Investigations of the Optical and EPR Spectra for Cr³⁺ Ions in Diammonium Hexaaqua Magnesium Sulphate Single Crystal

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The relations between spin-Hamiltonian parameters and local structure around Cr³⁺ in diammonium hexaaqua magnesium sulphate single crystal were established. On the basis of this, the spin-Hamiltonian parameters, optical spectra and the local structure were investigated successfully. The calculated results are in good agreement with experimental data. This shows that the distortion model adopted in this paper is reasonable.

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1. Introduction

In the past decades, the microscopic spin-Hamiltonian (MSH) theory has been extensively used in the area of electron paramagnetic resonance (EPR) of transition metal (TM) ions [1–6]. The MSH theory enables to correlate optical spectroscopy and structural data with the spin-Hamiltonian (SH) parameters extracted from the EPR spectra. Theoretical and experimental studies show that the SH parameters for TM ions in crystals reflect very sensitively the local structure. So, the SH theory is used extensively in the study on the crystal microstructure. Recently, Kripal et al. [7] determined the optical and EPR spectra of $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ (DAHAMS) crystals. Using Macfarlane's perturbation formulae [8, 9], Ciresan et al. calculated the SH parameters by considering the angular distortion along C₃-axis [2]. In the present work, the local structure, SH parameters and optical spectra of doped Cr³⁺ ions are investigated systematically by using complete diagonalization method.

2. Theory

In the crystal field (CF) framework, the total Hamiltonian is written as [10]:

$$H = H_{ee}(B, C) + H_{CF}(B_{kq}) + H_{SO}(\zeta), \quad (1)$$

where H_{ee} represents the Coulomb interactions, H_{CF} represents CF interactions, and H_{SO} represents the magnetic spin–orbit interaction parameterized by ζ. The CF Hamiltonian for tetragonal symmetry in the Wybourne notation can be given as

$$H_{CF} = B_{20}C_0^{(2)} + B_{40}C_0^{(4)} + B_{44}C_4^{(4)} + B_{4-4}C_{-4}^{(4)}, \quad (2)$$

where the CF parameters B_{kq} measure the strength of interaction between the open-shell electrons of paramagnetic ions and their surrounding crystalline environment

[11, 12] and hence play an important role in the CF studies. $C_q^{(k)}$ is the tensor operator defined by [13]:

$$C_q^{(k)} = \sqrt{\frac{4\pi}{2k+1}} Y_{kq} \quad (3)$$

with Y_{kq} denoting spherical harmonic functions. The methods of calculation of the matrix elements for H_{ee}, H_{SO}, and H_{CF} have been described in Ref. [14].

Cr³⁺ is of $3d^3$ configurations. The free-ion ^4F ground term of $3d^3$ ions splits in octahedral symmetry into $^4A_{2g}$, $^4T_{2g}$ and $^4T_{1g}$ states, where $^4A_{2g}$ is the ground state, and not split in tetragonal CF, but its irreducible representation changed into $^4B_1$. Due to the combined action of the tetragonal CF and magnetic interactions, $^4B_1$ will split further, and this procedure can be expressed by group theory as

$$B_1 \otimes D^{(3/2)} \to B_1 \otimes (E' \oplus E'') \to E' \oplus E'', \quad (4)$$

the value of splitting is $2D$, where D is the zero field splitting (ZFS) parameter of ground state.

For $3d^3$ ions with the tetragonal symmetry, the matrices of Hamiltonian in Eq. (1) are of the dimension 120×120 and can be partitioned into four 30×30 matrices, i.e., $E'\alpha'$, $E'\beta'$, $E''\alpha''$, $E''\beta''$. In zero magnetic field, $E'\alpha'$ and $E'\beta'$, $E''\alpha''$ and $E''\beta''$ are the Kramers doublets. Diagonalization of the full Hamiltonian matrices yields the energy levels and eigenvectors as functions of the Racah parameters B and C, CF parameters B_{kq}, and SO coupling constant ζ. The ground state eigenvectors will be used in calculating the spectroscopic splitting g-factors. For Cr³⁺ ions at tetragonal symmetry, the effective spin Hamiltonian, taking into account the ZFS and Zeeman terms, can be written as [15]:

$$H_S = D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + \mu_B g_\parallel B_z S_z$$
$$+ \mu_B g_\perp (B_x S_x + B_y S_y). \quad (5)$$

The symbols appearing in Eq. (5) have their usual meanings. According to SH theory, the ZFS parameter D and

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g factors can be expressed as

$$D = \frac{1}{2}\Big[\varepsilon(|E'(^4F \downarrow\ ^4A_{2g} \downarrow\ ^4B_1)\rangle)$$
$$- \varepsilon(|E''(^4F \downarrow\ ^4A_{2g} \downarrow\ ^4B_1)\rangle)\Big], \tag{6}$$

$$g_\parallel = 2\Big[k\langle\psi_{1/2}|\sum_{i=1}^{N} l_z(i)|\psi_{1/2}\rangle$$
$$+ g_e\langle\psi_{1/2}|\sum_{i=1}^{N} s_z(i)|\psi_{1/2}\rangle\Big], \tag{7}$$

$$g_\perp = k\langle\psi_{1/2}|\sum_{i=1}^{N} l_x(i)|\psi_{-1/2}\rangle$$
$$+ g_e\langle\psi_{1/2}|\sum_{i=1}^{N} s_x(i)|\psi_{-1/2}\rangle, \tag{8}$$

where k is the orbital reduction factor, and g_e is the free--spin g value of 2.0023.

3. Calculation and discussions

For $(NH_4)_2Mg(SO_4)_2\cdot 6H_2O$ crystals, the lattice constants of monoclinic unit cell are $a = 9.316$ Å, $b = 12.580$ Å, and $c = 6.202$ Å, with the angle $\beta = 107.09°$ [16]. There are 40 H, 2 Mg, 4 N, 28 O, and 4 S atoms in one unit cell, where Mg atoms occupy the 2a sites with coordination of six oxygen neighbors, and other atoms lie in 4e sites. Two of the six Mg–O bond lengths are $R_{10} = 2.05$ Å, and the other four are $R_{20} = 2.08$ Å (see Fig. 1). When Cr^{3+} ions are doped into DAHAMS crystals, Cr^{3+} will replace Mg^{2+} ions, and occupy the C_{4v} site. On account of the differences between the impurity ions and host ions, the local environment of the paramagnetic ion may be unlike that of the replaced host ion. We assume that the bond lengths will be changed. The increment of bond lengths can be described by the distortion parameters ΔR_1 and ΔR_2, i.e., $R_1 = R_{10} + \Delta R_1$, $R_2 = R_{20} + \Delta R_2$. According to superposition model [12, 17], the relationship between the CF parameters and local structure parameters can be expressed as

$$B_{20} = -2\bar{A}_2\left(\frac{R_0}{R_{10} + \Delta R_1}\right)^{t_2}$$
$$- 4\bar{A}_2\left(\frac{R_0}{R_{20} + \Delta R_2}\right)^{t_2}, \tag{9}$$

$$B_{40} = 16\bar{A}_4\left(\frac{R_0}{R_{10} + \Delta R_1}\right)^{t_4}$$
$$+ 12\bar{A}_4\left(\frac{R_0}{R_{20} + \Delta R_2}\right)^{t_4}, \tag{10}$$

$$B_{44} = 2\sqrt{70}\bar{A}_4\left(\frac{R_0}{R_{20} + \Delta R_2}\right)^{t_4}, \tag{11}$$

where R_0 is the reference distance. Herein, we take the mean value of all six bond lengths as the reference distance. $\bar{A}_k$ is the intrinsic parameter and t_k is the power--law exponent [13, 17, 18].
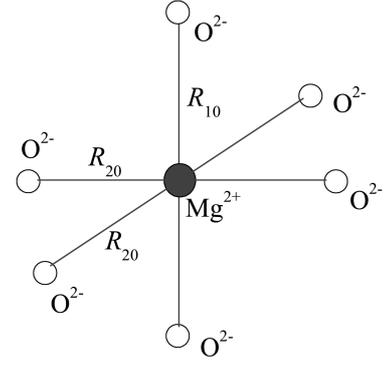
Fig. 1. Local structure of $(MgO_6)^{10-}$ in DAHAMS.

In our calculation, we take the optical parameters $B = 450$ cm^{-1} and $C = 3450$ cm^{-1} for Racah parameters, $\zeta = 259$ cm^{-1} for SO coupling constant, $Dq = 1958$ cm^{-1} for cubic CF parameter. The orbital reduction factor $k = (\sqrt{B/B_0} + \sqrt{C/C_0})/2 = 0.8$, where $B_0 = 1030$ cm^{-1} and $C_0 = 3850$ cm^{-1} are the Racah parameters for free Cr^{3+} ions. Substituting these parameters into Hamiltonian, then the complete energy matrix can be obtained. Diagonalizing the matrix, one can obtain the optical spectra and the eigenvectors. The obtained eigenvectors can be used to calculate the g-factors. Thus, the optical and EPR spectra can be obtained. Taking the local structure distortion parameters ΔR_1 and ΔR_2 as tunable parameters, the local structure distortion parameters $\Delta R_1 = -0.071$ Å and $\Delta R_2 = -0.008$ Å can be obtained by fitting the experimental optical and EPR spectra. The comparisons between theoretical results and observed values are given in Tables I and II.

It can be seen from Tables I and II that the inclusion of small lattice distortion leads to agreement between experimental and theoretical results. This indicates that the distortion model we used is reasonable. The distortion parameters ΔR_1 and ΔR_2 are negative, this shows that the bond length of Cr–O is smaller than that of Mg–O. Since the charge of Cr^{3+} is larger than that of Mg^{2+}, and then the electrostatic Coulomb interaction between Cr^{3+} and O^{2-} should be larger than that between Mg^{2+} and O^{2-}. Thus, the bond length of Cr–O should be smaller than that of Mg–O. This shows that our calculations are reliable in its physical meanings.

Ignoring the structural distortions yields remarkably smaller values of D (see row (b) in Table I). In this case, it is found that $D_{cal.}/D_{exp.} = 0.38$. When considered the distortion, the calculated parameters D and g factor are much closer to the experimental data. This indicates that local structure distortions do occur and play an important role in making contributions to the ZFS parameters. Comparing the calculated results in row (a) and (b) in Table II, one can see that the contributions to optical spectra from local structure distortion are remarkable. Especially, for $^4T_1(F)$, this contribution reaches 2789 cm^{-1}. Therefore, the structural distortion must be

considered in the investigations of optical spectra. In Ref. [7], the spectral line 36645 cm^{-1} was assigned to $^2T_{2g}(H)$. But our calculation shows that this line should be assigned to $^2E_g(H)$.

TABLE I

Distortion and SH parameters of Cr^{3+} ions in DAHAMS.

	ΔR_1 [Å]	ΔR_2 [Å]	D [cm^{-1}]	$g_\parallel$	$g_\perp$	$g = (g_\parallel + 2g_\perp)/3$
Cal. (*a*)			0.0611	1.9733	1.9728	1.9729
Cal. (*b*)	0.000	0.000	0.0233	1.9738	1.9733	1.9735
Cal. (*c*)	−0.074	−0.009	0.0610	1.9766	1.9749	1.9755
Exp. [7]			0.0611(2)			1.9763(2)

(*a*) calculated in Ref. [2] by perturbation formulae;
(*b*) this work, with ignoring the local distortion;
(*c*) this work, with considering the local distortion

TABLE II

Optical spectra of Cr^{3+} ions in DAHAMS (in cm^{-1}).

	$^2E_g(G)$	$^4T_{2g}(F)$	$^4T_{2g}(F)$	$^4T_{1g}(F)$	$^2A_{1g}(G)$	$^2E_g(H)$
Cal. (*a*)	13889	19522	19887	25062	31740	35109
Cal. (*b*)	13930	20478	22042	27851	33116	36957
Exp. [7]	13923	20433	21872	27863	33168	36645

(*a*) this work, with ignoring the local distortion;
(*b*) this work, with considering the local distortion

4. Summary

In the doped DAHAMS, Cr^{3+} impurity ions are substituted for Mg^{2+}. The differences in charge and ionic radius between Cr^{3+} and Mg^{2+} induce the local structural distortion around Cr^{3+}. On the basis of superposition model, the relationship between the optical and EPR spectra and structural parameters is established. Considering local distortion, the calculated results agree well with observed values. The bond lengths are shortened 0.071 Å and 0.008 Å, respectively. Thus, optical and EPR spectra are interpreted systematically.

Acknowledgments

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