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Research Article

EPR STUDY OF VO²⁺ DOPED TRISODIUM CITRATE PENTAHYDRAT SINGLE CRYSTALS

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ABSTRACT

X-band Electron Paramagnetic Resonance study of VO²⁺ doped trisodium citrate pentahydrate (Na₃C₆H₅O₇·5H₂O) single crystal has been examined at room temperature. The observed spectra of VO²⁺ are characteristic of tetragonally compressed octahedral site. The EPR study shows single site occupying substitutional position in the lattice along Na⁺. The angular variation of the EPR spectra in three planes ba*, bc and ca* are used to determine principal g and A tensors. The values obtained are: g_x=2.013±0.002, g_y=1.982±0.002, g_z=1.925±0.002, A_x=(71±2)×10⁻⁴ cm⁻¹, A_y=(69±2) ×10⁻⁴ cm⁻¹, and A_z=(178±2)×10⁻⁴ cm⁻¹. These data are compared with those of VO²⁺ in other lattices.

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INTRODUCTION

Electron paramagnetic resonance (EPR) technique of transition metal ions in crystals can lead to a detailed description of the electronic structure of these compounds. It is also useful in solving problems related to binding of metals to inorganic and organic ligands. EPR studies have been usually carried out on paramagnetic impurities doped in diamagnetic hosts. Because of broadening of impurity resonance line, EPR study of paramagnetic ion in paramagnetic hosts is less common. However, sharp EPR spectra are observed in many paramagnetic hosts [1-7]. Due to its higher stability, vanadyl ion is used extensively as an impurity probe to study defect properties, structural changes and host lattice effects on molecular ion using EPR studies [8]. Vanadyl complexes have been the subject of interest to a number of workers over recent years [9-14] in different crystalline field environments. In alkali halides and ammonium nitrates VO²⁺ ion has a random orientation at room temperature. The behavior of unpaired electron in VO²⁺ complexes is dominated by the strong V=O bonding, as a result most of the complexes possess C_{4v} symmetry. In view of above we have studied VO²⁺ impurity ions in trisodium citrate pentahydrate.

Trisodium citrate pentahydrate is a tribasic salt of citric acid. It is widely used in food, beverages and different technical applications. Citrates are also very important for biological and medical applications [15, 16]. In the present investigation, EPR

on VO²⁺ ion in trisodium citrate pentahydrate single crystals have been done at room temperature. The purpose of study is to find the site symmetry of the metal ion and to have better knowledge about physical interactions present in the system. The EPR study of VO²⁺ doped trisodium citrate pentahydrate has been done earlier [17] where the authors observed two sites of VO²⁺ but in the present study only one of VO²⁺ is observed.

Crystal Structure

The molecular formula of trisodium citrate pentahydrate is Na₃C₆H₅O₇·5H₂O. The structure of sodium citrate was studied first by Burns and Iball [18] and then by Fischer and Palladino [19]. Sodium citrate crystals are monoclinic and belong to space group C2/c. The dimensions of its unit cell are a = 15.7044 (4), b = 12.5010 (4) and c = 11.2837(4) Å⁰. There are eight molecules of C₆H₅O₇·Na₃·5H₂O per unit cell and d = 1.814 Mg m⁻³. There is an ambiguity regarding the space group of this crystal. Burns and Iball [18], from the systematic absence in the X-ray diffraction, mention that space group should be either C_{2v}⁹ or D_{2h}¹⁶. The detailed atomic positions are also not known.

Experimental

Single crystals of trisodium citrate pentahydrate [Na₃C₆H₅O₇·5H₂O TSCP hereafter] were grown by slow evaporation from the saturated aqueous solution. The VO²⁺ impurity was added by mixing 0.02 mole % of VOSO₄·3H₂O.

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After a few days good single crystals of VO²⁺ doped TSCP with well-defined faces were obtained.

The EPR spectra were recorded at room temperature (300 K) on X-Band (~9.5GHz) EPR spectrometer (Make: Varian, USA), Model: E-Line century series E-112) located at I. I. T. Powai, Mumbai. Single crystal was mounted at the end of goniometer with the help of quick fix along three mutually perpendicular axes a*, b and c (a* is perpendicular to b and c axis). The angular variations were recorded at every 10⁰ rotations by rotating the crystal about above three axes. The g-factors were corrected by comparing with a diphenylpicrylhydrazil sample with g=2.0036. The magnetic field was measured with the help of Varian flux meter using proton probe and Hewlett-Packard frequency counter.

RESULTS AND DISCUSSION

At room temperature VO²⁺ doped trisodium citrate pentahydrate [Na₃C₆H₅O₇·5H₂O TSCP hereafter] gives strong EPR spectrum. Observed EPR spectrum is strongly orientation dependent. EPR spectrum of VO²⁺ doped sodium citrate, when magnetic field is 90⁰ away from a* axis, is shown in Fig.1.

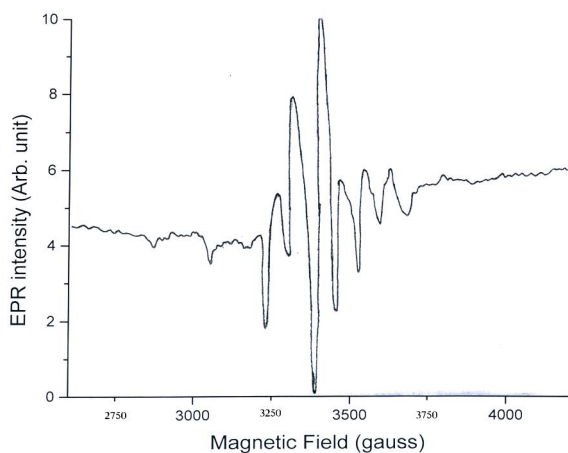


Fig 1 EPR spectrum of VO²⁺ doped TSCP single crystals when magnetic field is when magnetic field is 90⁰ away a* axis.

The spectrum consists of only one set of eight lines with different intensities which arise due to interaction of electron spin (S=1/2) with ⁵¹V nucleus (I=7/2). Computer simulation of the EPR spectrum were performed the EasySpin program [20-23] and spin-Hamiltonian parameters: g_x=2.013±0.002, g_y=1.982±0.002, g_z=1.925±0.002, A_x=(71±2)×10⁻⁴ cm⁻¹, A_y=(69±2)×10⁻⁴ cm⁻¹ and A_z=(178±2)×10⁻⁴ cm⁻¹ obtained from EPR spectra at 9.223 GHz. The simulation was based upon the numerical diagonalization of the entire S=1/2, I=7/2 energy matrix and the first derivative line shapes were used. The simulated EPR spectrum does not exactly match the experimental EPR spectrum due to assumption of a Lorentzian line shapes in the simulation while the actual line shape may be different. The simulated EPR spectrum given in Fig. 2. is in reasonable agreement with the experimental one.

The line positions of eight EPR lines are plotted against the rotation angle in three mutually perpendicular planes and are shown in Figs. 3, 4 and 5. The following spin Hamiltonian can be used to analyze the observed EPR spectra [24-27].

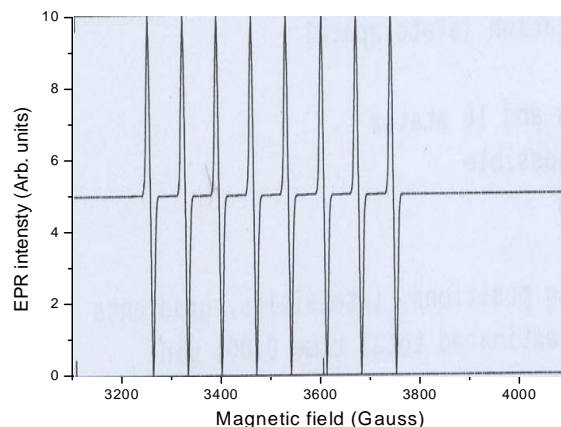


Fig 2 Simulated EPR spectrum of VO²⁺ doped TSCP single crystals when magnetic field is with simulation frequency 9.223 Ghz.

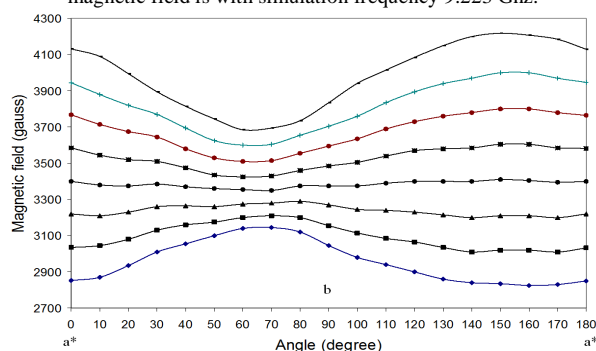


Fig 3 Angular variation of EPR line positions of VO²⁺ doped TSCP single crystals in a*b plane

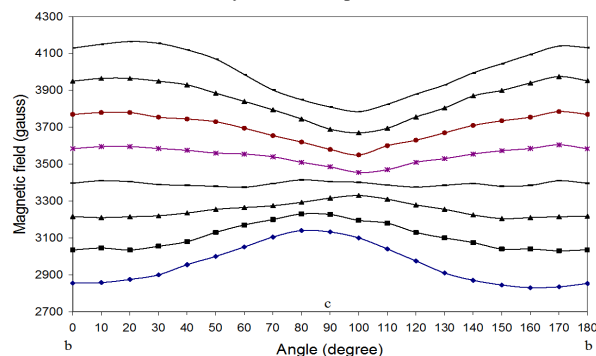


Fig 4 Angular variation of EPR line positions of VO²⁺ doped TSCP single crystals in bc plane.

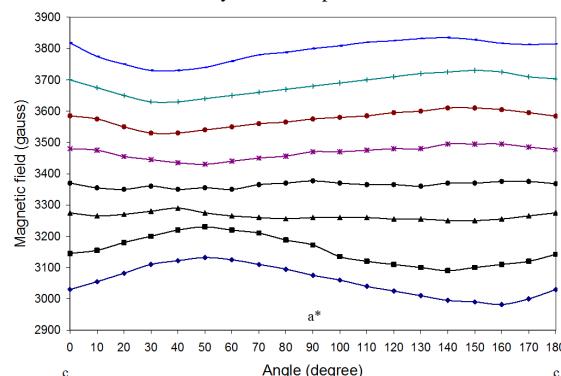


Fig 5 Angular variation of EPR line positions of VO²⁺ doped TSCP single crystals in ca plane.

$$\mathcal{H} = \mu_B (g_x B_x S_x + g_y B_y S_y + g_z B_z S_z) + A_z I_z S_z + A_y I_y S_y + A_x I_x S_x \quad (1)$$

which consists of only Zeeman and hyperfine interaction terms. Being negligibly small nuclear Zeeman, nuclear quadrupole and spin-orbit interactions are neglected.

The observed EPR spectra are fitted to a spin-Hamiltonian (1) of orthorhombic symmetry with:

$$g_x=2.013\pm 0.002, g_y=1.982\pm 0.002,$$

$$g_z=1.925\pm 0.002,$$

$$A_x = (71\pm 2)\times 10^{-4} \text{ cm}^{-1}, A_y = (69\pm 2)\times 10^{-4} \text{ cm}^{-1} \text{ and } A_z=178\pm 2)\times 10^{-4} \text{ cm}^{-1}$$

Table 1 Spin Hamiltonian parameters for Vanadyl ions in trisodium citrate pentahydrate.

g_x	g_y	g_z	A_x ($\times 10^{-4}$) cm^{-1}	A_y ($\times 10^{-4}$) cm^{-1}	A_z ($\times 10^{-4}$) cm^{-1}
2.013	1.982	1.925	71	69	178
± 0.0002	± 0.0002	± 0.0002	± 2	± 2	± 2

The above spin-Hamiltonian parameters are evaluated using self-developed computer program and the well-known Schonland procedure [28]. The spin-Hamiltonian parameters indicate that the symmetry of VO^{2+} ions in the lattice is orthorhombic and the spectral features indicate that the symmetry may be a little lower.

The variation of spectroscopic splitting factor g is fitted to the following expression

$$g^2(\theta) = \alpha + \beta \cos 2\theta + \gamma \sin 2\theta \tag{2}$$

$$2\alpha = (g_{\max}^2 + g_{\min}^2)$$

$$2\beta = (g_{\max}^2 - g_{\min}^2) \cos 2\phi$$

$$2\gamma = (g_{\max}^2 - g_{\min}^2) \sin 2\phi$$

where θ is the angle specifying the direction of the magnetic field in the plane of measurement and ϕ is the angle at which g_{\max} or g_{\min} occurs.

The g and A values were evaluated using Schonland method and are given in Table 1. The behavior of unpaired electron in vanadyl complexes is determined by a strong V=O bond.

Table 2 Spin Hamiltonian parameters of VO^{2+} in different lattices (*A is in unit of 10^{-4} cm^{-1} except for S. No 4, 5 and 7 for which A is in Gauss).

S.No.	Systems	g_x	g_y	g_z	A_x	A_y	A_z	References
1.	TSCP	2.013	1.982	1.925	71.0	69.0	178.0	Present Work
2.	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 5\text{H}_2\text{O}$	1.934	1.992	1.998	70.0	66.6	175.4	[17]
3.	Sodium Citrate							
	Complex I	1.968	2.005	1.912	79.0	76.0	185.0	[31]
	Complex II	1.965	2.007	1.942	78.0	70.0	186.0	[31]
4*.	$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	1.940	1.988	1.988	73.5	43.5	177.0	[32]
5*.	KHC_2O_4	1.936	1.989	1.989	88.5	73.5	186.5	[32]
6.	$\text{Cs}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.933	1.979	1.979	73.9	73.9	183.3	[33]
7*.	$(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.936	1.981	1.979	81.0	79.0	196.0	[34]
8.	$\text{Mg}(\text{H}_2\text{O})_6\text{H}_2$ EDTA	1.952	1.987	1.983	64.8	80.7	151.3	[33]
9.	$\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.930	2.005	1.997	77.0	67.0	178.5	[35]
10.	$(\text{NH}_4)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	1.940	1.978	1.978	67.0	67.0	176.0	[36]

Table 3 Direction cosines of different bonds and distortion axes in TSCP single crystals

Bonds	Distance (Å^0)	a*	b	c
Na1-O8 ⁱ		± 0.2578	± 0.0799	± 0.9629
Na1-O1		± 0.4878	± 0.8298	± 0.2712
Na1-O6 ⁱⁱ	2.4942	± 0.4951	± 0.4681	± 0.1367
Na1-O9 ⁱⁱⁱ	2.2743	± 0.8730	± 0.9969	± 0.0591
Na1-O5	2.3288	± 0.6343	± 0.4838	± 0.6029
Na1-O5 ^{vi}	2.4539	± 0.7768	± 0.6274	± 0.0543
Na1-Na2 ⁱ	3.1395	± 0.0606	± 0.6561	± 0.7522
Na1-Na3 ⁱⁱⁱ	2.7437	± 0.9600	± 0.2674	± 0.0830
Na1-Na1 ⁱⁱ	3.3601	± 0.8066	± 0.0249	± 0.5905
Na(2)-O2 ⁱⁱⁱ	3.4778	± 0.9277	± 0.3674	± 0.0663
Na2-O6 ^{iv}	3.8990	± 0.5174	± 0.0773	± 0.8522
Na2-O6	2.2825	± 0.9693	± 0.0895	± 0.2289
Na2-O8	2.6217	± 0.1796	± 0.9824	± 0.0514
Na2-O1	2.2653	± 0.3398	± 0.0826	± 0.9369
Na2-Na3	2.6659	± 0.3453	± 0.9255	± 0.1554
Na2-Na2 ^{iv}	3.3666	± 0.9001	± 0.0000	± 0.4349
Na2-Na3 ⁱⁱⁱ	3.9450	± 0.6566	± 0.2466	± 0.7127
Na3-O4 ^{iv}	4.7746	± 0.5450	± 0.0679	± 0.8357
Na3-O7	2.6314	± 0.8606	± 0.4499	± 0.2388
Na3-O1 ⁱⁱⁱ	2.2863	± 0.8609	± 0.3696	± 0.3497
Na3-O9	2.5896	± 0.4987	± 0.8665	± 0.0195
Na3-O2 ⁱⁱⁱ	2.3988	± 0.3730	± 0.8896	± 0.2635
Na3-O3 ^{vi}	2.5598	± 0.2997	± 0.9469	± 0.1166
Distortion Axis: (g_z)	2.7889			
		0.7369	0.6569	0.0521

As a result, both *g* and *A* of all complexes are found to be nearly axially symmetric, as usual for most of the VO²⁺ complexes reported in the cited papers [17, 29-30].

For comparison, the spin-Hamiltonian parameters of VO²⁺ ion in different systems are also given in Table 2. It can be seen from Table 2 that the spin-Hamiltonian parameters obtained in the present work are similar to the results of earlier workers [31-36] and hence the assumption that VO²⁺ has entered an octahedral coordination is valid one. Thus the wave functions and expression for spin-Hamiltonian parameters in the present study will be the same as that for vanadyl ions in other lattices. Theoretical investigation to verify spin-Hamiltonian parameters and site symmetry is in progress and will be reported soon.

Assuming that the VO²⁺ enters the two Na-O bond directions, the EPR spectrum showed one set of octet hyperfine lines along three crystallographic axes and four sets of hyperfine lines in general orientations. Keeping this in view, the spin Hamiltonian parameters are calculated for one vanadyl site along Na-O vectors in the three mutually perpendicular planes. The EPR spectra show that vanadium ion of the V⁴⁺=O²⁻ group replaces the Na⁺ in the host lattice. Since V⁴⁺ is more active and smaller the atomic radii (are 0.98Å for Na⁺ and 0.64Å for V⁴⁺). The V=O orientations can be obtained by correlating the experimentally obtained direction cosines with those calculated from the crystal structure data [19]. The calculated direction cosines from the crystal structure data are given in Table 3. The difference in bond length is reflected in the EPR spectra showing different intensities corresponding to different V = O orientations [12]. It is clear from Table 3 that V = O orientation is along Na1 – O5^{vi} bond direction (Fig. 6).

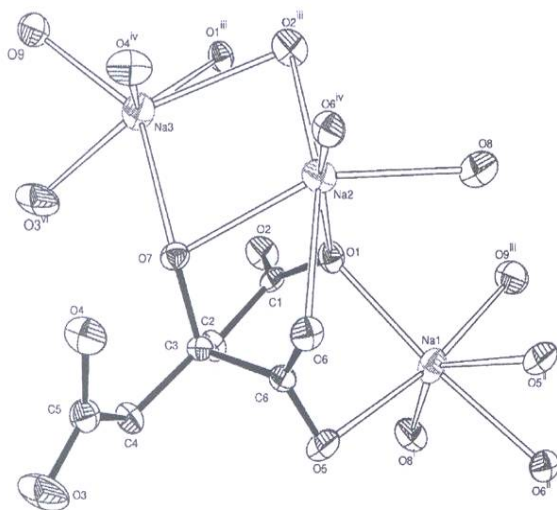


Fig 6 The citrate ion and three Na⁺ ions with their complete coordination environments in the structure of trisodium citrate pentahydrate.

CONCLUSIONS

EPR and optical absorption studies of VO²⁺ ions in trisodium citrate pentahydrate single crystals have been done at room temperature. The *g* and *A* parameters and their respective direction cosines have been evaluated from EPR data. The comparison of direction cosines obtained from EPR data with those evaluated from crystal structure data shows that VO²⁺ ions are expected to occupy substitutional site in the lattice. In the present study only one site having orthorhombic symmetry in EPR spectra has been observed while in earlier study of the

same system two different VO²⁺ complex groups each containing two magnetically distinct sites with orthorhombic symmetry were reported.

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