Electron Paramagnetic Resonance of Cu$^{2+}$ Doped Na$_2$HAsO$_4$·7H$_2$O Single Crystals

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The electron paramagnetic resonance spectra of Cu$^{2+}$ doped Na$_2$HAsO$_4$·7H$_2$O single crystals were studied at room temperature. The results indicate the substitutional entrance of Cu$^{2+}$ in two magnetically inequivalent Na$^+$ sites. Charge compensation is supposed to be fulfilled by proton vacancies. The spin Hamiltonian parameters were determined. The ground state for Cu$^{2+}$ seems to indicate the dominance of the d$_{2z}$ orbital and therefore a compression of the distorted octahedron along its C$_4$ axis.

Key words: EPR; Cu$^{2+}$; Sodium Hydrogen Arsenate.

Introduction

The electron paramagnetic resonance (EPR) method is very useful for obtaining a detailed description of the ground state of a paramagnetic ion, and it enables one to understand the nature of the electric field symmetry produced by the ligands around the metal ions. Particularly, Cu$^{2+}$ has been extensively used as a probe to obtain information about crystalline electric fields and phase transitions [1 - 6]. In lattices containing divalent cations Cu$^{2+}$ was mostly found to enter the lattice substitutionally at the place of the divalent cation. However, when a divalent impurity cation enters the host lattice substitutionally, replacing the monovalent cation, an electric charge imbalance arises, and this must be compensated by some means. Mostly, this charge compensation is supposed to be fulfilled by another monovalent cation vacancy, and in some cases it has been found that the magnetic coupling tensors have their principal axes pointing towards the divalent impurity – monovalent cation vacancy direction [1].

In the majority of Cu$^{2+}$ systems studied so far, the ion was found to have a d$_{2z}$ ground state, corresponding to axial lengthening of the octahedron of ligands in which the Cu$^{2+}$ ion resides. On the other hand, the d$_{2z}$ ground state, which corresponds to the axial compression, has been observed only in a few cases, like Cu$^{2+}$ in Hoffman type benzene aniline clathrates [7], K$_2$CuF$_4$ [8], Cu(NH$_3$)$_2$Cl$_2$ [9], Cu(NH$_3$)$_2$Br$_2$ [9], Cu(dien)$_2$(NO$_3$)$_2$ [10], (NH$_4$)$_2$Zn(NH$_3$)$_2$(CrO$_4$)$_2$ [11] etc. In all these cases, the axial compression arises from two of the octahedrally disposed ligands coming closer to copper due to crystal packing. Furthermore, the low symmetry crystal fields cause mixed d$_{2z}$ and d$_{xy}$ ground states [12], and such mixed ground states lead to orthorhombicity of g tensors and low magnitudes of hyperfine coupling. In the light of these studies we looked for a suitable crystal. Since in Na$_2$HAsO$_4$·7H$_2$O single crystals, the Na$^+$ ion is surrounded by a distorted octahedron of oxygens of water molecules, it seemed interesting to study Cu$^{2+}$ in this compound. To our knowledge such a study has not been carried out so far.

Experimental

The Na$_2$HAsO$_4$·7H$_2$O single crystals, doped with Cu$^{2+}$, were grown at room temperature by slow evaporation of saturated aqueous solution. Well developed good crystals were obtained in about three weeks. Concerning crystal data, Na$_2$HAsO$_4$·7H$_2$O crystallizes in the monoclinic system, space group P2$_1$/n; the unit cell parameters are $a = 1.065$, $b = 1.101$ and $c = 0.939$ nm, $\beta = 95°\ 26'$. The unit cell contains four molecules. The structure consists of layers normal to
[101] in which the two crystallographically independent Na atoms coordinate six oxygen atoms of the water molecules [13]. The Na-polyhedra form chains along [010], which are joined by hydrogen bonds. The AsO₄ tetrahedra lie between these layers and link them by hydrogen bonds involving their own oxygen atoms and those of the water molecules.

The spectra were recorded using a Varian E-109C model X-band EPR spectrometer. The magnetic field modulation frequency was 100 kHz. The single crystals were mounted on a goniometer and the spectra were recorded in the three mutually perpendicular planes (ac*, bc*, ab) at 10° intervals at room temperature. The g values were found by comparison with a diphenylpicrylhydrazyl sample of g = 2.0036.

**Results and Discussion**

Two typical EPR spectra of Cu²⁺ doped Na₂HAsO₄·7H₂O single crystals are shown in Fig. 1 for two different orientations of the magnetic field. These spectra are obviously belonging to Cu²⁺ for which S = 1/2 and I = 3/2. The angular variations of the spectra in (ac*), (bc*) and (ab) planes at every 10° orientations of the magnetic field are shown in Figure 2. It can be seen from these that two sets of hyperfine lines were observed for all orientations in the (bc*) and (ab) planes, whereas only a single set of four hf lines was observed in the (ac*) plane. The whole spectra can be fitted to the spin Hamiltonian

\[ H = \beta B \cdot g \cdot S + I \cdot A \cdot S. \]
Fig. 2. Angular variation of the hyperfine lines of Cu$^{2+}$ in Na$_2$HAsO$_4$.7H$_2$O single crystal at room temperature.

Table 1. Spin-Hamiltonian parameters (g and A) and their direction cosines with respect to a, b, and c* axes for Cu$^{2+}$ in Na$_2$HAsO$_4$.7H$_2$O single crystal at room temperature. ($\Delta g = \pm 0.0005$ and $\Delta A = \pm 0.005$ mT).

<table>
<thead>
<tr>
<th>Sites</th>
<th>Principal values of g and A (mT)</th>
<th>Direction cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$g_{xx}$</td>
<td>$g_{yy}$</td>
</tr>
<tr>
<td>I</td>
<td>2.1697</td>
<td>1.9771</td>
</tr>
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<tr>
<td>II</td>
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<tr>
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<td>0.5324</td>
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</tbody>
</table>

The principal values of the g and A tensors and their direction cosines were found by diagonalization procedure [14]. The results are given in Table 1.

From these results it can be inferred that the Cu$^{2+}$ ions enter two inequivalent Na$^+$ places in the Na$_2$HAsO$_4$.7H$_2$O single crystals. This is consistent with the single crystal data, since the crystal has monoclinic symmetry and contains 4 molecules in the unit cell. In a monoclinic crystal, at most two inequivalent sites can be observed, and this is was indeed observed. We suggest that the charge compensation is fulfilled by proton vacancies of the nearest water molecules around the Na$^+$ ions, but this cannot be proved by means of the direction cosines in Table 1. Since the Na$^+$ ions are distant from one another, charge compensation cannot be fulfilled by Na$^+$ ion vacancies. The spin Hamiltonian parameters indicate a rhombic symmetry which is expected as the 6 oxygen atoms of the water molecules in the crystal form irregular octahedrons around the Na$^+$ ions.

It is known that, when $R = (g_{xx} - g_{yy})/(g_{zz} - g_{xx})$ is greater than unity, a predominantly d$_{z^2}$ ground state, and for $R$ less than unity a predominantly d$_{x^2-y^2}$
ground state would be expected for rhombic $g$ values with $g_{zz} > g_{xx} > g_{yy}$ [16]. The observed $R$ values for the two sites, $R_I = 1.2$ and $R_{II} = 1.2$, are larger than unity and therefore suggest predominantly $d_{z^2}$ ground state. Since the principal values of the $g$ tensor, and the principal values of the hyperfine tensor indicate rhombic symmetry, we could not obtain an observable powder spectrum of this compound. This is due to the intensity distribution to every component. The principal values of the $g$ tensors are similar to the ones observed for benzene and aniline clathrates with $d_{z^2}$ ground state [7], and therefore this shows the compression of the distorted octahedron of oxygens around the Cu$^{2+}$ ion along its $C_{4v}$ axis. The orthorhombicity of the $g$ and $A$ tensors indicate some $d_{x^2-y^2}$ mixing.

As a conclusion we can state that the Cu$^{2+}$ ion doped in Na$_2$HAsO$_4$·7H$_2$O largely has a $d_{z^2}$ ground state character and seems to constitute another example to this rarely observed case.