Multi-Frequency and Single-Crystal EPR on V^{4+} in W-Doped β -Vanadyl(V) Phosphate: Hyperfine Coupling- and g -Tensor Values and Orientation

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Abstract

Different structure types of vanadyl(V) orthophosphate [i.e. $(V^V \equiv O)^{3+}$ orthophosphate] have been subjects of research due to their catalytic activity in the oxidation of n -butane to maleic anhydride. Electron paramagnetic resonance (EPR) spectroscopy can be exploited to elucidate the electronic structure of such compounds. When tuning the oxidation state of vanadium in $(V_{1-x}W_x)OPO_4$, X-band EPR spectra have confirmed the presence of paramagnetic V^{4+} ions. However, some of the features in these spectra could not be explained. Here, powder samples of β -($V_{0.99}^{IV}V_{0.01}^{V}W_{0.01}^{VI}$) OPO_4 are investigated at S-, X- and Q- band, along with X-band EPR measurements on single crystals. Thereby, the discrepancies between the spectra and their simulations could be resolved. In particular, it could be shown that the g and A tensors are not coaxial. The resulting consistent EPR picture and the refined paramagnetic parameters are reported. The work underlines the indispensability of a multi-frequency approach in EPR for unequivocal conclusions.

1 Introduction

Vanadyl(IV) pyrophosphate [that is, $(V^{IV}O)_2P_2O_7$] has long been used industrially for the selective oxidation of n -butane to maleic anhydride (MAN) [1]. The catalyst is often referred to as vanadium phosphorus oxide (VPO) due to the presence of multiple vanadium(V) orthophosphate by-phases. Structure types of such by-phases or single stable phases are α_I -VOPO₄, α_{II} -VOPO₄, β -VOPO₄, γ -VOPO₄, and δ -VOPO₄ [2, 3]. These were subject of various studies into their structures and their

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catalytic properties [2, 3]. It was found that the catalytic reaction mechanism may involve vanadium in an intermediate oxidation state [4]. This, in turn, has encouraged experimental efforts to introduce mixed-valency in vanadyl phosphates, hoping for new catalyst materials [5–7].

Electron paramagnetic resonance spectroscopy (EPR) is an established powerful method for investigating systems with unpaired electrons [8]. The dependency of the electron and nuclear Zeeman effects on the external magnetic field, in contrast to the field independence of other terms of the EPR Hamiltonian, such as hyperfine and quadruple interactions, renders acquiring EPR spectra at multiple microwave frequencies helpful and often essential for an unequivocal determination of the plethora of involved magnetic parameters [8, 9]. When a single crystal of the system under investigation is present, the orientation of the magnetic tensors (such as the $\mathbf{g}$ and $\mathbf{A}$) and consequently the relative orientations of molecular units and chemical bonds with respect to the crystal axes can be determined by recording EPR spectra at different orientations of the crystal [10].

While vanadium(V) has no unpaired electrons ($S=0$) and thus is EPR silent, vanadium(IV) has one unpaired electron ($S=1/2$). Thus, continuous wave (cw) EPR spectroscopy has been invoked previously to study the solid solution $(V^{IV}_x V^{V}_{1-2x} W^{VI}_x)OPO_4$, which adopts the β -VOPO₄ structure type for $x \leq 0.01$ [5]. However, some features of the spectra, and a small splitting of ca. 0.7 mT in particular, could not be explained [5]. Here, this system is revisited by recording cw X-band EPR spectra of a single crystal of such a β -VOPO₄ mixed valence species in addition to S-, X- and Q-band EPR spectra of its powder. The resulting consistent set of magnetic parameters from the simulation of all the data sets is reported, and reveals a significant rotation of the $\mathbf{g}$ - and $\mathbf{A}$ -tensors with respect to each other.

2 Experimental Details

2.1 Synthesis and Crystallization

The previously reported literature procedures were used for the synthesis of β -VOPO₄, $W^{VI}OPO_4$, $(V^{IV}_x V^{V}_{1-2x} W^{VI}_x)OPO_4$, and the making of the single crystals of $(V_{1-x} W_x)OPO_4$ [5].

2.2 EPR Measurement

The cw EPR spectra of all samples were acquired on a Bruker Elexsys E580 spectrometer at ambient temperature. Powdered samples were measured at S-, X- and Q-band frequencies (Figs. 1, 2, left), with MgO:Mn²⁺ as magnetic field calibration standard [11]. For S-, X- and Q-band frequencies (corresponding to ca. 3.5 GHz, ca. 9.7 GHz and ca. 33.7 GHz), resonators ER4118MS5, ER4119HS and EN5107D2 from Bruker were utilized, respectively. Single-crystal EPR measurements (Fig. 4) were performed at X-band, using a programmable E218-1001 goniometer also from Bruker. The crystals were mounted on a homemade mounting rod, which consisted

Fig. 1 EPR spectra of the powder sample of $(V^{IV}_{0.01}V^V_{0.98}W^{VI}_{0.01})OPO_4$ **a** at S-band and **b** at Q-band microwave frequencies. The simulations are overlaid as red lines. All spectra were acquired at ambient temperature. The simulation parameters are listed in Table 1 (colour figure online)

Fig. 2 Shortcoming of the single-frequency EPR. **a** The experimental X-band EPR spectrum of $(V^{IV}_{0.01}V^V_{0.98}W^{VI}_{0.01})OPO_4$ (black, identical to that of [5]), the simulation with multifrequency parameters (red), and the previously reported simulation [5] (magenta). **b** The top inset focuses on a small but significant mismatch at the central region, if g and A are considered to be collinear. **c** The two insets at the bottom zoom in on the most pronounced set of smaller peaks, which are suspected to stem from hyperfine coupling to one or more of the phosphorus atoms. **d** Q-band comparison of the multifrequency simulation (red), and the simulation with previously reported X-band-extracted parameters in [5] (magenta) (colour figure online)

of a quartz tube equipped with a flat-faced Teflon tip. All spectral simulations were performed using *EasySpin*, a MATLAB® toolbox for simulating and fitting EPR spectra [12].

3 Results and Discussion

The solid solution β -(V_{0.99}W_{0.01})OPO₄, which assumes the β structure type (β -(V^{IV}_{0.01}V^V_{0.98}W^{VI}_{0.01})OPO₄) [13], gives rise to an EPR spectrum due to the presence of paramagnetic V(IV) in its structure [5]. The *cw* S-, X- and Q-band EPR spectra of powdered (V_{0.99}W_{0.01})OPO₄, are shown in Fig. 1. These spectra are dominated by the octuplet hyperfine peaks brought about by the ⁵¹V (*I*=7/2) nuclei. A previously reported effort in the simulation of the X-band EPR spectrum of the compound resulted in a presentable spectral agreement albeit failing to reproduce some small but significant features of the spectrum [5]. Using here the previously reported values of the *g* (*g*_{||}=1.935, *g*_⊥=1.965) and *A*(⁵¹V) tensor (*A*_{||}=504 MHz, *A*_⊥=159 MHz) drastically fails to reproduce the spectrum at Q-band (Fig. 2, right). A close inspection of the Q-band spectrum, where the *g* resolution is larger than at S- or X-band, reveals that *g* is actually orthorhombic and not as previously reported axial. In addition, initial attempts to simultaneously simulate the EPR spectra from all three frequencies indicated that *g* and *A* are not collinear.

The orientation of the two tensors with respect to each other was then established via single crystal X-band EPR measurements (Fig. 3).

Since the *g* tensor is practically axial at X-band, it was sufficient to record two sets of EPR spectra, with incremental rotation of the crystal around two perpendicular rotation axes, one parallel to *a* and one in the *b* and *c* plane (Fig. 4) [13]. Figure 3 shows the resulting spectra and their simulations. The agreement is very good and the parameters are consistent with the powder EPR data at S-, X-, and Q-band microwave frequencies. Successful simulation of the single crystal and Q-band powder measurements were only possible with Euler rotation angles α , β , γ of 0°, 18° and 0°, respectively, that is, the *g* and *A* tensors are off by an 18° rotation around the *y* axis (Fig. 4). A comparison with the previously reported parameters (Table 1) shows also that indeed a small *g* and *A* orthorhombicity has to be included to fully describe the spectra as well as a non-collinearity of the tensors. Figure 4 also shows the zigzag of the octahedra, and how *g*_z closely aligns with the *a* axis of the crystal, while *A*_z aligns with the V≡O bonds.

Although the presented simulation model demonstrates a consistent and good agreement over three frequency bands and for powder as well as single crystal, it is

Fig. 3 Single crystal EPR measurement of β -($V_{0.99}W_{0.01}$) OPO_4 at X-band. The angles refer to the rotations around the crystal axis a (right), and a perpendicular rotation axis in the b - c plane (left) (Fig. 4)

not perfect. Of particular interest are the two sets of line splittings at X-band, each about 0.7 mT, centered around 328 mT and 360 mT, respectively (Fig. 2, left—bottom insets). We suspect that these doublets may rise from unaccounted-for hyperfine interactions of the phosphorus atoms, as opposed to the presence of two virtually identical species at a 1:1 ratio. There are three types of P atoms, connected to each V through O bridges, at distances ranging from 3.1 to 3.3 Å [13]. These phosphorus atoms were not included in the simulations to avoid overfitting the data.

4 Conclusion

Here, we have shown that multi-frequency EPR in combination with single-crystal EPR was necessary to obtain a full picture of the g and $A(^{51}V)$ tensors of β -($V_{0.99}W_{0.01}$) OPO_4 . However, the improvement with respect to the previous reported tensors is fairly subtle and does not change the conclusions drawn in the earlier paper [5].

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Fig. 4 Relative orientation of the molecular units and crystal axes in β -($V_{0.99}W_{0.01}$) OPO_4 (adopted from [13]). The atoms are colour coded as follows: phosphorus yellow, oxygen in vanadyl purple, other oxygen atoms white, vanadium grey. $g_z \parallel a$ and A_z tilted away from a by 18° (whether A_z is in the a - c or a - b plane could not be determined) (colour figure online)

Table 1 Simulation parameters for the powder sample of ($V_{0.01}^{IV}V_{0.98}^{V}W_{0.01}^{VI}$) OPO_4 at S-, X-, and Q-band microwave frequencies (Figs. 1, 2, left) as well as its single crystal EPR spectra at X-band (Fig. 4)

Parameter	This work	Literature
g	1.9666(4) ^a	1.965
	1.9636(4)	1.965
	1.9330(2)	1.935
$A(^{51}V)/\text{MHz}$	163(3)	159
	157(4)	159
	503(1)	504
$\alpha, \beta, \gamma/^\circ$	0(3), 18(1), 0(3)	0, 0, 0 (implicit)

Previously reported values are tabulated alongside [5]

^aThe numbers in parentheses indicate the errors in the last reported digits

Author contributions Chemical synthesis, assessment, and crystallization was done by SCR and supervised by RG. EPR measurements and data simulations were performed by YN and supervised by OS. The manuscript was written by YN, with contributions from RG and OS.

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Compliance with ethical standards

Conflict of interest The authors declare no conflicting/competing interests.

Availability of data, material and code The experimental data, materials and simulation code can be made available upon request.

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