
EPR of Vanadyl Ion Impurities in Single Crystals of RbHC_2O_4

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The EPR of VO^{2+} in RbHC_2O_4 single crystals has been studied in X-band at ≈ 290 K. Three sites have been observed. VO^{2+} enters the lattice at substitutional and interstitial sites. Spin-Hamiltonian parameters are evaluated.

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1. Introduction

The electron paramagnetic resonance (EPR) of vanadyl ion, VO^{2+} , has been studied in a variety of host lattices which fall into two categories, those in which the VO^{2+} ion is free to rotate (at least at normal temperature) and those in which it is preferentially oriented. The second type usually occurs when the lattice contains a number of oxygens which are coordinated to vanadyl as is the lattice containing water of hydration, sulfate ions, or other oxygen rich groups [1]. A rotating vanadyl ion is usually observed when it is coordinated by halogen or when the nitrate ion is involved in the coordination. In this paper we report the EPR of VO^{2+} doped RbHC_2O_4 (RHO) single crystals at ≈ 290 K.

2. Crystal structure

RHO is isomorphous to KHC_2O_4 (KHO) [2]. The detailed crystal structure studies of RHO are not available. However, RHO is expected to have the same structure as that of KHO. The crystal structure of KHO is monoclinic with group $P(2_1/c)$ [3]. The unit cell has dimensions $a = 0.4319$ nm, $b = 1.2890$ nm, $c = 0.7660$ nm and $\beta = 101.96^\circ$ and contains four formula units. The crystal is built of infinite chain of hydrogen oxalate ions held together by short hydrogen

bonds of 0.2534 nm parallel to $(10\bar{2})$ planes. The potassium (rubidium) ions are situated between the oxalate chains. Each monovalent ion is coordinated to seven oxalate oxygens originating from five different oxalate ions at a distance (for KHO) from 0.2704 nm to 0.2964 nm with a mean K–O distance of 0.2827 nm. All the monovalent ions lie on general positions in the lattice.

3. Experimental

Single crystals of RHO doped with VO^{2+} were grown by slow evaporation of an aqueous solution at room temperature (≈ 300 K). The VO^{2+} was introduced into the host lattice by adding 0.5–1 wt% of vanadyl sulfate. The EPR experiments were performed with an X-band JEOL FE-3X spectrometer equipped with a TE_{011} cylindrical cavity and 100 kHz field modulation. As a reference for magnetic field strength the resonance line of diphenyl picrylhydrazyl (DPPH) with 2.0036 is used.

4. Result and discussion

The EPR spectra consisted of a number of overlapping angular dependent eight line hyperfine patterns, each produced by ions located at a specific site. These eight line hyperfine patterns result from the hyperfine coupling of a single unpaired electron with a ^{51}V (99.8% abundant, spin $I = 7/2$) nucleus. At least three distinct hyperfine patterns of differing intensities were observed, indicating at least three chemically distinct ion sites which will be called I, II and III (Fig. 1) in order of decreasing intensity. Detailed analysis has been carried out only for the intense VO^{2+} centers (site I and II) because it was not possible to follow the angular variation of the hyperfine lines of VO^{2+} centers of low intensity (site III).

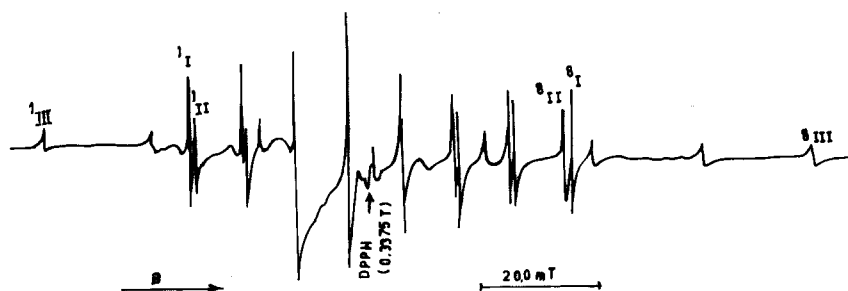


Fig. 1. The EPR spectrum of VO^{2+} in RbHC_2O_4 single crystals for an arbitrary orientation at ≈ 290 K.

Angular variation studies in ab , bc' (c' is at 90° to a and b axes) and $c'a$ planes indicate a set of eight lines of VO^{2+} at site I and II. However, all the lines of VO^{2+} at site II are not resolved at all orientations. A fully resolved sixteen line spectrum could not be obtained at all, although it is clear that the spectrum

consists of two sets of eight lines (Fig. 1). For certain orientations, at most six lines of site II get separated in either extremity from the lines of site I. The two sets corresponding to site I and II thus move almost together for different orientations of the crystal. A maximum field separation of 2.3 mT between the two extreme high field hyperfine lines of site I and II are observed for some orientations. The spectra exhibit high anisotropy in bc' ($c'a$) plane while in ab plane the anisotropy is very small. The z axis of site I and site II make an angle of $\approx 3^\circ$ and $\approx 9^\circ$, respectively, with c' axis in bc' plane while x and y axes nearly coincide with a and b axes. The z axis of site III makes an angle of $\approx 5^\circ$ with the b axis.

The VO^{2+} EPR spectra have been analysed using the spin-Hamiltonian for an orbitally non-degenerate electron

$$\mathcal{H} = \beta_e \mathbf{SgB} + \mathbf{SAI},$$

where the terms have their usual meaning. The quadrupole and nuclear Zeeman interaction are ignored, as they contribute negligibly.

The spin-Hamiltonian parameters observed for VO^{2+} in RHO are given in Table. The spin-Hamiltonian parameters (\parallel , \perp) were also determined from the spectra taken with finely crushed crystals (Fig. 2) and are included in Table. The

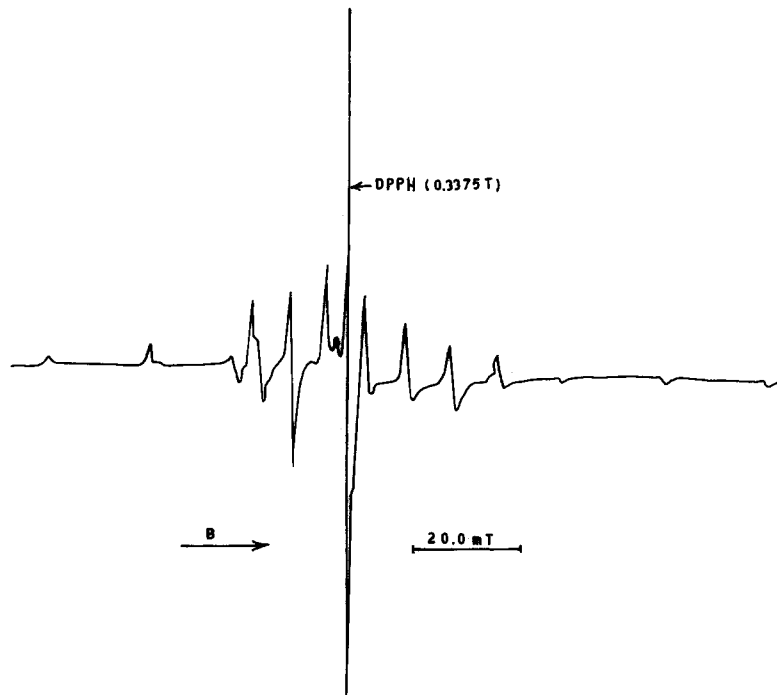


Fig. 2. The EPR spectrum of finely crushed $\text{RbHC}_2\text{O}_4:\text{VO}^{2+}$ single crystals at ≈ 290 K.

TABLE

Spin-Hamiltonian parameters for VO^{2+} ions in RbHCO_4 at ≈ 290 K. Values of A are in units of 10^{-4} cm^{-1} .

Parameters	Site I	Site II	Site III	Powder
A_z	176(1)	175(1)	172(1)	173
A_x	72(2)	72(2)	74(2)	69
A_y	66(2)	66(2)	–	–
g_z	1.933(1)	1.936(1)	1.935(1)	1.939
g_x	1.976(2)	1.976(2)	1.990(2)	1.979
g_y	1.978(2)	1.978(2)	–	–

accuracy of the parameters determined from the powder spectrum is limited by the line shapes.

The results suggest that VO^{2+} occupies two magnetically distinguishable site I and site II in the lattice. It is also seen from the angular variation studies that the two sites are not related by any symmetry element in the lattice (like twofold axis or mirror plane) and that the vanadyl ions corresponding to site I and II are inclined to each other by $\approx 6^\circ$. Further, the fact that the two sites show the least anisotropy in ab plane and that g_z and A_z are nearly along the c' axis suggest that VO^{2+} are oriented with V–O axis nearly perpendicular to the ab plane.

In vanadyl containing materials including complexes in solution, the vanadium is usually coordinated with other groups, and particularly with oxygens. The total coordination number for vanadium in these complexes is usually six (sometimes five as well) and one very short V–O bond generally preserves the identity of VO^{2+} bond [4]. In order to experimentally determine the orientation of V–O bond in the host, one must consider the position of principal axes of g and A . It is reasonable to assume that g_z and A_z coincide with the V–O bond. Thus z axis can be taken along the V–O bond direction.

It can be seen from the crystal structure that Rb^+ is the most probable site available to VO^{2+} for substitution. A search for possible interstitial sites in the crystal lattice revealed that in each unit cell there are on the average four quadrangular planes of oxygens. These planes form two sets oriented differently in the lattice. One set of planes is almost perpendicular to the c' axis. This can also provide a suitable site for VO^{2+} . On comparing experimentally determined direction of the z axis of the EPR spectrum of VO^{2+} at site I and II with the structure of the lattice, it is found that the direction of the z axes are almost parallel to the $\text{K(Rb)}\text{--O}$ ($r = 0.2834$ nm, direction cosines $-0.0480, 0.2047, 0.9986$) and which is nearly parallel to the c' axis. This indicates that VO^{2+} is entering the lattice at substitutional as well as interstitial sites. In $(\text{NH}_4)_2\text{SeO}_4$ lattice also

VO^{2+} was found to enter at substitutional and interstitial sites [5]. However, it is difficult to conclude which VO^{2+} spectrum belongs to substitutional site.

Since two chemically identical but differently oriented interstitial sites are available in the lattice, one would expect VO^{2+} impurity to show no preference for a particular site and one would anticipate spectra of sixteen lines of equal intensity corresponding to two interstitial sites in addition to the substitutional sites. However, the observation of the spectra of only one interstitial site indicate that perhaps there is a large difference in intensities corresponding to two interstitial sites. A similar difference in intensities was observed in $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ [6] and $\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ [7]. The observed behaviour is explained on the basis of the dynamics of crystal growth [8]. The z axis of site III is at about $\approx 5^\circ$ with the b axis. This direction is very close to that of $\text{K(Rb)-O}'_2$ ($r = 0.27044$ nm, direction cosines $-0.00566, -0.9556, -0.2946$) indicating that perhaps spectra of site III are due to VO^{2+} substituting for Rb^+ with V=O bond nearly along the $\text{K(Rb)-O}'_2$ direction which is shortest bond direction.

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