EPR and optical absorption spectra of Cu(II) doped zinc potassium phosphate hexahydrate

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EPR and optical absorption spectra of copper-doped zinc potassium phosphate hexahydrate (ZPPh) are recorded both at room temperature and liquid nitrogen temperature. Both, EPR and optical spectra are characteristic of Cu(II) ion in rhombically distorted octahedral symmetry. Spin-Hamiltonian and bonding parameters have also been evaluated as follows: $g_1=2.372$, $g_2=2.188$, $g_3=2.032$, $A_1=78 \times 10^{-4}$ cm$^{-1}$, $A_2=48 \times 10^{-4}$ cm$^{-1}$, $A_3=63 \times 10^{-4}$ cm$^{-1}$; $\alpha=0.55$.

Zinc potassium phosphate hexahydrate (ZnKPO$_4$.6H$_2$O), hereafter called ZPPh is analogous to the bio-mineral, struvite (MgNH$_4$PO$_4$.6H$_2$O), which belongs to the orthorhombic space group, Pmn2$_1$ with two molecules per unit cell. In struvite, Mg(II) is octahedrally coordinated by six water molecules. Cu(II) ($d^9$) is the simplest and the most sensitive paramagnetic probe that enters easily into a number of hexa-aqua coordinated host lattices. Cu(II) ion replaces the central metal ion and therefore exhibits distorted octahedral coordination. The present study on the EPR and optical absorption spectra of Cu(II) doped in ZPPh has been undertaken with a view to ascertain distortion in the hexa-aqua coordinated site and the bonding nature of Cu(II) dopant.

**Experimental**

Equal volumes of equimolar solutions of potassium dihydrogen phosphate and zinc sulphate were mixed and to this was added 0.1 mole percent of copper sulphate. Good crystals were grown by slow evaporation in about ten days. Crystals of ~2 mm thickness were selected for optical absorption studies. The spectra were recorded in the UV-vis-NIR region on a Hitachi U-3400 spectrophotometer both at room temperature as well as liquid nitrogen temperature.

The EPR spectra of the polycrystalline sample were recorded on a Varian E-112 X-band spectrometer operating at 9.12 GHz with 100 kHz modulation at laboratory and liquid nitrogen temperatures.

**Results and discussion**

The EPR spectrum recorded at liquid nitrogen temperature is shown in Fig. 1. It consists of four lines each in the low field ($g_1$), mid field ($g_2$) and high field ($g_3$) regions. From the peak positions and their separations, the spectroscopic splitting factors ($g$-values) and hyperfine structure constants ($A$-values) were determined to be $g_1=2.372$, $g_2=2.188$, $g_3=2.032$, $A_1=78 \times 10^{-4}$ cm$^{-1}$, $A_2=48 \times 10^{-4}$ cm$^{-1}$ and $A_3=63 \times 10^{-4}$ cm$^{-1}$.

From the above data, information on the electronic ground state of Cu(II) can easily be inferred. If for $g$-values, $g_1 > g_2 > g_3$, the quantity $R=(g_2-g_3)/(g_3-g_2)$ is greater than unity, the ground state is predominantly $^2A_1(d_{xy-z^2})$ and if it is less than unity it is $^2A_1(d_{xy-z^2})$ (ref. 9). In the present study the value of $R$ was found to be of the order 0.85, i.e. less than unity, indicating that the ground state is $^2A_1(d_{xy-z^2})$.

From the EPR data, the covalency parameter ($\alpha^2$) has been calculated making use of the relevant formula and assuming the value of the free ion dipolar term $P$ to be 0.036 cm$^{-1}$ and $g_a=2.0023$ to be $\alpha^2 = (7/6)(A_1 - A_2)/P - (g_r-g_a) + (11/14)(g_r-g_1) - (6/14)(g_r-g_3)$. The value of $\alpha^2$ was found to be 0.55.

![Fig. 1—EPR spectrum of Cu(II) in ZPPh at liquid nitrogen temperature.](image-url)
The optical absorption spectra at room (RT) and liquid nitrogen temperature (LNT) are shown in Fig. 2. At RT, two bands are observed at 845 nm (11831 cm\(^{-1}\)) and 1300 nm (7690 cm\(^{-1}\)). At LNT, the bands show shifts towards higher frequency and are observed at 825 (12117 cm\(^{-1}\)) and 1290 nm (7750 cm\(^{-1}\)) respectively. Two more weak bands are observed at 750 (13330 cm\(^{-1}\)) and 1040 nm (9613 cm\(^{-1}\)). For Cu(II) in rhombic symmetry, the general ordering of the energy levels is as follows\(^\text{10}\):

\[
{^2A_f(d_{2z^2})} < {^2A_f(d_{z^2-x^2})} < {^2A_f(d_{xy})} < {^2A_f(d_{y^2})} < {^2B_f(d_{y^2})} < {^2B_f(d_{x^2-y^2})}.
\]

Accordingly, the optical absorption bands at 1290, 1040, 825 and 750 nm are attributed to transitions from \({^2A_f(d_{2z^2})}\) to \({^2A_f(d_{z^2})}\), \({^2A_f(d_{xy})}\), \({^2B_f(d_{x^2})}\), and \({^2B_f(d_{y^2})}\) respectively. These observations are in tune with those reported earlier\(^\text{11}\) and the bands accordingly are ascribed to Cu(II) in octahedral coordination with rhombic distortion (\(C_{2v}\)). The band head data and their assignments are presented in Table 1.

The quartet structure of the \(g_0\), \(g_2\), and \(g_1\) components of the EPR spectrum suggests rhombically distorted nature of the hexa-aqua coordinated Cu(II) ion in ZPPH. The bonding parameter \(\alpha'\) (=0.55) indicates predominant covalency for the in-plane \(\sigma\)-bonding\(^\text{10}\). The optical absorption spectrum is characteristic of rhombically distorted octahedral Cu(II) exhibiting four bands. The observed shifts of the bands to higher frequency at LNT are in accordance with the theoretical prediction for the hexa-aqua coordinated Cu(II) ion. Thus the results of the optical and EPR investigations reported in the present note conclusively prove that the site symmetry of Cu(II) ion in ZPPH is rhombically distorted octahedral with the ground state \({^2A_f(d_{x^2-y^2})}\).

### Table 1—Band head data and the assignments for Cu(II) in ZPPH

<table>
<thead>
<tr>
<th>Transition</th>
<th>300K (cm(^{-1}))</th>
<th>77K (cm(^{-1}))</th>
</tr>
</thead>
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<tr>
<td>(2A_f(d_{2z^2})) (\rightarrow) (2A_f(d_{2z}))</td>
<td>1300</td>
<td>7690</td>
</tr>
<tr>
<td>(2A_f(d_{2z^2})) (\rightarrow) (2A_f(d_{x^2}))</td>
<td>—</td>
<td>1290</td>
</tr>
<tr>
<td>(2A_f(d_{2z^2})) (\rightarrow) (2B_f(d_{x^2}))</td>
<td>845</td>
<td>11831</td>
</tr>
<tr>
<td>(2A_f(d_{2z^2})) (\rightarrow) (2B_f(d_{y^2}))</td>
<td>—</td>
<td>750</td>
</tr>
</tbody>
</table>

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### References