3 = \Delta + 9B + 3C, \qquad D_4 = \Delta + 12B,$$
$$D_5 = 2\Delta + 3B, \qquad D_7 = \Delta + 6B, \qquad D_8 = \Delta + 6B,$$
$$D_{10} = \Delta, \qquad D_{12} = \Delta + 14B + 3C, D_{13} = \Delta + 5B.$$

The trigonal field parameters ν and ν' can be expressed using the superposition model of crystal field [10] as:

$$\nu = \frac{18}{7}\overline{A}_2(R)(3\cos^2\theta - 1) + \frac{40}{21}\overline{A}_4(R)(35\cos^4\theta - 30\cos^2\theta + 3) + \frac{40\sqrt{2}}{3}\overline{A}_4 \sin^3\theta\cos\theta \quad (5)$$

$$\nu' = -\frac{6\sqrt{2}}{7}\overline{A}_2(R)(3\cos^2\theta - 1) + \frac{10\sqrt{2}}{21}\overline{A}_4(R)(35\cos^4\theta - 30\cos^2\theta + 3) + \frac{20}{3}\overline{A}_4 \sin^3\theta\cos\theta \quad (6)$$

where: $\overline{A}_2(R)$ and $\overline{A}_4(R)$ are the intrinsic parameters of the model, θ is the angle between the C_3 axis and metal-ligand chemical bond. In an ideal octahedron, $\theta = \arccos(1/\sqrt{3}) \approx 54.7^0$; in a real (even undoped) crystal this angle differs from that value because of distortions.

For the transition metal ions in octahedral impurity centers $\overline{A}_4(R) = 3Dq/4$ [11].

In our calculation we use $\overline{A}_2(R)/\overline{A}_4(R) \approx 10.5$ [12].

Using the equations (2, 3, 4, 5, 6) we calculate the EPR parameters and compare the results with experimental data as you can see in table 1.

Table 1. EPR parameters (zero–field splitting D, g – factors $g_{\|}$, $g_{\perp}$) of Cr^{3+} doped in $CdIn_2S_4$

$CdIn_2S_4$	$D(cm^{-1})$	$g_{\|}$	$g_{\perp}$
Calculated (a)	-0.186	1.974	1.972
Experimental (b)	-0.187	1.995	2.000

a) This paper b) Paper [13]

3. Conclusion

This work presents a cluster approach for the calculation of the EPR parameters D, g – factors $g_{\|}$, $g_{\perp}$ for Cr^{3+} in laser crystal $CdIn_2S_4$. For that we use the single spin-orbit coupling parameter model. With this model, the calculated results are found to agree well with experimental data.

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