EPR Spectra of VO^{2+} Doped Ammonium Oxalate Monohydrate Single Crystals

B. Karabulut and R. Tapramaz

Ondokuz Mayıs University, Faculty of Art and Sciences, Department of Physics,
55139-Samsun, Turkey

Reprint requests to Dr. B. K.; e-mail: bbulut@SAMSUN.omu.edu.tr

The EPR spectra of VO^{2+} ions in ammonium oxalate monohydrate, [(NH$_4$)$_2$C$_2$O$_4$·H$_2$O], single crystals have been studied at room temperature and at 113 K in mutually three perpendicular planes. The spin Hamiltonian parameters are determined using a numerical technique together with a trial and error procedure to resolve the single crystal spectra. The parallel and perpendicular components of axially symmetric **g** and hyperfine tensors for VO^{2+} ion in ammonium oxalate monohydrate single crystal are determined, and the results are discussed.

Key words: EPR; (NH$_4$)$_2$C$_2$O$_4$·H$_2$O; VO^{2+}; Ammonium Oxalate Monohydrate.

1. Introduction

The electron paramagnetic resonance, (EPR), method provides detailed description of the nature of the electrical field symmetry produced by the ligands around the paramagnetic ions. The EPR spectra of the vanadyl ions, (VO^{2+}), in different diamagnetic host lattices have studied by many workers. A number of papers on magnetically or chemically distinct metal ion complexes in a single host crystal are published in recent years, [1 - 6]. When the number of distinct metal ions in a single host crystal is larger, the resolution of the spectra is not so easy and some techniques for resolution must be utilised. The difficulty in resolution of the spectra arises basically from overlapping of large number of lines in different orientation. In this work we have undertaken the resolution and identification of VO^{2+} spectra in ammonium oxalate monohydrate single crystal [AOMH, hereafter]. Large number of lines in the spectra of single crystal were observed and a numerical technique is used to resolve the spectra.

2. Experimental

The single crystals of AOMH were grown by slow evaporation of a saturated aqueous solution of the commercially obtained compound in polycrystalline form. A very small amount of VOSO$_4$ was added to the solution to supply VO^{2+} ions as dopants. The single crystals, grown in one week, were investigated. The crystal structure of AOMH is orthorhombic with the space group P2$_1$2$_1$2 (D$_2^3$). There are two molecules, in a unit cell. The unit cell dimensions are $a = 8.04$ Å, $b = 10.25$ Å and $c = 3.82$ Å [7].

The EPR spectra were recorded with a Varian E-109 C model EPR spectrometer using 2 mW microwave power and 100 kHz magnetic field modulation. The single crystals were glued on a Lucit pillar and rotated in three mutually perpendicular planes (*ab, ca, bc*). The spectra were recorded with 10° steps. The g factors were found by comparison with a diphenylpicrylhydrazyl sample ($g = 2.0036$).

3. Results and Discussion

The VO^{2+} ion has the electron configuration 3d^1 [8]. The EPR spectra of the vanadyl ions can be satisfactorily explained in terms of the unpaired electron ($S = 1/2$) interacting with the ^{51}V nucleus ($I = 7/2$). The spectrum can be described in terms of a spin Hamiltonian of the form

$$\mathcal{H} = \beta B \cdot \mathbf{g} \cdot \vec{S} + \vec{S} \cdot \mathbf{A} \cdot \vec{I}, \qquad (1)$$

which includes only electronic Zeeman and hyperfine interactions and where Nuclear Zeeman, quadrupole and spin orbit interactions are neglected.

Fig. 1. EPR spectrum of VO^{2+} doped AOMH single crystal. The magnetic field is in the *ab* plane making an angle of a) 0° and b) 80° with the *b* axis.

The EPR spectra of VO^{2+} ions in AOMH single crystals consist of many hyperfine lines as shown in Figure 1. The number and spacings of lines change rapidly with orientation. The lines appearing at one orientation, disappear almost completely at some other orientation. We therefore used a simple technique to resolve and identify the lines as discussed below.

The g^2 values of all detected lines are plotted against the rotation angle in mutually three perpen-

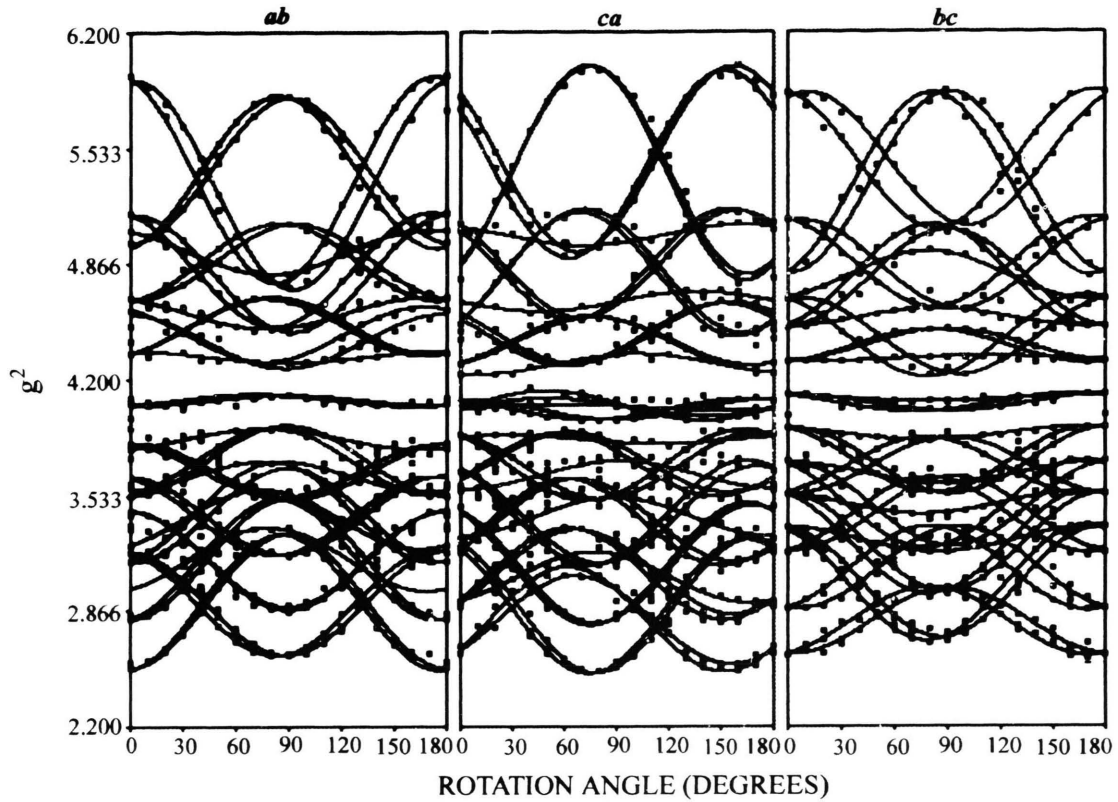Fig. 2. Variation of the g^2 values of all lines in three mutually perpendicular planes of VO^{2+} doped AOMH single crystal.

dicular planes, as shown in Figure 2. The g^2 variation of a specific line with respect to the rotation angle in each plane must fit to the expression

$$g_k^2(\theta) = g_{ii}^2 \cos^2 \theta_i + g_{jj}^2 \sin^2 \theta_j + 2g_{ij}^2 \sin \theta_i \cos \theta_j, \quad (2)$$

where $i, j, k = x, y, z$ are cyclical laboratory coordinates and θ is the rotation angle. g_{ii}^2, g_{jj}^2 and g_{ij}^2 are the **g** tensor elements which will be found by fitting [9].

One can guess and choose the points belonging to a specific line on the graph and fit them to (2). The goodness of fitting can be controlled either visually or by the regression coefficient. If the result is satisfactory, the line is accepted. Otherwise the operation is cancelled and another line is tried. The operation is repeated until all detectable lines are determined. The results of the line determination process are shown in Figure 2. Since the number of lines is large, visual selection of hyperfines belonging to a specific complex is rather difficult, and another technique must be used.

The groupings of each eight lines belonging to the same complex are made referring to the parallelisms and testing the spacings with the second order approximation given as

$$B_m = B_0 - ma - \frac{a^2[I(I+1) - m^2]}{2B_0}, \quad (3)$$

where $B = h\nu/g\beta$, and hyperfine splittings a are functions of the rotation angle, $I = 7/2$ and $m = -7/2...7/2$ [10]. The hyperfine splitting expressions as a function of the rotation angle are obtained by replacing g by a in (2). For the determination of the unknown parameters a and g let the spacing between lines corresponding to m and $-m$ be $(\Delta B)_m$, which is measurable on spectra. Equation (3) gives the expression for this spacing as

$$(\Delta B)_m = 2|m|a. \quad (4)$$

Putting this expression into (3), a quadratic expression for B_0 is obtained as
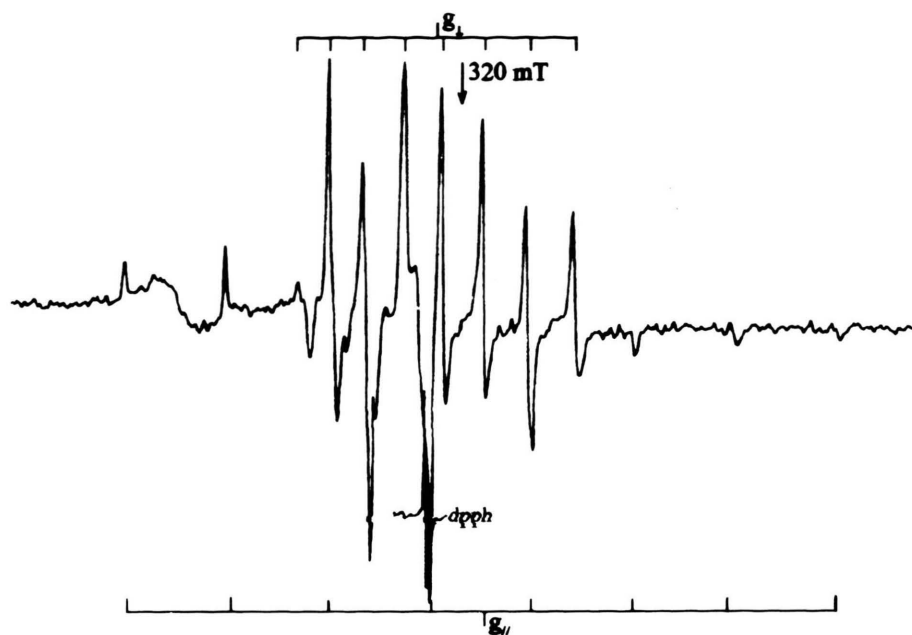
Fig. 3. Powder spectrum of VO^{2+} doped AOMH.

$$B_0 = \frac{1}{2}\left(B_0 - \frac{\Delta B}{2}\right) \quad (5)$$

$$+ \frac{1}{2}\sqrt{\left(\frac{\Delta B}{2} - B_m\right)^2 + 2\left(\frac{\Delta B}{2|m|}\right)^2 [I(I+1) - m^2]}.$$

Each m and $-m$ pairs of lines at a specific orientation must give almost the same a and g values. For example, at a specific orientation, the a and g values calculated from the spacing between $m = 7/2$ and $m = -7/2$ lines must be almost be the same as those obtained from $m = 5/2$ and $m = -5/2$ lines. Therefore it is more reasonable to calculate all a and g values corresponding to $m = \pm 7/2$, $\pm 5/2$, $\pm 3/2$ and $\pm 1/2$ lines and average the results if they are close to each other. Otherwise other lines are tried. The technique works well and gives g and hyperfine tensors by fitting to (2). The tensors can be diagonalised and the principal values are obtained, Table 1.

The interest in AOMH arises from the arrangement of atoms around the NH$_4^+$ cation which is expected to substitute VO^{2+}. Around the ammonium group, there are eight oxygen atoms. Four of these oxygens form a tetrahedron with distances of 2.8 Å from nitrogen atoms, while the other four are at about 3.2 Å from the nitrogen atoms forming another tetrahedron [11].

Eight sets of octets are clearly identified in the spectra of AOMH, Table 1 and Figure 2. The number

Table 1. Principal **g**, hyperfine (**A**), P, and κ parameters for paramagnetic vanadyl complexes in AOMH single crystals at room temperature.

Site	$g_{\parallel}$	$g_{\perp}$	g_{IZO}	$A_{\parallel}$ 10^{-4}cm^2	$A_{\perp}$ 10^{-4}cm^2	A_{IZO} 10^{-4}cm^2	$|P|$ 10^{-4}cm^{-1}	κ
Complex I:								
1	1.897	1.987	1.957	196.28	69.80	111.96	138.17	0.79
2	1.894	1.987	1.956	196.80	67.27	110.44	135.12	0.76
3	1.899	1.985	1.956	194.90	78.90	117.01	122.55	0.90
4	1.904	1.984	1.957	189.20	76.26	113.90	119.02	0.89
Complex II:								
1	1.906	1.980	1.955	198.27	86.60	123.82	118.10	0.98
2	1.903	1.981	1.955	201.7	85.10	123.96	122.81	0.94
3	1.906	1.980	1.955	198.27	86.60	123.82	118.10	0.98
4	1.903	1.981	1.955	201.7	85.10	123.96	122.81	0.94
Powder:								
	1.905	1.993	1.963	193.25	75.51	114.75	131.56	0.84

of complexes, at first sight, is incompatible with the orthorhombic symmetry of AOMH. Referring to their spectral behaviour, the complexes can be collected into two groups, each having four sites. In other words, there are two different VO^{2+} complexes located in different chemical environments, and each environment contains four magnetically distinct sites, which is compatible with orthorhombic crystal symmetry. The distortion primarily takes place along the V = O direction, and the degeneracy of the ground state d$_{xy}$ of the V atom in 3d^1 splits into d$_{x^2-y^2}$

and d_{xz}, d_{yz} states. Similar studies were made by Kasthurirengenan and Soundararajan [1], who resolved four distinct sites in $K_2Zn(SO_4)\cdot 6H_2O$ and $K_2Mg(SO_4)\cdot H_2O$ single crystals, and by Chand et al. [6], who resolved three distinct sites in the single crystal of tutton salt.

The principal values of the **g** and **A** tensors were calculated, and the results are listed in Table 1 for two groups. The isotropic values of the **g** and **A** tensors for four sites are nearly equal. Figure 3 shows the powder EPR spectrum of VO^{2+} doped AOMH single crystal. It can be clearly seen from the powder spectrum that the complex symmetry in the crystal is axial. The powder EPR spectrum was clearly resolved and the $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ values were measured. The second order approximation was used to determine the spin Hamiltonian parameters. The obtained values are given in Table 1 together with single crystal values. These parameters are in good agreement with those obtained from the single crystal EPR data. No detectable changes were observed in the spectra at lower temperatures down to 113 K, so all measurements were made at room temperature.

The degree of distortion can be estimated from the Fermi contact κ and the $|P|$ parameters which are related to radial distribution of the wave function of the ion given as $|P| = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle$. The Fermi contact and $|P|$ parameters for the VO^{2+} ions, reported so far, vary around $\kappa = 0.84$ and $|P| = 135 \times 10^{-4}$ cm^{-1}. Therefore, these two values can be taken as criteria for the distortion of th VO^{2+} complexes. In order to find these two parameters, the expressions given for $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ can be used [1, 2]. The four equations given in [1, 2] can be reduced to two equations including the unknowns κ and $|P|$:

$$
\begin{aligned}
A_\parallel &= -P\left[\kappa - \frac{4}{7} - (g_e - g_\parallel) - \frac{3}{7}(g_e - g_\perp)\right], \\
A_\perp &= -P\left[\kappa - \frac{2}{7} - \frac{11}{14}(g_e - g_\perp)\right]
\end{aligned}
\tag{6}
$$

where $g_e = 2.0023$. Calculated κ and $|P|$ values are given in Table 1. The parameters of the first group are clearly in the same range and close to the values given in the cited papers. The second group, however, has smaller $|P|$ and conversely greater κ values.

[1] S. Kasthurirengan and S. Soundararajan, J. Magn. Reson. **19**, 357 (1975).

[2] B. P. Maurya, A. Punnoose, M. Umar, and R. J. Singh, Solid State Commun. **89**, 59 (1994).

[3] S. K. Misra and J. Sun, Physica B, **162**, 331 (1990).

[4] M. Venkateshwarlu and T. B. Rao, Solid State Commun. **82**, 837 (1992).

[5] K. Liu, J. Yu, S. Lou, C. Lee, Y. Huang, and K. Lii, J. Phys. Chem. Solids **55**, 1221 (1994).

[6] P. Chand, R. M. Krishna, J. L. Rao, and V. J. Lak-

shman, Radiation Effects and Defects in Solids **127**, 245 (1993).

[7] J. H. Robertson, Acta Cryst. **18**, 410 (1965).

[8] T. B. Rao and M. Venkateshwarlu, Solis State Commun. **44**. 1617 (1982).

[9] N. M. Atherton, Electron Spin Resonance Theory and Applications, John-Wiley and Sons, New York 1973.

[10] J. Harriman, J. Chem. Phys., **37**, 111 (1978).

[11] S. Radhakrishna and M. Salagram, Phys. Stat. Sol. (a) **62**, 441 (1980).