



# Investigation of the zero-field splitting parameters using crystal-field parameters from the superposition model for an $\text{Fe}^{3+}$ centre in single-crystal diammonium indium pentachloride monohydrate (DIPM)

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## ABSTRACT

The zero-field splitting parameters (ZFSPs) for an  $\text{Fe}^{3+}$  centre in single-crystal diammonium indium pentachloride monohydrate ( $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ ; DIPM) are calculated using perturbation formulae and crystal-field parameters from the superposition model. The calculated second-order axial and rhombic ZFSPs at the  $\text{In}^{3+}$  site turn out to be similar to those obtained from experiments. This supports the notion that the  $\text{Fe}^{3+}$  impurity substitutes for the  $\text{In}^{3+}$  ion in DIPM.

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## 1. Introduction

Electron paramagnetic resonance (EPR) studies of  $\text{Fe}^{3+}$  impurities in single-crystal diammonium indium pentachloride monohydrate ( $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ ; DIPM) have been reported [1]. There are two possibilities for site of the  $\text{Fe}^{3+}$  centre in this crystal, namely substitution in place of  $\text{In}^{3+}$  and interstitial. It was indicated [1] that  $\text{Fe}^{3+}$  enters the lattice substitutionally in place of  $\text{In}^{3+}$ . It is interesting to determine the site of this impurity. The superposition model (SPM) has been widely used as being quite reliable for determining the probable site of an impurity dopant [2]. The SPM has been tested for  $3d^5$  ions with  $\text{O}^{2-}$  ligands [3]. The values of rank-2 parameters have been studied for both  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  in tetrahedral and octahedral oxygen-coordinated sites in the garnets. An alternative approach to test the validity of the SPM for  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  has been explored, and good agreement with the experiment was obtained [4]. Using  $\text{Fe}^{3+}$ -substituted chiolite ( $\text{Na}_5\text{Al}_3\text{F}_{14}$ ), the SPM gives a satisfactory interpretation of the order of magnitude and the signs of the phenomenological spin Hamiltonian parameters [5]. Full allowance was made for local distortion effects in the study of  $\text{Fe}^{3+}$ -doped and  $\text{Mn}^{2+}$ -doped alkaline-earth metal oxides. The data for  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  with a variety of ligands were collected, and strong correlations of the parameter values with both

covalency and ligand polarizability were demonstrated. The use of the SPM in understanding the coordination of  $3d^5$  and  $4f^7$  ions in glasses has been discussed [6]. It has been found useful in explaining the coordination of  $\text{Fe}^{3+}$  ion in quartz.

In this paper, we present the calculated zero-field splitting parameters (ZFSPs) using perturbation formulae and crystal-field parameters from the SPM for the  $\text{Fe}^{3+}$  ion present at the  $\text{In}^{3+}$  site in DIPM. The result derived from this model is consistent with experimental observations.

## 2. Crystal structure

The crystal structure of DIPM has been studied using X-ray diffraction by Lindqvist [7] and by Klug et al. [8]. It is orthorhombic bipyramidal (space group  $D_{2h}^{16}$ ,  $P_{nma}$ ). The dimensions of the unit cell for the indium salt are  $a = 1.410$  nm,  $b = 1.017$  nm and  $c = 0.716$  nm [8], whereas those for the iron salt are  $a = 1.368$  nm,  $b = 0.988$  nm and  $c = 0.702$  nm. The lattice is constituted by  $\text{NH}_4^+$  ions and  $(\text{MCl}_5 \cdot \text{H}_2\text{O})^{2-}$  ions, where  $\text{M} = \text{In}$ , the latter forming an octahedral complex. The octahedra are distorted due to the difference in the strength of the crystal field between the  $\text{Cl}^-$  ion and the  $\text{H}_2\text{O}$  molecule, the latter being situated at a corner of the  $(\text{MCl}_5 \cdot \text{H}_2\text{O})^{2-}$  octahedron. The structure viewed along the [010] direction is shown in Fig. 1(a). Indium is surrounded by five chlorine atoms and a water molecule at the corners of a distorted octahedron. The various chlorine atoms of one octahedron are designated with Roman numerals. Each chlorine IV stands for two

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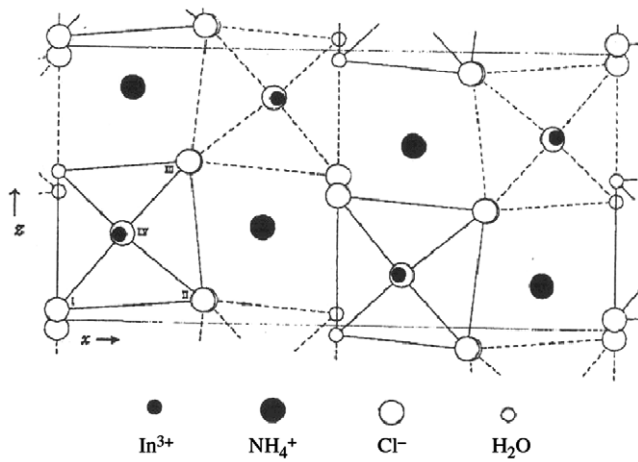


Fig. 1(a). Schematic diagram of the structure viewed along [010].

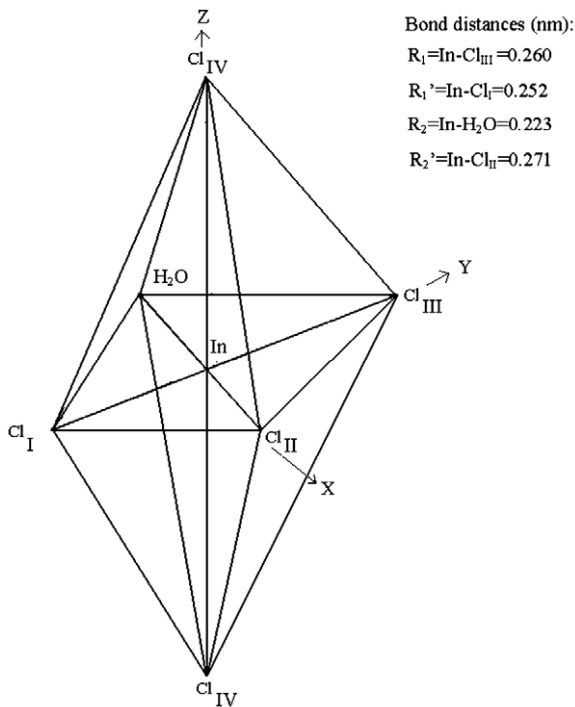


Fig. 1(b). Coordination of indium in DIPM.

such chlorines at equal distances above and below the symmetry plane (Fig. 1(b)). The  $\text{NH}_4^+$  ions are surrounded by a distorted cube of six chlorine atoms and two water molecules. At the  $\text{NH}_4^+$  positions there are actually two  $\text{NH}_4^+$  groups separated from each other by half the length of the  $b$ -axis. There are also four chlorine IV atoms at a slightly greater average distance surrounding each  $\text{NH}_4^+$  ion. The structure is thus a packing of  $\text{NH}_4^+$  ions and  $[\text{InCl}_5 \cdot \text{H}_2\text{O}]^{2-}$  ions, and the formula of the salt should be  $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ .

### 3. Theoretical investigation

Theoretical studies on the SHPs of  $d^5$  ( $^6S$ ) ions have been the subject of good amount of work [9,10]. For  $^6S$ -state ions,  $\langle \Gamma_0 | \mathbf{L} | \Gamma_0 \rangle = 0$  ( $\mathbf{L}$  is orbital angular momentum) for the orbital singlet ground state ( $\Gamma_0$ ), and this leads to considerable difficulty in explaining the observed effects of the crystal field. Various mechanisms have been suggested to contribute to ground-state splitting of the magnetic ions interacting with the lattice.

The spin Hamiltonian (SH) appropriate for orthorhombic site symmetry expressed in terms of the extended Stevens (ES) operators  $O_k^q(S_x, S_y, S_z)$  defined in [11] and generalized in [12] was chosen to fit the EPR line positions of  $\text{Fe}^{3+}$  in DIPM [13–15]:

$$\mathcal{H} = \mu_B (g_{zz} B_z S_z + g_{xx} B_x S_x + g_{yy} B_y S_y) + 1/3 (b_2^0 O_2^0 + b_2^2 O_2^2) + 1/60 (b_4^0 O_4^0 + b_4^2 O_4^2 + b_4^4 O_4^4). \quad (1)$$

In the SH,  $\mu_B$  is the Bohr magneton,  $S$  ( $=5/2$ ) is the electron spin of the  $\text{Fe}^{3+}$  ion,  $g_{zz}$ ,  $g_{xx}$  and  $g_{yy}$  are the spectroscopic splitting factors, the  $b_l^m$  are the fine-structure parameters (or ZFSPs), and the  $O_l^m$  are the spin operators as defined in [13,15]. The direction of the maximum overall splitting of EPR spectrum is taken as the  $z$ -axis and that of the minimum as the  $y$ -axis [16]. The  $(x, y, z)$  system is parallel to the crystallographic axes. The local site symmetry axes, i.e. the symmetry adapted axes (SAAs) are the nearly orthogonal directions of metal–ligand bonds [17]. The SH (1) is given in SAA system.

The effect of the spin–orbit interaction is considered as a part of the perturbation due to the free-ion and crystal-field Hamiltonians [9]. However, the spin–spin interaction is neglected because its contribution to the spin Hamiltonian parameters is much smaller than that due to the spin–orbit interaction [18–20]. In an orthorhombic symmetry of first kind (OR-I) [21], the zero-field splitting (ZFS) parameters  $D$  ( $=b_2^0$ ) and  $E$  ( $=b_2^2/3$ ) [16] are derived as [22,23]

$$D^{(4)}(SO) = (3\zeta^2/70P^2D)(-B_{20}^2 - 21\zeta B_{20} + 2B_{22}^2) + (\zeta^2/63P^2G)(-5B_{40}^2 - 4B_{42}^2 + 14B_{44}^2) \quad (2)$$

$$E^{(4)}(SO) = (\sqrt{6}\zeta^2/70P^2D)(2B_{20} - 21\zeta)B_{22} + (\zeta^2/63P^2G)(3\sqrt{10}B_{40} + 2\sqrt{7}B_{44})B_{42}, \quad (3)$$

where Wybourne notation is used for the crystal-field parameters,  $B_{kq}$ ;  $P = 7B + 7C$ ,  $G = 10B + 5C$ , and  $D = 17B + 5C$ , where  $B$  and  $C$  are the Racah parameters. Since the first-, second-, third-, and fifth-order perturbations of  $D$  and  $E$  are zero, the sixth-order term is negligibly small [24], so only the fourth-order perturbations are considered. Eqs. (2) and (3) are appropriate for weak-field cases. These are still correct even when the low-symmetry components are comparable with the cubic part [23].

In fact, the experimental values of the different parameters ( $B$ ,  $C$ ,  $\zeta_d$ ) in a crystal are less than those of the free ion. We may use the average covalency parameter  $N$  to take into account the covalency. The Racah parameters and the spin–orbit coupling parameter are given by the following relations [25]:  $B = N^4 B_0$ ,  $C = N^4 C_0$ , and  $\zeta_d = N^2 \zeta_d^0$ , where  $B_0$  and  $C_0$  denote the Racah electrostatic parameters,  $\zeta_d^0$  the spin–orbit coupling parameter for the free ion, and  $0 < N < 1$  ( $N = 1$  for the pure ionic bond). The parameter  $N$  depends mainly on the property of the transition-metal–ligand bond. From experimental data [26] for  $\text{YAG}:\text{Fe}^{3+}$ , the value of  $N$  is in the range 0.8–0.9 for the  $\text{Fe}^{3+}-\text{O}^{2-}$  bond. Therefore, we may take the middle point ( $N = 0.85$ ) as the average covalency parameter for  $\text{Fe}^{3+}-\text{Cl}^-$  and  $\text{Fe}^{3+}-\text{H}_2\text{O}$  bonds [26]. Zhao et al. [27] obtained the following values for the free  $\text{Fe}^{3+}$  ions:  $B_0 = 1130 \text{ cm}^{-1}$ ,  $C_0 = 4111 \text{ cm}^{-1}$ , and  $\zeta_d^0 = 589 \text{ cm}^{-1}$ . Thus, the numerical values of  $B$ ,  $C$ , and  $\zeta_d$  can be calculated with the help of the above relations.

### 4. Results and discussion

The crystal-field parameters  $B_{kq}$  are related to the crystal structure. The SPM is used to calculate the  $B_{kq}$  parameters for  $\text{Fe}^{3+}$

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