EPR and optical absorption studies of VO$^{2+}$ ions doped in cobalt maleate tetrahydrate (CoMTH) single crystals

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1. Introduction

Electron paramagnetic resonance (EPR) provides a great deal of information about the magnetic properties of transition metal ions doped in crystals. EPR studies are usually carried out on paramagnetic impurities doped in diamagnetic hosts. Similar studies can, in principle, be carried out by incorporating paramagnetic ions in paramagnetic hosts. The EPR study of paramagnetic impurity ions in paramagnetic hosts is less common because of the broadening of impurity resonance lines due to the host impurity interaction. However, if sharp spectra are observable, these studies can be used to obtain additional information on magnetic interactions themselves and on the paramagnetic host ion properties, besides the usual information obtained from the diamagnetic hosts. Reasonably sharp EPR spectra have been observed in many paramagnetic hosts [1–8].

The vanadyl ion (VO$^{2+}$) is the most stable cation among a few molecular paramagnetic transition metal ions, which is used extensively as an impurity probe for EPR studies. Since the EPR spectrum is very sensitive to the crystalline environment, extensive EPR studies on VO$^{2+}$ ions in a variety of lattices [9–14] have been reported. Recently, Narasimhulu and Rao [5] have studied the EPR spectra of Mn$^{2+}$ ions in cobalt maleate tetrahydrate single crystal. They found that the Mn$^{2+}$ ion is in a highly distorted orthorhombic symmetry. In this chapter, the author presents a detailed EPR and optical absorption spectral studies of paramagnetic impurity (VO$^{2+}$) in paramagnetic host (cobalt maleate tetrahydrate) single crystal.
2. Crystal structure

Cobalt maleate tetrahydrate (hereafter to be referred as CoMTH) belongs to a group of compounds with general formula \( \text{H}_2\text{M} (\text{C}_4\text{H}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O} \) where M is a cation such as Zn, Co, Mn or Ni [15,16]. A detailed structure of CoMTH is not available. However, the unit cell dimensions were reported [15] for isomorphous nickel maleate tetrahydrate. The unit cell dimensions for nickel maleate tetrahydrate given are \( a = 0.520 \text{ nm}, b = 0.729 \text{ nm}, c = 0.973 \text{ nm}, \alpha = 60^\circ 12', \beta = 104^\circ 54', \gamma = 102^\circ 12' \) and \( Z = 1 \). The metal ions are octahedrally coordinated by six oxygen atoms, four from water molecules and two from maleate ligands.

3. Experimental

Single crystals of CoMTH were grown by slow evaporation method. Stoichiometric amount of cobalt sulphate (\( \text{CoSO}_4 \cdot 5\text{H}_2\text{O} \)) was taken and precipitated as hydroxide using ammonium hydroxide. After eliminating excess ammonia by warming the solution, the resultant hydroxide was treated with 100% excess of hot maleic acid. To this solution, 0.3 mol% of VO\(^{2+}\) was added as dopant. The solution was filtered and kept at room temperature (300 K) for slow evaporation. Reddish-coloured transparent crystals with well-developed faces were separated out on concentrating the solution.
The EPR experiments were performed on a JEOL FEIX ESR spectrometer operating at X-band microwave frequency equipped with TE011 cylindrical cavity with 100 kHz field modulation. The resonance line of Diphenyl Picryl Hydrazyl (DPPH) was used as a standard field marker. The angular variation spectra were recorded for every 5° interval. The temperature variation studies were performed using a JES UCT 2AX variable temperature controller. Optical absorption spectrum was recorded on a JASCO UV–VIS–NIR spectrophotometer (Model V-570) at room temperature, taking the pure CoMTH crystal as the reference in the UV–VIS region.

4. Theory

4.1 Electron paramagnetic resonance studies

Vanadium (Z = 23), the iron group transition metal ion having electronic configuration [Ar] 3d3 4s1 readily reacts with atmospheric oxygen to form a number of oxycations and the simplest is the vanadyl ion, VO2+ with electronic configuration [Ar] 3d1.

As vanadyl ion contains a single unpaired electron (S = 1/2) interacting with a single nucleus (51V, 99.8% abundant, I = 7/2), one expects eight (2I + 1) hyperfine lines in the EPR spectrum. The energy level splitting and allowed transitions for VO2+ ion in an external magnetic field with nuclear interactions is shown in Fig. 1. The following spin-Hamiltonian, including the electron-Zeeman and nuclear hyperfine terms can be used to analyse the EPR spectra.
Fig. 1: The energy level diagram and allowed transitions for VO$^{2+}$ ion in an external magnetic field with nuclear interactions.
\[ H = \beta H \cdot g \cdot S + \hbar S \cdot A \cdot I \]  

(1)

where \( \beta \) is the Bohr magneton, \( S \) the electron spin operator, \( I \) the nuclear spin operator, \( H \) the applied magnetic field, \( g \) the \( g \)-value tensor and \( A \) the hyperfine interaction tensor.

In single crystals, one usually observes orientation dependent EPR spectra. For VO\(^{2+} \) complexes, \( g \) and the hyperfine tensor \( A \) are found to be axially symmetric, thus permitting one to use the perturbation results for the axial symmetry which were first given by Bleaney [17]. The resonant magnetic field \( H_m \) for the \( m^{th} \) hyperfine line \((m = 1, 0, -1, \ldots, -1) \) with \( S = 1/2 \) is given by the expression

\[
H_m = H_k - ma - \left[ I (I + 1) - m^2 \right] \frac{a_{2z}^2 (a_{2x}^2 + a_{2y}^2)}{4 a^2 G} \\
+ \frac{m^2 \sin^2 \theta}{g^2} \left( \frac{g_{m} g_{I}^2}{g^2} \right) \frac{(a_{m}^2 - a_{y}^2)^2}{8 a^2 G} 
\]  

(2)

here \( \theta \) is the angle between the magnetic field and the symmetry axis. The effective \( g \)-factor is given by \( g^2 = g_{m}^2 \cos^2 \theta + g_{y}^2 \sin^2 \theta \).

The effective hyperfine splitting constant \( A \) is then given by

\[
g^2 A^2 = g_{m}^2 A_{m}^2 \cos^2 \theta + g_{y}^2 A_{y}^2 \sin^2 \theta
\]  

(3)
which along with $A_{||}$ and $A_{\perp}$ are converted into gauss using expressions of the form $a = \frac{hcA}{g\beta}$. The microwave frequency is also converted into gauss, thus reducing all parameters in equation (2) to magnetic field units.

The magnetic field positions for parallel and perpendicular components are given by

$$H_{\parallel} = H_0 - A_{||} m - \frac{A_{\perp}^2}{2 H_0 \beta^2 g^2} \left[ I(I+1) - m^2 \right] \quad (4)$$

$$H_{\perp} = H_0 - \frac{A_{\perp}}{g} m - \frac{A_{||}^2 + A_{\perp}^2}{4 H_0 \beta^2 g^2} \left[ I(I+1) - m^2 \right] \quad (5)$$

4.2 Optical absorption spectra

The vanadyl (VO$^{2+}$) ion has one unpaired electron in the 3d shell. Therefore, according to Hund's rule the ground state term for the VO$^{2+}$ ions is $^2D$. In an octahedral (Oh) symmetry, the $^2D$ orbital energy will split as upper $e_g$ level and the ground $t_{2g}$ level. Thus $e_g$ orbital gives rise to a $^2E_g$ state and $t_{2g}$ orbital gives rise to a $^2T_{2g}$ state. The d electron occupies the $^2T_{2g}$ ground state. In Oh symmetry, VO$^{2+}$ ion gives only one band corresponding to $^2T_{2g} \rightarrow ^2E_g$ transition. However, due to the non-symmetrical alignment of the $V=O$ bond, VO$^{2+}$ site symmetry lowers to tetragonal or rhombic. In a tetragonal symmetry, the lower $^2T_{2g}$ level splits into $^2B_{2g}$ and $^2E_g$ levels and the upper $^2E_g$ level splits into $^2B_{1g}$ and $^2A_{1g}$ levels. The schematic diagram of the splitting of energy levels
of vanadyl ion is shown in Fig. 2. In tetragonal symmetry, three bands due to $^{2}B_{2g} \rightarrow ^{2}E_{g}$, $^{2}B_{2g} \rightarrow ^{2}B_{1g}$ and $^{2}B_{2g} \rightarrow ^{2}A_{1g}$ are expected. It has been reported by Kivelson and Lee [18] that $^{2}B_{2g}$ state lies at the lowest. Ballhausen [19] reported that the $^{2}A_{1g}$ state is less stable than the $^{2}B_{1g}$ state in VO$^{2+}$. The order of the energy levels is therefore represented as shown in Fig. 2.

The above crystal field theory considers only $\sigma$-bonding and hence it could not provide an adequate description of the electronic structure of VO$^{2+}$ ion. To explain the complete electronic structure, Ballhausen and Gray [20] proposed a molecular orbital scheme by considering both $\sigma$- and $\pi$-bonds between vanadium and oxygen. The Ballhausen and Gray molecular orbital (MO) scheme for VO$^{2+}$ in VOSO$_4$·5H$_2$O lattice is shown in Fig. 3. As is seen from the figure, the energy level order obtained $b_{2} < e^{*} < b_{1}^{*} < 1a^{*}$ ($^{*}$ represents antibonding nature of the orbital) is the same as given by the crystal field model (Fig. 2).

5. Results and discussion

5.1 EPR studies

The EPR studies on paramagnetic ions in carboxylic acids have yielded many interesting results [21–24]. In spite of the fact that there should be line broadening due to interaction of paramagnetic host and impurity ions, reasonably sharp EPR spectra were observed in VO$^{2+}$ doped CoMTH single crystals. EPR spectra were recorded in three mutually perpendicular planes, defined by X, Y and Z axes. The Z-axis is chosen to be parallel to the direction.
Fig. 2: The schematic representation of the energy levels of the VO$^{2+}$ ion as split in octahedral ($O_h$) and tetragonal ($C_{4v}$) distortion.
Fig. 3: Molecular orbital scheme for the VO(H₂O)₅²⁺ ion.

(b - Bonding, n - Non-Bonding, * - Anti-Bonding)
of the magnetic field for which the absolute maximum separation of the hyperfine lines occurs. Fig. 4 shows the EPR spectrum of VO$^{2+}$ ions doped CoMTH single crystals at room temperature for H||Z axis in the ZX' plane. Two magnetic VO$^{2+}$ molecular ions in the unit cell of CoMTH giving rise to two sets of eight lines with differing intensities were observed. This octet spectrum is due to the interaction of electron spin ($S = 1/2$) with $^{51}$V nucleus ($I = 7/2$). These two VO$^{2+}$ ions are denoted as I and II in Fig. 4. In addition, another set of much weaker EPR lines was also observed and is denoted as III in Fig. 4. The ratios of the intensities of the EPR lines corresponding to the VO$^{2+}$ complexes I, II and III were found to be 12 : 6 : 1. This reveals the presence of three vanadyl complexes with different populations. The EPR spectra corresponding to complex III were not studied in detail due to their much weaker intensities. The octet patterns of these complexes coincide along the crystallographic axes. Fig. 5 shows the spectrum of the two complexes I and II coinciding along the crystallographic axis in ZX' plane.

The angular variation spectra were studied corresponding to two sets of intense vanadyl lines (I & II) in all the three crystallographic planes. The analysis has been carried out only for two intense signals I and II, since the weak lines (III) were quite difficult to follow. The angular variation plots of intense vanadyl complexes in the, ZX', Y'Z and X'Y' plane are shown in Figures 6(a), (b) and (c) respectively. The angular variation studies reveal that the sites of complexes I and II are substitutional. This can also be judged well by the
Fig. 4: EPR spectrum of VO$^{2+}$:CoMTH single crystal at room temperature for $H \parallel Z$ axis in the $ZX'$ plane.
Fig. 5: EPR spectrum of VO$^{2+}$:CoMTH single crystal for two complexes I and II coinciding along the X-axis in ZX' plane. The spectrum observed at 103 K is also shown in the same figure.
Fig. 6(a): A plot of angular variation EPR spectra of VO$_2^+$:CoMTH single crystal in ZX$^c$ plane. The open circles and triangles represent experimental data, while the continuous lines connect data points belonging to the same transition.
Fig. 6(b): A plot of angular variation EPR spectra of VO$^{2+}$:CoMTH single crystal in Y'Z plane. The open circles and triangles represent experimental data, while the continuous lines connect data points belonging to the same transition.
Fig. 6(c): A plot of angular variation EPR spectra of VO$^{2+}$:CoMTTH single crystal in XY plane. The open circles and triangles represent experimental data, while the continuous lines connect data points belonging to the same transition.
comparable ionic radii of V" (0.63 Å) and Co²⁺ (0.72 Å). From the angular variation studies, these complexes are found to be physically equivalent, but magnetically inequivalent. The two vanadyl complexes may therefore orient themselves along different directions in the unit cell, i.e. along one of the Co-H₂O bond directions. Thus, the orientation of the two VO²⁺ sites substituting the Co²⁺ ions in the unit cell are different. Therefore, it appears that the site of Co²⁺ ion is the most probable site for substitution by VO²⁺ ion.

5.2. Spin-Hamiltonian parameters

As the vanadyl ion has a single unpaired electron (S = 1/2) interacting with its nucleus (⁵¹V, 99.8% abundant, I = 7/2), the following spin-Hamiltonian can be used to analyse the EPR spectra [25].

\[
\mathcal{H} = \beta (g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z \quad \text{(6)}
\]

where the terms have their usual meaning. The g and A values were calculated at each interval from the angular variation spectra in the three mutually perpendicular planes. The diagonalization procedure was carried out following the standard procedure given by Schonland [26] in the analysis of EPR spectra, for obtaining the principal g and A tensors and the direction cosines of \(g^2\) and \(g^2A^2\) tensors corresponding to the three principal directions. The g and A values and the direction cosines of \(g^2\) and \(g^2A^2\) tensors for VO²⁺ ions-doped CoMTH single crystals are given in Table 1.
Table I: Spin-Hamiltonian parameters and direction cosines for g and A tensors of VO$^{2+}$:CoMTH single crystal and polycrystalline sample. A and P values are in units of $10^{-4}$ cm$^{-1}$.

<table>
<thead>
<tr>
<th>Site</th>
<th>$g_x$, $A_x$, $P$ and $K$ Parameters</th>
<th>Direction cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single crystal</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$g_x = 1.935$</td>
<td>0.7943</td>
</tr>
<tr>
<td></td>
<td>$g_y = 1.975$</td>
<td>0.5014</td>
</tr>
<tr>
<td></td>
<td>$g_k = 2.016$</td>
<td>0.4552</td>
</tr>
<tr>
<td></td>
<td>$A_x = 188$</td>
<td>0.9841</td>
</tr>
<tr>
<td></td>
<td>$A_y = 79$</td>
<td>0.1617</td>
</tr>
<tr>
<td></td>
<td>$A_z = 71$</td>
<td>0.2998</td>
</tr>
<tr>
<td></td>
<td>$P = 122$</td>
<td>0.5858</td>
</tr>
<tr>
<td></td>
<td>$k = 0.89$</td>
<td>0.8564</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4847</td>
</tr>
<tr>
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<td>0.1612</td>
</tr>
<tr>
<td>Complex - I</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>$g_x = 1.975$</td>
<td>0.4553</td>
</tr>
<tr>
<td></td>
<td>$g_y = 1.985$</td>
<td>0.7054</td>
</tr>
<tr>
<td></td>
<td>$g_k = 2.005$</td>
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</tr>
<tr>
<td></td>
<td>$A_x = 188$</td>
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<tr>
<td></td>
<td>$A_y = 77$</td>
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<tr>
<td></td>
<td>$A_z = 67$</td>
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<tr>
<td></td>
<td>$P = 122$</td>
<td>0.0964</td>
</tr>
<tr>
<td></td>
<td>$k = 0.89$</td>
<td>0.8851</td>
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<td></td>
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<td>0.5138</td>
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<td></td>
<td></td>
<td>0.9307</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.3804</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1055</td>
</tr>
<tr>
<td>Polycrystalline sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$g_0 = 1.950$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$g_0 = 1.990$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_0 = 187$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_0 = 73$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$P = 126$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k = 0.85$</td>
<td></td>
</tr>
</tbody>
</table>

The errors in g and A values are $\pm 0.002$ and $\pm 3 \times 10^{-4}$ cm$^{-1}$ respectively.
The spin-Hamiltonian parameters indicate that the symmetry of VO$^{2+}$ ions in this lattice is orthorhombic. The higher symmetry ($C_{2v}$) of vanadyl sites as indicated by EPR data, suggests a local relaxation to create the observed rhombicity around VO$^{2+}$ ions in this host. Hence, one can safely confirm that by the introduction of VO$^{2+}$ ions into the CoMTH lattice, the environment around the VO$^{2+}$ ions rearranges itself to provide the observed rhombic symmetry at Co$^{2+}$ sites.

The spin-Hamiltonian parameters can be determined more easily by recording EPR spectra of polycrystalline sample (the crystals are crushed to a fine powder). The polycrystalline spectrum can be used as a cross-check for the single crystal data. Fig. 7 shows the EPR spectra of a polycrystalline sample of VO$^{2+}$:CoMTH at room temperature and at 123K respectively. The spin-Hamiltonian parameters obtained from the polycrystalline sample are also presented in Table 1.

6. Optical absorption studies

Fig. 8 shows the optical absorption spectrum of VO$^{2+}$:CoMTH single crystal at room temperature. The spectrum exhibits two bands centred at 750 nm (13325 cm$^{-1}$) and 622 nm (16060 cm$^{-1}$). These bands are assigned to d–d transitions $^2B_{2g} \rightarrow ^2E_g$ and $^2B_{2g} \rightarrow ^2B_{1g}$ respectively [27]. By correlating EPR and optical absorption data, the molecular orbital coefficients ($\beta_1^2$ and $\epsilon^2$) are calculated for vanadyl ion.
Fig. 7: The EPR spectra of polycrystalline sample of VO$^{2+}$:CoMTH at room temperature and at 123 K
Fig. 8: The optical absorption spectrum of VO\textsuperscript{2+}:CoMTH single crystal at room temperature.
7. Calculation of molecular orbital bonding coefficients, the Fermi contact term \((k)\) and the dipolar hyperfine coupling parameter \((P)\)

The molecular orbital bonding coefficients \((\beta_1^2 \text{ and } \epsilon^2)\), the Fermi contact term \(k\) and the dipolar hyperfine coupling constant \(P\) are calculated from the following formulae given by Kivelson and Lee [18]

\[
\begin{align*}
g_\parallel &= g_e - 8 \left( \lambda \beta_1^2 / E_2 \right), \\
g_\perp &= g_e - 2 \left( \lambda \epsilon^2 / E_1 \right)
\end{align*}
\]

and

\[
\begin{align*}
A_\parallel &= P \left[ - (4/7 + k) - 8 \left( \lambda \beta_1^2 / E_2 \right) - 6/7 \left( \lambda \epsilon^2 / E_1 \right) \right], \\
A_\perp &= 2 \left[ (2/7 - k) - 11/7 \left( \lambda \epsilon^2 / E_1 \right) \right]
\end{align*}
\]

where the terms \(\beta_1^2\) and \(\epsilon^2\) are bonding coefficients of \(| x^2 - y^2 >\) and \(| xz >\) orbitals, which represent the in-plane \(\sigma\)-bonding and out-of-plane \(\pi\)-bonding, respectively. \(\lambda\) is the spin–orbit coupling coefficient, which is assumed to be 170 cm\(^{-1}\) for VO\(^{2+}\) ion [18]. \(E_1\) and \(E_2\) are energy separations from the ground state \(^3\)B\(_{2g}\) to the two nearest higher states \(^2\)E\(_g\) and \(^3\)B\(_{1g}\), respectively. \(g_e\) is the free electron \(g\) value \((g_e = 2.0023)\). \(P\) represents the dipole–dipole interaction of the electronic and nuclear moments \((P = g_e g_N \beta_e \beta_N < r^3 >)\), \(k\) is the Fermi contact parameter, which is related to the unpaired electron density at the vanadium nucleus and the other symbols have their usual meaning. Using the EPR and optical data, Eqs. (7) to (10) can be solved to get \(\beta_1^2\), \(\epsilon^2\), \(P\) and \(k\).
The values of molecular orbital coefficients obtained in the present work are $\beta_1^2 = 0.62$ and $\varepsilon^2 = 0.48$ respectively. The parameters $(1 - \beta_1^2)$ and $(1 - \varepsilon^2)$ are the measures of the covalency rates [3,10,23]. The former gives an indication of the influence of $\sigma$-bonding between vanadium atom and equatorial ligands while the latter indicates the influence of $\pi$-bonding with the vanadyl oxygen. The calculated values of $\beta_1^2$ and $\varepsilon^2$ indicate that the in-plane $\sigma$-bonding is moderately ionic and out-of-plane $\pi$-bonding is significantly covalent.

The values of $P$ and $k$ can be calculated using the above expressions. The calculated values of $P$ and $k$ are listed in Table 1. The parameter $k$ indicates extreme sensitivity to the deformations of the electron orbitals of the central vanadium ion. The large value of $k$ indicates a large contribution to the hyperfine constant by the unpaired electron and also probably a contribution from spin polarization. The standard value of $P$ for a free ion is $160 \times 10^4$ cm$^{-1}$. The calculated value of $P$ in the present system is $126 \times 10^4$ cm$^{-1}$, which is considerably reduced (78%), which indicates a significant amount of covalent bonding in the complex. The values of $P$ and $k$ are close to the values reported for VO$^{2+}$ ions in other lattices [10,11,22,23].

8. EPR spectra at different temperatures

EPR spectra of VO$^{2+}$ ions doped in CoMTH have been studied at various temperatures from 103 to 373 K. The linewidth variation studies were carried out choosing the EPR spectrum of VO$^{2+}$:CoMTH in ZX' plane when the magnetic field is along the X-axis. An appreciable linewidth variation of
The observation of narrow signals at room temperature and the broadening of the lines at low temperatures can be explained on the basis of a model proposed by Mitsuma [29]. If the motional narrowing is due to exchange between the host ions, the impurity linewidths will be temperature independent until the temperature is very much lowered and a change in g-value with temperature is also expected. In the present work, an appreciable change in
Fig. 9: A plot of inverse of temperature versus logarithmic intensity for the hyperfine line $M_z = 5/2$
linewidth with temperature has been observed and there is no change in g-values. This can be explained on the basis of spin-lattice relaxation, where the fast spin-lattice relaxation of the paramagnetic host provides sufficient modulation of the dipolar interactions between the host and the impurity ions [29,30], which is mainly responsible for these linewidth variations of hyperfine lines of VO$^{2+}$ ions in Co$^{2+}$ lattices.

9. Estimation of spin-lattice relaxation time

The linewidth variations of VO$^{2+}$ hyperfine lines in CoMTH can be understood on the basis of host spin-lattice relaxation mechanism. The fast spin-lattice relaxation of the host ions can randomly modulate the dipolar interaction between paramagnetic host and impurity ions, resulting in what is called host spin-lattice relaxation narrowing [29].

When the host spin-lattice relaxation narrowing mechanism is effective, the host spin-lattice relaxation time ($T_1$) is given by [29,30]

$$T_1 = \frac{3}{10} \left( \frac{\hbar}{2 \gamma_1 \beta} \right) \left( \Delta B_{\text{imp}} / B_d^2 \right)$$  ----- (11)

with

$$B_d^2 = 5.1 \left( \gamma_1 \beta \eta \right)^2 S_h (S_h + 1)$$

In the above equation, $\hbar$ is Planck's constant, $\beta$ is Bohr magneton, $\gamma_1$ is the host g-value, $S_h$ is the effective host spin and is taken to be 1/2. $\eta$ is the number of host spins per unit volume which can be calculated from crystallographic data.
of the crystal lattice and $B_{\text{imp}}$ is the impurity linewidth. As the crystal structure of CoMTH is not available, the crystal structure data of isomorphous $\text{H}_2\text{Ni(C}_6\text{H}_2\text{O}_4)_2\cdot4\text{H}_2\text{O}$ has been used in the calculation of $n$. The $g$ value for $\text{Co}^{2+}$ ions in $\text{Co}^{2+}:(\text{NH}_4)_2\text{Zn(SO}_4)_2\cdot6\text{H}_2\text{O}$ has been taken to be the $g_h$ in the present work. The detailed linewidth studies in $\text{VO}^{2+}:\text{CoMTH}$ were carried out for $M_i = 5/2$ hyperfine line at different temperatures.

From the observed linewidth of $\text{VO}^{2+}$ in CoMTH, the order of spin-lattice relaxation time ($T_1$) obtained for $\text{Co}^{2+}$ ions at room temperature is $2.51 \times 10^{-12}$ s. The $T_1$ values calculated for this system along with the other $\text{VO}^{2+}$ doped systems are given in Table 2. The $T_1$ values have been calculated at different temperatures.

Table 2: Host spin-lattice relaxation time ($T_1$) of $\text{Co}^{2+}$ in some high-spin cobalt complexes at 300 K

<table>
<thead>
<tr>
<th>System</th>
<th>$T$ ($10^{-12}$ s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{VO}^{2+}:\text{Cs}_5\text{Co(SO}_4)_6\text{H}_2\text{O}$</td>
<td>1.90</td>
<td>[10]</td>
</tr>
<tr>
<td>$\text{Mn}^{2+}:\text{CoH}<em>6\text{CoMo}</em>{12}\text{O}_{42}\cdot12\text{H}_2\text{O}$</td>
<td>2.60</td>
<td>[7]</td>
</tr>
<tr>
<td>$\text{Mn}^{2+}:\text{Co(H}_2\text{O})_6\cdot(\text{C}_3\text{H}_2\text{N}_3\text{SO}_3^-)\cdot4\text{H}_2\text{O}$</td>
<td>0.54</td>
<td>[8]</td>
</tr>
<tr>
<td>$\text{VO}^{2+}:\text{Rb}_2\text{Co(SeO}_4)_2\cdot6\text{H}_2\text{O}$</td>
<td>2.00</td>
<td>[31]</td>
</tr>
<tr>
<td>$\text{VO}^{2+}:\text{H}_2\text{Co(C}_4\text{H}_2\text{O}_4)_3\cdot4\text{H}_2\text{O}$</td>
<td>2.51</td>
<td>Present Work</td>
</tr>
</tbody>
</table>
The temperature dependence of $T_1$ can be approximately given by the relation [25]

$$\frac{1}{T_1} = A T + B T^n$$ ---- (12)

Fig. 10 shows a logarithmic graph of the estimated $T_1$ as a function of temperature for the Co$^{2+}$ host ion when the magnetic field is parallel to Z-axis. It is found from the slope that $T_1 \propto T^n$ where $n = 1.0$. $T_1$ is found to be of the same order as observed for other cobalt salts [1,5,7,8,10,31]. From the nature of the graph, it is postulated that two-phonon Raman process may be the main mechanism for the spin-lattice relaxation.

10. Conclusions

1. EPR spectra of VO$^{2+}$ ions in cobalt maleate tetrahydrate (CoMTH) have been studied in the temperature range 103–373 K. Three vanadyl complexes have been identified; two are magnetically inequivalent and one set of weaker lines possess intensity much distinguishable than other two. The detailed EPR analysis indicates that the magnetically inequivalent complexes occupy the Co$^{2+}$ substitutional sites in the lattice.

2. The spin-Hamiltonian parameters suggest that the symmetry is orthorhombic.
Fig. 10: A logarithmic plot showing the spin-lattice relaxation time $T_1$ of Co$^{2+}$ in CoMTH single crystal as a function of temperature.
3. The widths of VO$^{2+}$ resonance lines increase with decreasing temperature. This has been explained as due to host spin-lattice relaxation narrowing mechanism. The host spin-lattice relaxation time ($T_1$) calculated from the linewidth of VO$^{2+}$ is comparable to the values reported for other cobalt systems.

4. From the temperature-dependent $T_1$, two-phonon Raman process is found to be the main mechanism for spin-lattice relaxation, as was observed in similar cases in Co$^{2+}$ hosts.

5. The optical absorption spectrum at room temperature shows two absorption bands characteristic of VO$^{2+}$ ions. By correlating EPR and optical data, the molecular orbital coefficients have been evaluated.
References


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