EPR Study of Cu^{2+} and VO^{2+} Ions in $[NH_4H_3(C_2O_4)_2]\cdot 2H_2O$ Single Crystals

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The EPR spectra of Cu^{2+} and VO^{2+} ions in $[NH_4H_3(C_2O_4)_2]\cdot 2H_2O$ single crystals were recorded at room temperature in three orthogonal planes. The spectra indicate that the Cu^{2+} and VO^{2+} ions substitute NH_4^+ ions. The principal values of the **g** and **A** tensors were determined. The ground state wave function of the Cu^{2+} ion in the lattice has been calculated and the covalancy and Fermi contact terms of the VO^{2+} ions were evaluated.

Key words: EPR; Ammonium Tetraoxalate; Vanadyl Ion; Cupper Ion.

1. Introduction

Studies on transition metal ions in diamagnetic host lattices are reported in [1 – 5]. Such ions form paramagnetic centers from which information about the local symmetry can be obtained. Using EPR, it is also possible to obtain information about the environmental effects and electrical fields of paramagnetic ions in complexes. For this, Cu^{2+} and VO^{2+} ions as probes have often been used [6 – 10]. In doped compounds, the Cu^{2+} and VO^{2+} ions mostly replace a divalent cation or a monovalent cation obtaining charge compensation with some other nuclei.

The present paper reports X-band EPR studies on Cu^{2+} and VO^{2+} doped ammonium tetroxalate di-hydrate (ATO) single crystals at room- and liquid nitrogen temperature. The principal values of the hyperfine parameters (**A**) and the **g** tensors have been evaluated.

2. Experimental

Ammonium oxalate, oxalic acid and sulphuric acid were obtained from Merck. Aqueous solution of the three compounds with equal molarities were mixed. Very small amounts of $CuSO_4\cdot 5H_2O$ and $VOSO_4\cdot 3H_2O$ were added as impurities in separate vessels, and the solutions were left for crystallization. Well-developed crystals, obtained within 6 – 7 days, were selected for the EPR study.

ATO is triclinic with space group P_1, and contains two molecules per unit cell, the dimensions of which are $a = 6.329$ Å, $b = 10.551$ Å, $c = 7.226$ Å, and the angles are $\alpha = 85.75^\circ$, $\beta = 97.62^\circ$, and $\gamma = 79.73^\circ$ [11].

A Varian E-109 C Model X-band EPR spectrometer was used to record the spectra with the magnetic field modulation frequency of 100 kHz. The single crystals were mounted on a goniometer, and the spectra were recorded in the three perpendicular planes (a^*c^*, a^*b, bc^*) at 10° intervals. A diphenylpicrylhydrazil sample ($g = 2.0036$) was used to correct the g value.

3. Results and Discussion

Figures 1 and 2 show EPR spectra of Cu^{2+} and VO^{2+} doped ATO single crystals, respectively. As can be seen the EPR spectra of both crystals yield single set data. The g^2 and A^2 (hyperfine) values of all lines are plotted against the rotational angle in each plane and are fitted to (1) to obtain $\mathbf{g}^2$ and $\mathbf{A}^2$ tensor elements.

$$\begin{aligned} g_k^2(\theta) &= g_{ii}^2\cos^2\theta_i + g_{jj}^2\sin^2\theta_j + 2g_{ij}^2\sin\theta_i\cos\theta_j, \\ a_k^2(\theta) &= a_{ii}^2\cos^2\theta_i + a_{jj}^2\sin^2\theta_j + 2a_{ij}^2\sin\theta_i\cos\theta_j, \end{aligned} \quad (1)$$

where i, j, and k stand for the x, y, and z axis, respectively.

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Table 1. Principal **g** and hyperfine values (**A**) and their direction cosines with respect to the d^*, b^*, and c axes for Cu^{2+} in ATO($\Delta g = \pm 0.005$, $\Delta A = \pm 0.5$ mT).

g	Direction cosines			Hyperfine(**A**)	Direction cosines		
	a^*	b	c^*	mT	a^*	b	c^*
$g_{xx} = 2.087$	0.280	0.007	0.959	$A_{xx} = 1.97$	−0.077	−0.475	0.876
$g_{yy} = 2.048$	−0.508	−0.847	0.154	$A_{yy} = 4.62$	0.573	0.697	0.429
$g_{zz} = 2.311$	0.814	−0.531	−0.236	$A_{zz} = 14.68$	0.815	−0.535	−0.219

Table 2. Principal **g**, hyperfine (**A**), β_2^2, and κ parameters for paramagnetic vanadyl complexes in ATO single crystals at room temperature.

$g_\parallel$	$g_\perp$	g_{ISO}	$A_\parallel(10^{-4}\,cm^{-1})$	$A_\perp(10^{-4}\,cm^{-1})$	$A_{ISO}(10^{-4}\,cm^{-1})$	β_2^2	κ
1.900	1.998	1.965	195.0	63.2	107.1	1	0.73

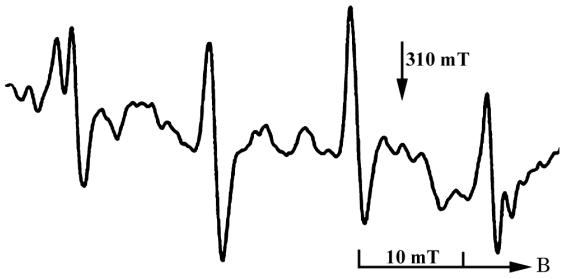

Fig. 1. EPR spectrum of Cu^{2+} doped in ATO single crystal. The magnetic field is in the bc^* plane and is 80° away from the b axis.

The Cu^{2+} and VO^{2+} spectra can be fitted to the spin Hamiltonian

$$\begin{aligned} \boldsymbol{H} = \beta(g_{xx}H_xS_x + g_{yy}H_yS_y + g_{zz}H_zS_z) \\ + A_{zz}I_zS_z + A_{yy}I_yS_y + A_{xx}I_xS_x, \end{aligned} \tag{2}$$

which includes only electron Zeeman and hyperfine interactions. The nuclear Zeeman, nuclear quadruple and spin-orbit interactions are neglected.

In order to find the g and A values, we have used an iterative numerical technique [12]. After the calculation, the **g** and **A** tensors were constructed and diagonalized to find the principal g and A values. The results are given in Tables 1 and 2 for Cu^{2+} and VO^{2+} ion complexes, respectively. The powder EPR spectra of the ATO crystals do not show any meaningful signal at room temperature for both ions. No significant changes of the Cu^{2+} and VO^{2+} ions are observed in the single crystals at room and liquid nitrogen temperature.

3.1. Cu^{2+} ions in ATO

From Fig. 1, the EPR spectra yield one set of four hyperfine lines. This is consistent with the triclinic symmetry. In Fig. 3 it is seen that, when the magnetic field is in the three planes, the angular variation of $A^2(\theta)$ shows only one site. These angular variations confirm the presence of one site in each plane and show the presence of only one magnetic site for Cu^{2+}. This result can be satisfactorily explained in terms of an unpaired electron interacting with a copper nucleus $[I = 3/2]$.

Figure 1 shows relatively broad lines of Cu^{2+} in ATO when the magnetic field makes 80° with the b axis in bc^* plane. The ^{65}Cu and ^{63}Cu lines are not clearly resolved in all orientations due to overlapping. From the EPR parameters, which are shown in Table 1 it can be seen that $g_{zz} > g_{xx} > g_{yy}$. When $R = (g_{xx} - g_{yy})/(g_{zz} - g_{xx})$ is less than unity, hence, the unpaired electron is dominantly in the $d_{x^2-y^2}$ state, and for R greater than unity it is in the $d_{3z^2-r^2}$ state. The observed R-values for Cu^{2+} is 0.180, which is much less than unity, so the ground state of the electron is $d_{x^2-y^2}$ [13–17]. In fact, when the site symmetry is rhombic, the ground state will be either $d_{x^2-y^2}$ or $d_{3z^2-r^2}$. The ground state wave function of the Cu^{2+} ion with $3d^9$ configuration in octahedral complexes was determined previously [1, 16, 17], so it can be written as

$$\Psi = \left(\alpha'^2\right)^{1/2}\left[\alpha|d_{x^2-y^2}\rangle + \beta|d_{3z^2-r^2}\rangle\right], \tag{3}$$

where the square of the α' is the covalancy parameter, which indicates the probability of finding the unpaired electron in the d orbital Cu^{2+}. The normalisation condition for mixing the coefficients α and β is

$$\alpha^2 + \beta^2 = 1. \tag{4}$$

Using (3) together with the experimental parameters obtained from the EPR spectra α, β, α'^2, and κ can be calculated. κ is the Fermi-contact term, and hence the ground-state wave function of Cu^{2+} in an ATO single crystal is evaluated. The values α'^2, α, β, and κ can be

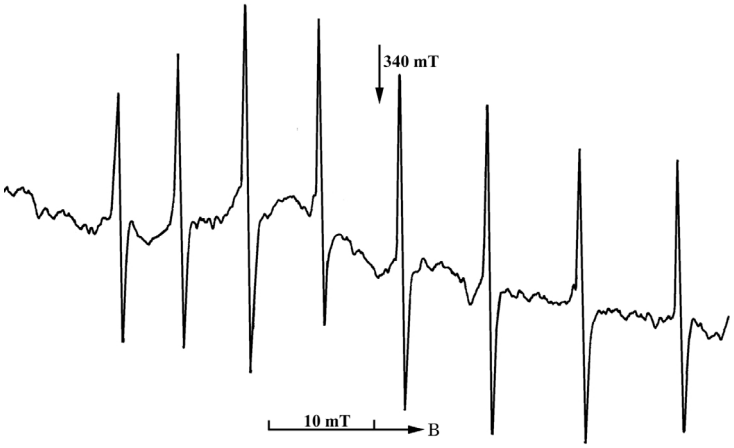

Fig. 2. EPR spectrum of VO^{2+} doped in ATO single crystal. The magnetic field is in the a^*c^* plane and is 40° away from the c^* axis.

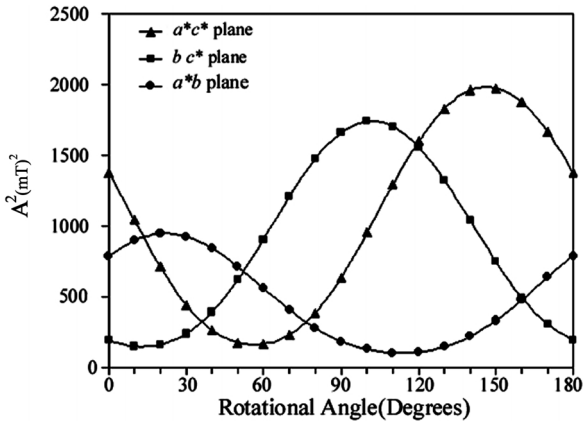

Fig. 3. Angular dependence of $A^2(\theta)$ for Cu^{2+} in an ATO single crystal.

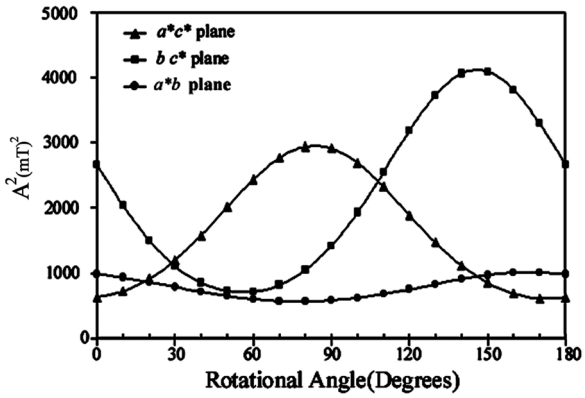

Fig. 4. Angular dependence of $A^2(\theta)$ for VO^{2+} in an ATO single crystal.

found as 0.917, 0.992, 0.126, and 0.295, respectively, utilizing the principal g and A values. Thus the ground state wave function of Cu^{2+} in the ATO lattice can be constructed as

$$\Psi = (0.917)^{1/2}\left[0,992|d_{x^2-y^2}\rangle + 0.126|d_{3z^2-r^2}\rangle\right]. \quad (5)$$

The covalancy parameter $\alpha'^2 = 0.917$ obviously explains that the unpaired electron spends 91.7% of its time on the Cu^{2+} d orbitals, and spends the rest in ligands. Since the coefficient of $d_{x^2-y^2}$ is significantly greater than that of $d_{3z^2-r^2}$, the unpaired electron spends most of its time on the $d_{x^2-y^2}$ orbital.

3.2. VO^{2+} Ions in ATO

The EPR spectrum of VO^{2+} ions in ATO single crystals consist of eight hyperfine lines, as shown in Fig. 2, which araises from the VO^{2+} ion with $I = 7/2$ and $3d^1$ configuration [18]. In Fig. 4 the positions of all lines are plotted against the rotational angle in mutually perpendicular three planes. Since the single crystal has triclinic symmetry, there is only one site in all orientations. These results suggest that the VO^{2+} ion has substitutes with the NH_4^+ ion. From Table 2, the principal g and A values have nearly axial symmetry. The determination of the parallel and perpendicular components of the g and A values from powder spectra was not successful due to the fact that the spectra of all orientations add up to zero. The VO^{2+} ion forming a $[VO(H_2O)_5]^{2+}$ complex with its nearest neighbours forms a tetragonally distorted octahedral symmetry. The distortion takes place along the V=O bond direction, and the degeneracy of the ground state d_{xy} of the vanadium atom in $3d^1$ configuration splits into

$d_{x^2-y^2}$, d_{xy} and d_{yz} [19]. The Hamiltonian parameters can be written as

$$A_{\parallel} = -P\left[\kappa - \frac{4}{7}\beta_2^2 - (g_e - g_{\parallel}) - \frac{3}{7}(g_e - g_{\perp})\right], \quad (6)$$

$$A_{\perp} = -P\left[\kappa - \frac{2}{7}\beta_2^2 - \frac{11}{14}(g_e - g_{\perp})\right], \quad (7)$$

where P is the dipol-dipol interaction constant between the magnetic moment of the electron and the vanadium nucleus, which is taken as 136 cm^{-1} [20]. κ is the Fermi contact parameter and represents the density of the unpaired electron. β_2^2 is the in-plane π-bonding coefficient of VO^{2+} with the ligands. From Table 2, using the expressions for the spin Hamiltonian parameters $A_{\perp}$, $A_{\parallel}$, $g_{\perp}$, $g_{\parallel}$ for $[VO(H_2O)_5]^{2+}$, the values of κ and β_2^2 are found to be 0.73 and 1, respectively. The deviation of β_2^2 from unity indicates the mixing of ligand orbitals due to the presence of low symmetry ligand fields of the surrounding structure. If the complex would have a smaller κ and unit β_2^2, the bonding would be nearly ionic and would represent poor π bonding of the ligands. Ballhausen and Gray reported that β_2^2 should be equal to unity for a nonbonding orbital in the case of an undistorted $[VO(H_2O)_5]^{2+}$ complex [19, 20].

[1] N. Satyanarayana, J. Phys. Chem. Solids. **47**, 55 (1986).
[2] N. O. Gopal, K. V. Narasimhulu, and J. L. Rao, Physica B **307**, 117 (2001).
[3] M. Korkmaz and B. Aktaş, J. Phys. Chem. Solids. **45**, 259 (1984).
[4] M. Venkateshwarlu and T. B. Rao, Solid State Comm. **82**, 837 (1992).
[5] K. V. Narasimhulu, C. S. Sunandana, and J. L. Rao, J. Phys. And Chem. Solids. **61**, 1209 (2000).
[6] S. K. Misra and J. Sun, Phys. Review B **42**, 8601 (1990).
[7] B. Karabulut, A. Bulut, and R. Tapramaz, Spect. Lett. **32**, 571 (1999).
[8] S. Radhakrishna and M. Salagram, Solid State Comm. **47**, 77 (1983).
[9] J. L. Rao, R. M. Krishna, S. V. J. Lakshman, and P. Chand, J. Phys. Chem. Solids. **51**, 323 (1990).
[10] F. Köksal, B. Karabulut, and Y. Yerli, J. Ing. Mater. **1**, 130 (2001).
[11] M. Currie and J. C. Speakman, J. Chem. Soc. (**A**) 1862 (1967).
[12] B. Karabulut and R. Tapramaz, Radiat. Phys. and Chem. **55**, 331 (1999).
[13] B. Bleanay, K. D. Bower, and M. H. L. Price, Proc. Roy. Soc. (London) A **228**, 166 (1955).
[14] Z. Sroubek and K. Zdansky, J. Chem. Phys. **44**, 3378 (1966).
[15] T. B. Rao and M. Narayana, Phys. Stat. Sol. B **106**, 601 (1981).
[16] P. Chand and M. Umar, Phys. Stat. Sol. B **127**, 179 (1985).
[17] P. Chand, G. C. Upreti, M. Uyar, and R. J. Singh, Phys. Stat. Sol. B **131**, 357 (1985).
[18] M. Narayana, S. G. Sathyanarayan, and G. S. Sastry. Mol. Phys. **31**(1), 203 (1976).
[19] C. J. Ballhausen and H. B. Gray, Inorg. Chem. **1**, 111 (1962)
[20] L. J. Boucher, E. C. Tynan, and T. F. Yen. Electron Spin Resonance of Metal Complexes. Plenum Press, New York 1969, p. 111 – 130.