

INVESTIGATION OF THE ANGULAR DISTORTION AROUND Cr^{3+} IN LiCaAlF_6

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Abstract

The local structure for Cr^{3+} in LiCaAlF_6 are theoretically investigated from the perturbation formulas of the EPR parameters (zero-field splitting, g_{\parallel} and g_{\perp}) and splitting of first excited states for a $3d^3$ ion, in trigonal symmetry, in the cluster approach. The results show that the local angle between the impurity-ligand bonding lengths and the C_3 axis in the Cr^{3+} centers are larger than the angle in the hosts matrix. The calculated EPR parameters show a reasonable agreement with experimental data.

Keywords: EPR, spin Hamiltonian parameters, Cr^{3+} , angular distortion.

1. Introduction

Single crystals of the collquirite fluoride family LiAMF_6 ($A=\text{Ca}$, Sr and $M=\text{Al}$, Ga), have been reported as efficient broadly tunable laser materials when doped with Cr^{3+} . The LiCaAlF_6 (LiCAF), LiSrAlF_6 (LiSAF), LiSrGaF_6 (LiSGaF) and LiCaGaF_6 (LiCGaF) crystals are very good as host matrices for laser crystals, due to easiness of their growth, their optical properties and laser performance [1-6].

It is well known that when the impurity ion substitutes a host ion in a crystal, the local structure surrounding the impurity becomes different from the corresponding structure in the host crystal. If the impurity is a paramagnetic ion, we can obtain useful information on the local structure of an impurity center by analyzing its EPR data [7, 8, 9], since the EPR parameters of a paramagnetic ion in crystal are sensitive to the local distortion of the impurity center. The distortion is associated with the relative rotations of the two opposite trigonal F^- faces, and as a result the site symmetry is lowered from O_h to D_3 . The electronic paramagnetic resonance (EPR) technique is sensitive to low-symmetry distortions, that are why collquirite crystals have been investigated by this technique [10-12]. The aim of this paper is to calculate the EPR parameters

(zero-field splitting D and g factors g_{\parallel} , g_{\perp}) of Cr^{3+} replacing Al in LiCaAlF_6 . The spectroscopic parameter for LiCaAlF_6 : Cr^{3+} are [13] $Dq=1587 \text{ cm}^{-1}$, $B=786 \text{ cm}^{-1}$, $C=3248 \text{ cm}^{-1}$.

We will follow the line of our earlier papers [14, 15].

2. Basic theoretical background and calculation

Effective spin-Hamiltonian (SH) for 3d ions in a trigonal crystal field is written as [16]:

$$H = D(S_z^2 - \frac{1}{3}S(S+1)) + \mu_B g_{\parallel} B_z S_z + \mu_B g_{\perp} (B_x S_x + B_y S_y) \quad (1)$$

The last two terms in Eq (1) are referred to as the Zeeman term, whereas the first term is known as the zero-field splitting (ZFS) term. D is the ZFS parameter and g_{\parallel} , g_{\perp} stand for the EPR g-factors. Besides these parameters we will consider also the splitting energy $\delta(^2E)$ of first excited state.

Macfarlane [17, 18] has considered a d^3 -ion in a trigonal octahedral center using the high-order perturbation approach. He obtained the following equations for calculating the EPR parameters D, g_{\parallel} , $\Delta g = g_{\parallel} - g_{\perp}$ and the first excited state splitting $\delta(^2E)$:

$$D = \frac{2}{9}\xi^2\nu\left(\frac{1}{D_1^2} - \frac{1}{D_3^2}\right) - \sqrt{2}\xi^2\nu\left(\frac{2}{3D_1D_4} + \frac{1}{D_2D_3} + \frac{1}{3D_3D_4} + \frac{1}{D_2D_4} + \frac{4\sqrt{2}B}{D_1D_4D_5} + \frac{4B}{D_3D_4D_5} + \frac{9B}{2D_2^2D_3}\right) \quad (2)$$

$$g_{\parallel} = g_s - \frac{8\xi k}{3D_1} - \frac{2\xi^2}{3D_2^2}(k + g_s) + \frac{4\xi^2}{9D_3^2}(k - 2g_s) + \frac{8\xi^2}{9D_1^2}(k - 2g_s) - \frac{4\xi^2 k}{3D_1D_2} + \frac{4\xi^2 k}{9D_1D_3} + \frac{4\xi^2 k}{3D_2D_3} + \frac{8\xi k}{9D_1^2}\nu - \frac{8\sqrt{2}\xi k}{3D_1D_4}\nu' \quad (3)$$

$$\Delta g = g_{\parallel} - g_{\perp} = \frac{4\xi k}{3D_1^2}\nu - \frac{4\sqrt{2}\xi k}{D_1D_4}\nu' \quad (4)$$

$$\delta(^2E) = E(\bar{E}) - E(2\bar{A}) = 4\xi\nu\left(-\frac{1}{3D_7} - \frac{4B}{D_7D_{12}} + \frac{B}{D_7D_{13}} - \frac{4B}{D_{10}D_{12}} + \frac{B}{D_{10}D_{13}}\right) + 2\sqrt{2}\xi B\nu'\left(\frac{4\sqrt{3}}{D_7D_{12}} - \frac{\sqrt{3}}{D_7D_{13}} - \frac{4}{D_8D_{12}} - \frac{1}{D_8D_{13}}\right) \quad (5)$$

where: $g_s=2.003$, $\xi = k\xi_0$ is the spin-orbit constant in a crystal, $k \approx (\sqrt{B/B_0} + \sqrt{C/C_0})/2$ [19] 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 [20]. For Cr^{3+} free ion we take [19] $B_0 = 1030 \text{ cm}^{-1}$, $C_0 = 3850 \text{ cm}^{-1}$ and $\xi_0 = 273 \text{ cm}^{-1}$.

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

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

The trigonal field parameters ν and ν' can be expressed using the superposition model of crystal field [21] as:

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

(6)

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

(7)

In these equations $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters of the model. For the transition metal ions in octahedral impurity centers $\bar{A}_4(R) = 3Dq/4$ [22].

θ is the angle between the C_3 axis and metal-ligand chemical bond. In an ideal octahedron, $\theta = \arccos(1/\sqrt{3}) \approx 54.7^\circ$; in a real (even undoped) crystal this angle differs from that value because of distortions.

The ratio $\bar{A}_2(R)/\bar{A}_4(R) \approx 10.5$ [23] we use for calculation.

Precise value of θ can be found from the X-ray diffraction data for a given crystal. The value of the angle θ differs for the doped crystal from that in the host crystal due to the differences in the mass and ionic radii between the substituted and substituting ions [19]. The value of θ can be determined by fitting the calculated spin-Hamiltonian parameters to those deduced from experimental EPR spectra. Equating D to the experimental value [15] yields the numerical value of θ , which corresponds to the angle between the C_3 axis and “impurity ion-ligand” chemical

bond in the doped crystal. Experimental [11] and calculated (this work) SH and trigonal parameters for LiCaAlF₆ doped with Cr³⁺:

$$k = 0.8960$$

$$D(10^{-4} \text{ cm}^{-1})(\text{exp.}[11]) = -1010$$

$$D(10^{-4} \text{ cm}^{-1})(\text{calc.}) = -1014$$

$$\theta(\text{deg}) = 54.97$$

$$\nu(\text{cm}^{-1}) = -296$$

$$\nu'(\text{cm}^{-1}) = 206$$

$$\delta(^2E), (\text{cm}^{-1}, \text{calc.}) = 5.75$$

$$g_{\parallel}(\text{exp.}[11]) = 1.974(1)$$

$$g_{\parallel}(\text{calc.}) = 1.963(8)$$

$$g_{\perp}(\text{exp.}[11]) = 1.974(2)$$

$$g_{\perp}(\text{calc.}) = 1.964(8)$$

As can be seen from above results, the calculated SH parameters are in reasonable agreement with experimental values. The value of the angle θ is very close to that one for an ideal octahedron, thus suggesting small trigonal deformation along the C₃ axis. In some other crystals this deformation is greater. For example, the values of θ for Cr³⁺ in Cs₂NaGaF₆ are [24] 55.2° and 53.2° for two Cr³⁺ positions in this crystal.

3. Conclusions

The main purpose of this paper was to study theoretically the local trigonal angles Cr³⁺ centers in hexagonal fluorides LiCa(Al)F₆, from their EPR spectra, by using the perturbation formulas for the spin Hamiltonian parameters (D , g_{\parallel} , g_{\perp}) in trigonally distorted octahedral, based on the cluster approach. The results of calculations of the EPR g-factors are in reasonable agreement with experimental values.

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