Theoretical investigations of ESR and optical spectra of crystalline $\text{KHSO}_4\text{:Mn}^{2+}$

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Calculations of $d-d$ transitions and the axial zero-field splitting parameter D in crystalline $\text{KHSO}_4\text{:Mn}^{2+}$ have been undertaken, with consideration of the ninth O^{2-} ligand. Energy level values calculated in a tetragonal field are in good agreement with experimentally observed values. Occasionally degenerate energy levels of $^4\text{A}_1(^4\text{E}_g(\text{G}))$ and $^4\text{A}_1(^4\text{A}_{1g}(\text{G}))$ were found in the tetragonal crystal field. The calculated value of D is in good agreement with experimental value for $\text{KHSO}_4\text{:Mn}^{2+}$.

nine coordinate, tetragonal crystal field, $d-d$ transition, axial zero-field splitting

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Research on the magneto-optical properties of transition metal ion-doped crystals has received widespread attention [1,2]. ESR (electron spin resonance) and optical spectra are two supplementary tools which can probe site symmetry and associated distortions by crystal structure parameters [2]. ESR can provide information about the magnetic properties of transition metal ions and also symmetry surrounding the metal ion [3]. Optical spectra are useful for studying the electronic structure of transition metal ions in crystals, and can provide information about energy levels and crystal field parameters. ESR of Mn^{2+} , a high spin d^5 ion, has been studied in depth, particularly for octahedral and tetrahedral coordinated ions [4,5].

Mn^{2+} has been shown to replace K^+ in crystalline KHSO_4 , with the excess charge being compensated for by nearby K^+ or H^+ vacancies [1]. Studies of Mn^{2+} in KHSO_4 have been carried out to ascertain whether Mn^{2+} enters the KHSO_4 lattice, as has been similarly observed for Cu^{2+} [1]. Results can be used to predict distortions, determine orbital level ordering and to probe the interaction between metal ion and ligands [1]. Mn^{2+} has five 3d electrons in a ground

state configuration of ^6S . ESR studies of Mn^{2+} have investigated structural and dynamic aspects of crystalline states, because zero-field splitting is sensitive to small distortions [6].

Four, six and eight coordination are most commonly observed in the crystal structures of transition metal ion clusters [7]. Theoretical investigations of ESR and optical spectra are usually based on the above coordination numbers, and $d-d$ transitions of nine coordinate Mn^{2+} species have received very little attention. For the case of Mn^{2+} doped KHSO_4 , Mn^{2+} replaces K^+ and there are nine O^{2-} ligands surrounding the central Mn^{2+} . One O^{2-} causes axial crystal field distortions in crystalline $\text{KHSO}_4\text{:Mn}^{2+}$ [7,8]. The current study investigates the effect of this ninth O^{2-} ligand on $d-d$ transitions and the axial zero-field splitting of Mn^{2+} in crystalline $\text{KHSO}_4\text{:Mn}^{2+}$.

1 Crystal structure

Potassium hydrogen sulfate has an orthorhombic crystal structure of space group $\text{D}_{2h}^{15}\text{-P}_{\text{bca}}$. The unit cell dimensions are $a = 8.40$, $b = 9.79$, $c = 18.93 \text{ \AA}$ and $Z = 16$ [9]. There is

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only one K^+ position and it is surrounded by nine oxygen ions. Eight form a distorted antiprism, with the ninth residing on top of one of the antiprism squares. Mn^{2+} replaces K^+ in crystalline $KHSO_4$: Mn^{2+} .

A geometry of eight coordinated oxygen atoms can be approximated as cubic symmetry. The average Mn-O bond length is 2.90 Å [9], and the average bond angle is $\theta = \arcsin \frac{\sqrt{6}}{3}$. The addition of a ninth oxygen atom results in a C_{4v} symmetry and $R_2 = 2.82$ Å [9] (Figure 1).

2 d-d transitions of Mn^{2+} in crystalline $KHSO_4$: Mn^{2+}

Mn^{2+} has a $3d^5$ electron configuration, and in a cubic field its energy levels are split into ${}^4T_{1g}(G)$, ${}^4T_{2g}(G)$, ${}^4E_g(G)$, ${}^4A_{1g}(G)$, ${}^4T_{1g}(P)$, ${}^4T_{2g}(D)$, ${}^4E_g(D)$, ${}^4A_{2g}(F)$, ${}^4T_{1g}(F)$, and ${}^4T_{2g}(F)$. The crystal-field parameter B_{kq} is related to the crystal structure parameters R_i , θ_i , φ_i , and can be shown as [10]

$$B_{kq} = A_{kq} \langle r^k \rangle, \quad (1-1)$$

$$A_{kq} = \sum_{i=1}^n \frac{eq_i}{R_i^{k+1}} (-1)^{q+1} C_{kq}(\theta_i, \varphi_i), \quad (1-2)$$

$$C_{kq} = \sqrt{\frac{4\pi}{2k+1}} Y_{kq}(\theta_i, \varphi_i), \quad (1-3)$$

where n and q_i are the number and charge of the ligand, respectively, e is the charge of the electron, $Y_{kq}(\theta_i, \varphi_i)$ is the spherical harmonic and $\langle r^k \rangle$ is the expectation values of the transition metal ion.

Figure 1 The crystal structure of Mn^{2+} - $9O^{2-}$.

In O_h symmetry, the crystal field parameters B_{44} and B_{40} are related to the band length R_1 and the angle θ . B_{kq} can then be obtained from eq. (1-1) as

$$B_{44} = B_{4-4} = \sqrt{\frac{35}{128}} eq \frac{8 \sin^4 \theta}{R_1^5} \langle r^4 \rangle, \quad (2-1)$$

$$B_{40} = -eq \left(\frac{35 \cos^4 \theta - 30 \cos^2 \theta + 3}{R_1^5} \right) \langle r^4 \rangle. \quad (2-2)$$

Considering the average covalent factor N for a reasonable analysis, the relationship between the expectation values $\langle r^k \rangle$ and the Racah parameters B and C in the crystal is [11,12]

$$\langle r^k \rangle = N^2 \langle r^k \rangle_0, B = N^4 B_0, C = N^4 C_0. \quad (3)$$

For a free Mn^{2+} the values of B_0 , C_0 , and $\langle r^k \rangle_0$ are [13]

$$\langle r^2 \rangle_0 = 2.7755 \text{ a.u.}, \langle r^4 \rangle_0 = 23.2594 \text{ a.u.} \quad (4-1)$$

$$B_0 = 911 \text{ cm}^{-1}, C_0 = 3273 \text{ cm}^{-1}. \quad (4-2)$$

From eqs. (2)–(4), for O_h symmetry the crystal field parameters B_{44} and B_{40} and Racah parameters B and C in crystalline $KHSO_4$: Mn^{2+} can be obtained as

$$B_{44} = -3466 \text{ cm}^{-1}, B_{40} = -5760 \text{ cm}^{-1},$$

$$B = 742 \text{ cm}^{-1}, C = 2666 \text{ cm}^{-1},$$

with $N=0.95$. The crystal field energy levels for Mn^{2+} in crystalline $KHSO_4$: Mn^{2+} can then be obtained using the HCF program [14]. Calculated energy levels for O_h symmetry are listed in Table 1. The energy levels ${}^4E_g(G)$ and ${}^4A_{1g}(G)$ are occasionally degenerate (According to the group theory, two levels are different irreducible representations, it should be separate, but the calculated results are consistent, that such situation is generally called occasionally degenerate.) [15].

Upon the addition of a ninth oxygen ion, the Mn^{2+} - $9O^{2-}$ cluster belongs to the C_{4v} symmetry group (Figure 1). The energy levels will be further split into ${}^4E({}^4T_{1g}(G))$,

Table 1 Mn^{2+} d-d transitions in crystalline $KHSO_4$: Mn^{2+} for O_h symmetry

Transition	Calculated (cm^{-1})	Observed [1] (cm^{-1})
${}^6A_{1g}(S)$		
${}^4T_{1g}(G)$	19310	14750
${}^4T_{2g}(G)$	20511	19750, 20650, 20661
${}^4E_g(G), {}^4A_{1g}(G)$	20750	20795, 21810
${}^4T_{1g}(P)$	25185	24015
${}^4T_{2g}(D)$	25515	24050
${}^4E_g(D)$	25944	28760
${}^4A_{2g}(F)$	34986	33670
${}^4T_{1g}(F)$	35097	36101
${}^4T_{2g}(F)$	35654	

${}^4A_2({}^4T_{1g}(G))$, ${}^4B_1({}^4E_g(G))$, ${}^4E({}^4T_{2g}(G))$, ${}^4B_2({}^4T_{2g}(G))$, ${}^4A_1({}^4E_g(G))$, ${}^4A_1({}^4A_{1g}(G))$, ${}^4E({}^4T_{1g}(P))$, ${}^4B_1({}^4E_g(D))$, ${}^4A_1({}^4T_{1g}(P))$, ${}^4B_2({}^4T_{2g}(D))$, ${}^4A_1({}^4E_g(D))$, ${}^4E({}^4T_{2g}(D))$, ${}^4A_1({}^4T_{1g}(F))$, ${}^4B_1({}^4T_{2g}(F))$, ${}^4E({}^4T_{1g}(F))$, ${}^4B_2({}^4A_{2g}(F))$, and ${}^4E({}^4T_{2g}(F))$ in the axial field. In a C_{4v} symmetry crystal field, the crystal field parameters B_{44} , B_{40} and B_{20} can be obtained as

$$B_{44} = B_{4-4} = \sqrt{\frac{35}{128}} e q \frac{8 \sin^4 \theta}{R_1^5} \langle r^4 \rangle, \quad (5-1)$$

$$B_{40} = -e q \left(\frac{35 \cos^4 \theta - 30 \cos^2 \theta + 3}{R_1^5} + \frac{1}{R_2^5} \right) \langle r^4 \rangle, \quad (5-2)$$

$$B_{20} = -\frac{1}{2} e q \left[\frac{8(3 \cos^2 \theta - 1)}{R_1^3} + \frac{2}{R_2^3} \right] \langle r^2 \rangle, \quad (5-3)$$

where R_2 is the bond length between metal ion and the ninth O^{2-} ion. In C_{4v} symmetry, the crystal field parameter B_{44} has the same formula as for the case of O_h symmetry (eq. (2-1)). However, B_{20} and B_{40} are related to the ninth O^{2-} ion and are different from the case in O_h symmetry (eqs. (5-2) and (5-3)). From eqs. (3)–(5), in C_{4v} symmetry these parameters can be obtained as

$$\begin{aligned} B_{44} &= -3466 \text{ cm}^{-1}, B_{40} = -3656 \text{ cm}^{-1}, \\ B_{20} &= 6681 \text{ cm}^{-1}, B = 742 \text{ cm}^{-1}, C = 2666 \text{ cm}^{-1}, \end{aligned} \quad (6)$$

with $N=0.95$. Crystal energy levels of Mn^{2+} in crystalline $KHSO_4 \cdot Mn^{2+}$ can then be obtained using the HCF program [14]. Calculated values of axial field splitting energy levels in C_{4v} symmetry are listed in Table 2. The ${}^4E_g(G)$ level will split into two different energy levels, ${}^4B_1({}^4E_g(G))$ and ${}^4A_1({}^4E_g(G))$. However, ${}^4A_1({}^4E_g(G))$ and ${}^4A_1({}^4A_{1g}(G))$ still remain occasionally degenerate. Numerous calculations show that ${}^4A_1({}^4E_g(G))$ and ${}^4A_1({}^4A_{1g}(G))$ still remain occasional degenerate, by changing bond length between the metal ion and ninth ligand R_2 . The energy levels ${}^4A_1({}^4E_g(G))$ and ${}^4A_1({}^4A_{1g}(G))$ will be occasionally degenerate, because of the tetragonal crystal field caused by the ninth O^{2-} ligand.

3 The axial zero-field splitting parameter for Mn^{2+} in crystalline $KHSO_4 \cdot Mn^{2+}$

Zero-field splitting is sensitive to small distortions, and the ninth O^{2-} ligand is thought to cause small axial distortion. From Yu and Zhao [10], the axial zero-field splitting parameter D can be calculated by

$$\begin{aligned} D &= \frac{\xi_d^2}{63E({}^4P)^2 E({}^4G)} (14B_{44}^2 - 5B_{40}^2) \\ &\quad - \frac{3\xi_d^2}{70E({}^4P)^2 E({}^4D)} B_{20} (B_{20} - 14\xi_d), \end{aligned} \quad (7)$$

Table 2 Mn^{2+} $d-d$ transitions in crystalline $KHSO_4 \cdot Mn^{2+}$ for C_{4v} symmetry

Further splitting levels	Calculated (cm^{-1})	Observed [1] (cm^{-1})
${}^6A_{1g}(S)$		
${}^4E({}^4T_{1g}(G))$	19171	14750
${}^4A_2({}^4T_{1g}(G))$	19310	19750
${}^4B_1({}^4E_g(G))$	20133	20650
${}^4E({}^4T_{2g}(G))$	20396	20661
${}^4B_2({}^4T_{2g}(G))$	20675	20795
${}^4A_1({}^4E_g(G)), {}^4A_1({}^4A_{1g}(G))$	20750	21810
${}^4E({}^4T_{1g}(P))$	23301	24015
${}^4B_1({}^4E_g(D))$	25038	24050
${}^4A_1({}^4T_{1g}(P))$	25185	
${}^4B_2({}^4T_{2g}(D))$	25795	
${}^4A_1({}^4E_g(D))$	25944	
${}^4E({}^4T_{2g}(D))$	26426	28760
${}^4A_1({}^4T_{1g}(F))$	35097	33670
${}^4B_1({}^4T_{2g}(F))$	35210	
${}^4E({}^4T_{1g}(F))$	35361	
${}^4B_2({}^4A_{2g}(F))$	36509	36101
${}^4E({}^4T_{2g}(F))$	36617	

where ξ_d is the spin-orbital parameter of the transition metal ion, $E({}^4P)$, $E({}^4G)$ and $E({}^4D)$ are the energy level separations between the excited quartets and the ground sextet. The parameters $E({}^4P)$, $E({}^4G)$ and $E({}^4D)$ can be calculated from the following formula [16]:

$$E({}^4P) = 7B + 7C, E({}^4G) = 10B + 5C, E({}^4D) = 17B + 5C. \quad (8)$$

Introducing the average covalent factor N , the relationship between the spin-orbital coupling coefficient ξ_d in the crystal and ξ_d^0 in the free ion is [15]

$$\xi_d = N^2 \xi_d^0 \quad (9)$$

and the spin-orbital coupling coefficient ξ_d^0 of the free Mn^{2+} is [15]

$$\xi_d^0 = 337 \text{ cm}^{-1}. \quad (10)$$

From eqs. (6)–(10), for crystalline $KHSO_4 \cdot Mn^{2+}$ we can obtain

$$D = 60 \times 10^{-4} \text{ cm}^{-1}.$$

This value of D was calculated using eq. (7). Because of the crystal field weakness ($D_q = 580 \text{ cm}^{-1}$), contributions from high energy excited states are less than one-tenth of the experimentally obtained value of D from eq. (7) [10]. We calculated $D_q = 286 \text{ cm}^{-1}$, thus the error is less than one-tenth. The calculated value of D is in good agreement with the experimentally obtained value ($D = 59 \times 10^{-4} \text{ cm}^{-1}$) [1], which indicates the axial zero-field splitting is

predominantly caused by the ninth O^{2-} ligand.

When divalent cation impurities are substituted for monovalent cations, the host crystal lattice has an electrical charge imbalance which must be compensated by some means. When Mn^{2+} is doped in crystalline $KHSO_4$, Mn^{2+} replaces K^+ to give $KHSO_4:Mn^{2+}$. Kripal and Mishra [1] suggested that this corresponded to the formation of an associated pair, $Mn^{2+}:O^{2-}$, where O^{2-} occupies an adjacent site. The symmetry axis is probably slightly tilted from the [001] axis because of a nearby anion vacancy in the [100] or [110] axes. This will result in a change of the orthorhombic symmetry E term of the spin-Hamiltonian equation [2]. In our calculations, the effect of this E term has not been included.

4 Conclusions

Calculations of $d-d$ transitions and the axial zero-field splitting parameter D in crystalline $KHSO_4:Mn^{2+}$ have been undertaken with consideration of the ninth O^{2-} ligand. The calculated energy levels in the tetragonal field are in good agreement with experimental values. Occasionally degenerate energy levels of $^4A_1(^4E_g(G))$ and $^4A_1(^4A_{1g}(G))$ were found in the tetragonal crystal field. The calculated axial zero-field splitting value D is in good agreement with experimental value for $KHSO_4:Mn^{2+}$.

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