Investigations of the Optical and EPR Spectra for \( \text{Cr}^{3+} \) Ions in Diammonium Hexaaqua Magnesium Sulphate Single Crystal

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The relations between spin-Hamiltonian parameters and local structure around \( \text{Cr}^{3+} \) 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 of the crystal microstructure. Recently, Kripal et al. [7] determined the optical and EPR spectra of \((\text{NH}_4)_2\text{Mg(SO}_4)_2\cdot6\text{H}_2\text{O}\) (DAHAMS) crystals. Using Macfarlane’s perturbation formulae [8, 9], Ciresan et al. calculated the SH parameters by considering the angular distortion along \(C_3\)-axis [2]. In the present work, the local structure, SH parameters and optical spectra of doped \( \text{Cr}^{3+} \) ions are investigated systematically by using complete diagonalization method.

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

\[
H = H_{\text{ee}}(B, C) + H_{\text{CF}}(B_{\text{eq}}) + H_{\text{SO}}(\zeta),
\]

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

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

where the CF parameters \(B_{\text{eq}}\) 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]:

\[
C_q^{(k)} = \sqrt{\frac{4\pi}{2k+1}} Y_{kq}
\]

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

\(\text{Cr}^{3+}\) 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

\[
B_1 \otimes D^{(3/2)} \rightarrow B_1 \otimes (E' \oplus E'') \rightarrow E' \oplus E'',
\]

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 \(\times\) 120 and can be partitioned into four \(30 \times 30\) matrices, i.e., \(E'\alpha', E'\beta', E''\alpha'', E''\beta''\). In zero magnetic field, \(E'\alpha'\) 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 \(B_{\text{eq}}\), and SO coupling constant \(\zeta\). The ground state eigenvectors will be used in calculating the spectroscopic splitting \(g\)-factors. For \(\text{Cr}^{3+}\) ions at tetragonal symmetry, the effective spin Hamiltonian, taking into account the ZFS and Zeeman terms, can be written as [15]:

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

The symbols appearing in Eq. (5) have their usual meanings. According to SH theory, the ZFS parameter \(D\) and
g factors can be expressed as

\[
D = \frac{1}{2} \left[ \epsilon (|E^r(4F \downarrow 4A_2g \downarrow 4B_1)|) \right. \\
- \epsilon (|E^r(4F \downarrow 4A_2g \downarrow 4B_1)|), \tag{6}
\]

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

\[
g_{\perp} = k \langle \psi_{1/2} | \sum_{i=1}^{N} l_z(i) | \psi_{-1/2} \rangle + g_c \langle \psi_{1/2} | \sum_{i=1}^{N} s_z(i) | \psi_{-1/2} \rangle, \tag{8}
\]

where \(k\) is the orbital reduction factor, and \(g_c\) is the free-spin \(g\) value of 2.0023.

### 3. Calculation and discussions

For \((\text{NH}_4)_2\text{Mg(SO}_4)_2\cdot 6\text{H}_2\text{O}\) crystals, the lattice constants of monoclinic unit cell are \(a = 9.316\ \text{Å}, b = 12.580\ \text{Å},\) and \(c = 6.202\ \text{Å},\) with the angle \(\beta = 107.09^\circ\) \cite{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 4c sites. Two of the six Mg–O bond lengths are \(R_{10} = 2.05\ \text{Å},\) and the other four are \(R_{20} = 2.08\ \text{Å}\) (see Fig. 1). When \(\text{Cr}^{3+}\) ions are doped into DAHAMS crystals, \(\text{Cr}^{3+}\) will replace \(\text{Mg}^{2+}\) 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 \(\Delta R_1\) and \(\Delta R_2,\) i.e., \(R_1 = R_{10} + \Delta R_1,\) \(R_2 = R_{20} + \Delta R_2.\) According to superposition model \cite{12, 17}, the relationship between the CF parameters and local structure parameters can be expressed as

\[
B_{20} = -2 A_2 \left( \frac{R_0}{R_{10} + \Delta R_1} \right)^{t_2}, \tag{9}
\]

\[
B_{40} = 16 A_4 \left( \frac{R_0}{R_{10} + \Delta R_1} \right)^{t_4} + 12 A_4 \left( \frac{R_0}{R_{20} + \Delta R_2} \right)^{t_4}, \tag{10}
\]

\[
B_{44} = 2 \sqrt{70} A_4 \left( \frac{R_0}{R_{20} + \Delta R_2} \right)^{t_4}, \tag{11}
\]

where \(R_0\) is the reference distance. Herein, we take the mean value of all six bond lengths as the reference distance. \(A_k\) is the intrinsic parameter and \(t_k\) is the power-law exponent \cite{13, 17, 18}.

In our calculation, we take the optical parameters \(B = 450\ \text{cm}^{-1}\) and \(C = 3450\ \text{cm}^{-1}\) for Racah parameters, \(\zeta = 259\ \text{cm}^{-1}\) for SO coupling constant, \(D_q = 1958\ \text{cm}^{-1}\) for cubic CF parameter. The orbital reduction factor \(k = (\sqrt{B/B_0} + \sqrt{C/C_0})/2 = 0.8,\) where \(B_0 = 1030\ \text{cm}^{-1}\) and \(C_0 = 3850\ \text{cm}^{-1}\) are the Racah parameters for free \(\text{Cr}^{3+}\) 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 \(\Delta R_1\) and \(\Delta R_2\) as tunable parameters, the local structure distortion parameters \(\Delta R_1 = -0.071\ \text{Å}\) and \(\Delta R_2 = -0.008\ \text{Å}\) 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 \(\Delta R_1\) and \(\Delta R_2\) are negative, this shows that the bond length of \(\text{Cr}–\text{O}\) is smaller than that of \(\text{Mg}–\text{O}.\) Since the charge of \(\text{Cr}^{3+}\) is larger than that of \(\text{Mg}^{2+},\) and then the electrostatic Coulomb interaction between \(\text{Cr}^{3+}\) and \(\text{O}^{2-}\) should be larger than that between \(\text{Mg}^{2+}\) and \(\text{O}^{2-}.\) Thus, the bond length of \(\text{Cr}–\text{O}\) should be smaller than that of \(\text{Mg}–\text{O}.\) 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 \(D_{\text{cal}}/D_{\text{exp}} = 0.38.\) 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 \(^4T'_2(F),\) this contribution reaches 2789 \text{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

<table>
<thead>
<tr>
<th></th>
<th>(\Delta R_1) [Å]</th>
<th>(\Delta R_2) [Å]</th>
<th>(D) [cm(^{-1})]</th>
<th>(g_\parallel)</th>
<th>(g_\perp)</th>
<th>(g = (g_\parallel + 2g_\perp)/3)</th>
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<td>Cal. (a)</td>
<td>0.0611</td>
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<td>1.9728</td>
<td>1.9759</td>
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<td></td>
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<td>1.9733</td>
<td>1.9735</td>
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<td></td>
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<tr>
<td>Cal. (c)</td>
<td>−0.074</td>
<td>0.0610</td>
<td>1.9766</td>
<td>1.9749</td>
<td>1.9755</td>
<td></td>
</tr>
<tr>
<td>Exp. [7]</td>
<td>0.0611(2)</td>
<td>1.9766</td>
<td>1.9749</td>
<td>1.9755</td>
<td>1.9763(2)</td>
<td></td>
</tr>
</tbody>
</table>

(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

<table>
<thead>
<tr>
<th></th>
<th>(^2E_g(G))</th>
<th>(^4T_{2g}(F))</th>
<th>(^4T_{2g}(F))</th>
<th>(^4T_{1g}(F))</th>
<th>(^2A_{1g}(G))</th>
<th>(^2E_g(H))</th>
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<tbody>
<tr>
<td>Cal. (a)</td>
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<td>19522</td>
<td>19887</td>
<td>25862</td>
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<td>35109</td>
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<tr>
<td>Cal. (b)</td>
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<td>22042</td>
<td>27851</td>
<td>33116</td>
<td>36957</td>
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<tr>
<td>Exp. [7]</td>
<td>13923</td>
<td>20433</td>
<td>21872</td>
<td>27863</td>
<td>33168</td>
<td>36645</td>
</tr>
</tbody>
</table>

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

### 4. Summary

In the doped DAHAMS, \(\text{Cr}^{3+}\) impurity ions are substituted for \(\text{Mg}^{2+}\). The differences in charge and ionic radius between \(\text{Cr}^{3+}\) and \(\text{Mg}^{2+}\) induce the local structural distortion around \(\text{Cr}^{3+}\). 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.

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### References