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# Angular Distortion around $\text{Cr}^{3+}$ Ions Doped Diammonium Hexaaqua Magnesium Sulphate Single Crystal

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The aim of the present study is to explain the local distortion around  $\text{Cr}^{3+}$  ions doped in the title crystal using the latest experimental data regarding optical and EPR spectra. We calculated  $g_{\parallel}$ ,  $g_{\perp}$ , and  $D$  spin-Hamiltonian parameter as function of angle between the  $C_3$  axis and metal–ligand chemical bond in local distorted octahedral cluster  $[\text{CrO}_6]^{9-}$  formed after doped crystal. The method is based on the single spin–orbit coupling parameter model, in the cluster approach using Macfarlane high order perturbation formulae. The results compared with experimental data give a reasonable agreement.

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## 1. Introduction

The EPR technique is used to find the local symmetry and to evaluate the zero-field splitting parameters of transition metal ions in crystals [1], to identify and characterize the defects responsible for charge compensation in impurity doped bulk crystals [2].  $\text{Cr}^{3+}$  ion in an octahedral environment is a very attractive system, which is continuously receiving considerable attention of many research groups. It is extensively used as a probe for studying the structure and the local symmetry of new materials [3–5]. It is well known that when a paramagnetic ion  $\text{Cr}^{3+}$  substitutes a host ion in a crystal like diammonium hexaaqua magnesium sulphate  $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (DAHAMS), it can obtain useful information on the local structure around impurity center by analyzing its EPR data. DAHAMS crystallizes with space group  $P2_1|a$  and its monoclinic unit cell has lattice constants  $a = 9.316$ ,  $b = 12.580$ , and  $c = 6.202$  Å,  $Z = 2$  and the angle  $\beta = 107.09^\circ$  [1].

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When  $\text{Cr}^{3+}$  is introduced in DAHAMS crystal it substitutes for  $\text{Mg}^{2+}$  in a distorted octahedral coordination and is bound electrically to the neighboring  $\text{NH}_4^+$  vacancies necessary for charge compensation [1].

In the DAHAMS crystal, the environment of the  $\text{Cr}^{3+}$  ion is an approximately octahedral array of oxygen ions.

In the present paper we analyze the EPR parameters (zero-field splitting  $D$  and  $g$  factors  $g_{\parallel}$  and  $g_{\perp}$ ) of  $\text{Cr}^{3+}$  ions in DAHAMS to obtain information about angular distortion which is associated with angle  $\theta$  between the  $C_3$  axis and metal–ligand chemical bond in local distorted octahedral cluster  $[\text{CrO}_6]^{9-}$  formed after doped crystal.

The spectroscopic parameters for  $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}:\text{Cr}^{3+}$  are [1]  $B = 676 \text{ cm}^{-1}$ ,  $C = 3371 \text{ cm}^{-1}$ ,  $Dq = 2043 \text{ cm}^{-1}$ .

The trivalent impurities in DAHAMS are compensated by monovalent ion ( $\text{NH}_4^+$ ) vacancies corresponding to a  $\text{M}^{3+}-\text{M}^+$  centre. In cases where monovalent ions are present  $\text{M}^{3+}-\text{M}^+$  centers are formed in preference to centers involving vacancies [1].

## 2. Calculation of spin-Hamiltonian parameters

Effective spin-Hamiltonian (SH) for  $3d$  ions in an octahedral crystal field is written as

$$H = \beta B(g_{\parallel}S_z + g_{\perp}S_x) + D \left[ S_z^2 - \frac{S(S+1)}{3} \right], \quad (1)$$

where  $\beta$  is the Bohr magneton,  $g_{\parallel}$ ,  $g_{\perp}$  are the spectroscopic splitting factors,  $D$  is the axial crystal field term. The first term of the above expression describes the electron Zeeman interaction, while the second term characterizes the zero-field splitting of the quartet ground state. For a  $d^3$  such as  $\text{Cr}^{3+}$ , the zero-field splitting arises from the interaction of the  $S = 3/2$  system with the noncubic components of the ligand field (via the spin–orbit coupling).

Macfarlane [6, 7] 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  $D$ ,  $g_{\parallel}$ ,  $\Delta g = g_{\parallel} - g_{\perp}$ :

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

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

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

Here  $g_s = 2.003$ ,  $\xi = k\xi_0$  is the spin-orbit constant in a crystal,  $k \approx (\sqrt{B/B_0} + \sqrt{C/C_0})/2$  [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. For  $Cr^{3+}$  free ion we take [9]  $B_0 = 1030 \text{ cm}^{-1}$ ,  $C_0 = 3850 \text{ cm}^{-1}$ , and  $\xi_0 = 273 \text{ cm}^{-1}$ .

The zeroth-order energy denominations  $D_i$  in Eqs. (2)–(5) are defined in terms of the Racah parameters and crystal field strength  $Dq$  as follows [2]:

$$D_1 = \Delta = 10DQ, \quad D_2 = 15B + 4C, \quad D_3 = \Delta + 9B + 3C, \quad D_4 = \Delta + 12B,$$

$$D_5 = 2\Delta + 3B, \quad D_7 = \Delta + 6B, \quad D_8 = \Delta + 6B, \quad D_{10} = \Delta,$$

$$D_{12} = \Delta + 14B + 3C, \quad D_{13} = \Delta + 5B. \quad (5)$$

The trigonal field parameters  $\nu$  and  $\nu'$  can be expressed using the superposition model of crystal field [10] as

$$\begin{aligned} \nu = & \frac{18}{7}\overline{A_2}(R)(3\cos^2\theta - 1) + \frac{40}{21}\overline{A_4}(R)(35\cos^4\theta - 30\cos^2\theta + 3) \\ & + \frac{40\sqrt{2}}{3}\overline{A_4}(R)\sin^3\theta\cos\theta, \end{aligned} \quad (6)$$

$$\begin{aligned} \nu' = & -\frac{6\sqrt{2}}{7}\overline{A_2}(R)(3\cos^2\theta - 1) + \frac{10\sqrt{2}}{21}\overline{A_4}(R)(35\cos^4\theta - 30\cos^2\theta + 3) \\ & + \frac{20}{3}\overline{A_4}(R)\sin^3\theta\cos\theta. \end{aligned} \quad (7)$$

In these equations  $\overline{A_2}(R)$  and  $\overline{A_4}(R)$  are the intrinsic parameters of the model. For the transition metal ions in octahedral impurity centers  $\overline{A_4}(R) = 3Dq/4$  [11].

$\theta$  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.

TABLE

Experimental [1] and calculated (this work) SH for  $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$  doped with  $Cr^{3+}$ .

$D [\text{cm}^{-1}]$ (exp.[1]) = 0.0611	$D [\text{cm}^{-1}]$ (calc.) = 0.0611
$g(\text{exp.}[1])=1.9763$	$g_{\parallel}(\text{calc.})=1.9733$
	$g_{\perp}(\text{calc.})=1.9728$
	$g = \frac{1}{3}(2g_{\perp} + g_{\parallel}) = 1.9729$
$\theta[\text{deg}] = 54.55$	

The ratio  $\overline{A_2}(R)/\overline{A_4}(R) \approx 10.5$  [12] was used for calculation. Precise value of  $\theta$  can be found from the X-ray diffraction data for a given crystal. The value

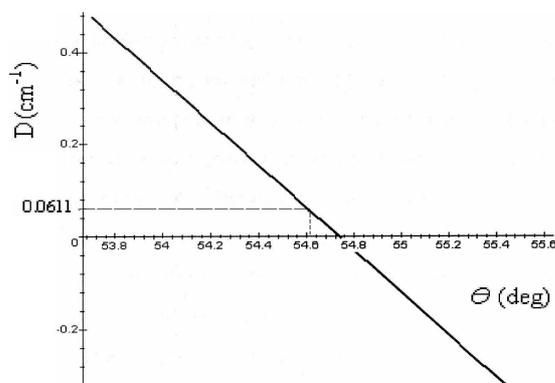


Fig. 1. Dependence of  $D$  on the angle between  $C_3$  axis and  $\text{Cr}^{3+}-\text{O}^{2-}$  chemical bond in  $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

of the angle 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 [8]. The value of  $\theta$  is determined by fitting the calculated spin-Hamiltonian parameters to those deduced from experimental EPR spectra. Equating  $D$  to the experimental value [13] yields the numerical value of  $\theta = 54.55^\circ$ , which corresponds to the angle between the  $C_3$  axis and “impurity ion–ligand” chemical bond in the doped crystal (Fig. 1).

By applying all the above parameters to Eqs. (2)–(4) we obtained the results given in Table.

The variation of the angle  $\theta$  corresponds to small trigonal distortions of the octahedral impurity centers. Comparison of the obtained values of  $\theta$  with that of an ideal octahedron suggests the character of the trigonal distortions. In the DAHAMS crystals, this angle is smaller than  $54.7^\circ$  (in cubic symmetry), and the deformation in this case is an elongation along the  $C_3$  axis.

### 3. Conclusions

In this paper we investigated theoretically the local trigonal distortion of trivalent chromium centers in diammonium hexaaqua magnesium sulphate  $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , from their EPR spectra. The perturbation formulae for the spin-Hamiltonian parameters ( $D$ ,  $g_{\parallel}$ ,  $g_{\perp}$ ) in trigonally distorted octahedral are based on the single spin–orbit coupling parameter model in the cluster approach. The results of calculations of the EPR  $g$ -factors are in reasonable agreement with experimental values.

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