

# EPR of $\text{VO}^{2+}$ in $\text{KTiOPO}_4$ Single Crystals

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*Dedicated to Prof. Dr. K. Recker on the occasion of his 65th birthday*

$\text{KTiOPO}_4$  single crystals doped with  $\text{V}_2\text{O}_4$  were grown from fluxes between 1323 and 1123 K with dimensions up to  $(10 \times 5 \times 5) \text{ mm}^3$ . Two crystallographically inequivalent centers of  $\text{VO}^{2+}$  in the occupation ratio of 10:1 were detected by EPR at room temperature. Their  $z$  axes of largest hyperfine splitting are oriented close to the directions of the very short Ti–O bonds of the two Ti in the structure. An energy difference for incorporation of  $\text{VO}^{2+}$  into these two sites of  $-9.4 \pm 1.7$  kJ/mol per pm difference in bond lengths was obtained from the occupation ratio, the large limits of error being mainly due to uncertainties in the bond lengths. Additional hyperfine splitting caused by  $^{31}\text{P}$  nuclei as next-nearest neighbors was also resolved in most orientations.

## Introduction

$\text{KTiOPO}_4$  (often referred to as KTP) has found important applications as a component with non-linear properties in laser and electro-optic systems. It is considered the material of choice for doubling of the  $1.064 \mu\text{m}$  Nd : YAG laser radiation [1]. The advantages offered by KTP are its large non-linear coefficients, broad spectral and temperature bandwidths, high mechanical and chemical stabilities and a high damage threshold.

EPR of  $\text{Fe}^{3+}$  in KTP has recently been studied [2]. Only one center was observed and assigned to Ti (1) on the basis of the orientation of the pseudosymmetry axes of the fourth-order zero-field splitting parameters [3]. This assignment is still questionable since the reliability of this pseudosymmetry method has never been tested rigorously, and it has been shown in the case of  $\text{Mn}^{2+}$  in  $\text{CaMgSi}_2\text{O}_6$  to lead to erroneous results [4]. According to general rules for incorporation of transition-metal impurities [5] Ti (2) with slightly longer average bond distances and less compression along the shortest bond should be preferentially occupied.

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The presence of one short Ti–O bond for both Ti sites should favor incorporation of the ion  $\text{VO}^{2+}$  as observed in titanite ( $\text{CaTiOSiO}_4$ ) [6], wavellite ( $\text{Al}_3(\text{OH})_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ ) [7] and other minerals. It was hoped that both sites would be occupied so that from their concentration ratio an estimate of the energy difference for the different bond lengths of the short Ti–O bonds could be obtained for the first time (assuming that the occupation ratio reflects the equilibrium at the growth temperature).

KTP crystallizes in the acentric space group  $\text{Pna}2_1$  ( $C_{2v}^9$ ) with the lattice parameters  $a = 1281.4$ ;  $b = 1061.6$ ;  $c = 640.4$  pm and  $Z = 8$  according to a crystal structure refinement [8]. Slightly different lattice parameters were reported recently [9].

Since KTP melts incongruently, crystals cannot be obtained from their own melt. The first attempts to grow it were reported by Ouvrard [10]. Patents by Bierlein and Gier [11] describe crystal growth by the flux and hydrothermal methods. The need for non-linear optical material of high efficiency has considerably promoted the efforts for growth of high-quality KTP [12–16]. The largest progress in crystal growth of KTP by the flux and in particular the top-seeded solution growth (TSSG) technique was achieved by Bordui [17].

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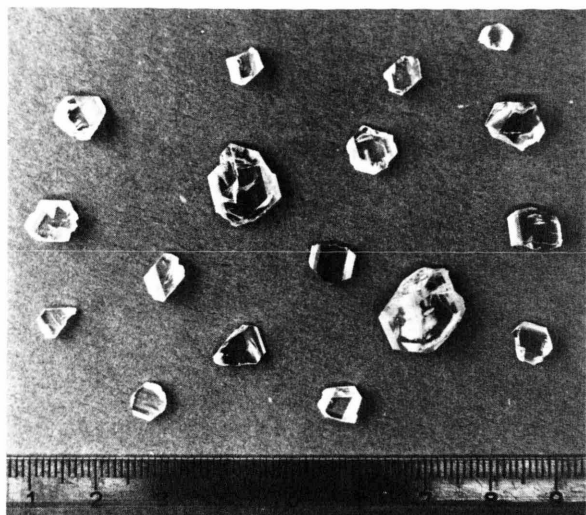


Fig. 1. Crystals of  $\text{KTiOPO}_4$  grown from a  $\text{K}_6\text{P}_4\text{O}_{13}$  flux. The scale is in centimeters.

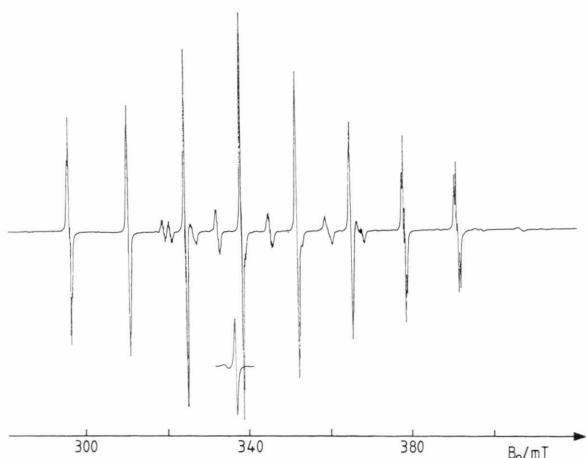


Fig. 2. EPR spectrum of  $\text{VO}^{2+}$  in  $\text{KTiOPO}_4$  at 9.4 GHz and 298 K for the magnetic field approximately along the  $a$  axis. Presence of two centers as well as additional hyperfine splitting due to  $^{31}\text{P}$  nuclei are clearly visible. The small signal below is due to piceine.

## Experimental

Our KTP crystals doped with 1 to 2 mol%  $\text{V}_2\text{O}_5$  were grown by the conventional flux technique in platinum crucibles (alloyed with Ir, Rh or Au). The furnace consisted of a Kanthal-Al heater with ceramic fiber insulation. Two different types of fluxes were used:  $\text{K}_6\text{P}_4\text{O}_{13}$  and  $3\text{KWO}_4 \cdot \text{P}_2\text{O}_5$ . They were crystallized after soaking periods of 3 hours by sponta-

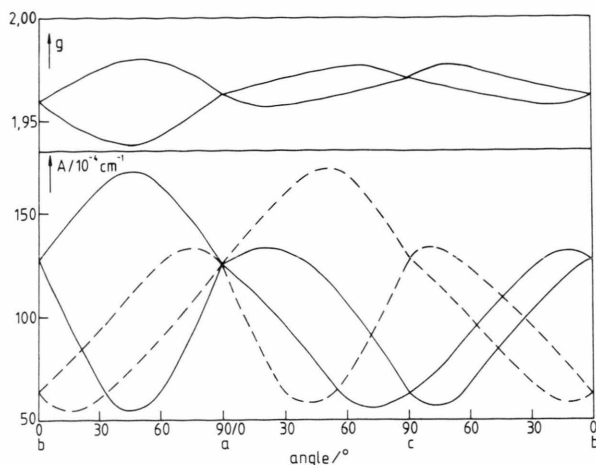


Fig. 3. Rotational diagrams of the  $^{51}\text{V}$  hyperfine splitting constants and  $g$  factors for  $\text{VO}^{2+}$  in  $\text{KTiOPO}_4$ . Full lines: Ti(1) site; dashed lines: Ti(2) site.

neous nucleation in the temperature range between 1323 and 1123 K with a cooling rate of 0.1 K/h and subsequent cooling to room temperature with 50 K/h.

After dissolution of the flux in hot water, yellow transparent KTP crystals with dimensions up to  $(10 \times 5 \times 5) \text{ mm}^3$  were obtained, see Figure 1. Details of the crystal growth, especially for samples doped with  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$ , will be reported in a subsequent paper.

EPR measurements were carried out at room temperature on an X-band spectrometer model 200 D of Bruker Analytische Meßtechnik GmbH, Karlsruhe using piceine as a standard for precise determination of  $g$  factors [18].

## Results and Discussion

The crystals were oriented according to their morphologies with (001) as the largest face. EPR spectra were recorded for rotations around the three crystal axes  $a$ ,  $b$  and  $c$ , where the orientations of the other two axes were found from coincidence of the pairs of magnetically inequivalent spectra. Two such crystallographically inequivalent pairs of spectra, each with a characteristic octet hyperfine splitting due to the  $^{51}\text{V}$  nucleus with  $I=7/2$  were observed with an intensity ratio close to 10 : 1. An example is shown in Figure 2. The rotational diagrams in Fig. 3 show that very similar hyperfine splittings result for the two centers with

their orientations converting into each other if the  $a$  and  $c$  axes are interchanged. The  $g$  factors are also very similar, but those of the center of lower symmetry are not shown because of the larger limits of error resulting from the fact that they are partially hidden under the more intense spectra for many orientations. Principal axes transformations for the more intense center resulted in the principal values and principal axes directions listed in Table 1. Clearly the results are typical for a  $\text{VO}^{2+}$  ion with a short  $\text{V}=\text{O}$  bond as a comparison with the results for titanite [6], wavellite [7] and many other systems listed in review articles [19] shows.

The orientations of these principal axes for the more intense center are drawn in the stereographic projection in Fig. 4 together with the orientations of the short  $\text{Ti}(1)-\text{O}(\text{T}_2)$  and  $\text{Ti}(2)-\text{O}(\text{T}_1)$  bonds. Also included in this Figure is the orientation of  $A'_{zz}$  for the less intense center resulting from interchange of  $a$  and  $c$  axes for  $A_{zz}$  of the more intense center. Clearly these orientations almost coincide within the limits of error with those of the two short  $\text{Ti}-\text{O}$  bonds of 171.3(4) and 173.8(4) pm for  $\text{Ti}(1)$  and  $\text{Ti}(2)$ , respectively [8]. Thus they can unambiguously be assigned to these two sites. The higher occupation of  $\text{Ti}(1)$  is most likely caused by the shorter  $\text{Ti}(1)-\text{O}(\text{T}_2)$  bond according to results for a number of other systems [5] including wavellite [7]. Assuming an effective growth temperature between 1223 and 1173 K (lower than the average because more material is deposited in the later, lower-temperature stages of crystal growth for the same linear growth) an estimate of the energy difference  $\Delta H$  can be obtained from the occupation ratio  $n_2/n_1$ :

$$\Delta H = RT \ln n_2/n_1 = -8.314 \cdot 2.303 \cdot T \quad (1)$$

resulting in a value of  $\Delta H = (-22.9 \pm 0.5) \text{ kJ/mol}$ . With the difference in bond lengths of  $(2.0 \pm 0.8) \text{ pm}$  this leads to an energy difference per pm decrease in bond length of  $(-13.7 \pm 5.5) \text{ kJ/mol}^*$ . To our knowledge this is the first estimate available. The large limits of error are mainly due to the uncertainties in bond lengths. It must be emphasized that the actual bond lengths are about 10 pm shorter than the  $\text{Ti}-\text{O}$  bond lengths according to the large values of  $A_{zz}$ . Thus in

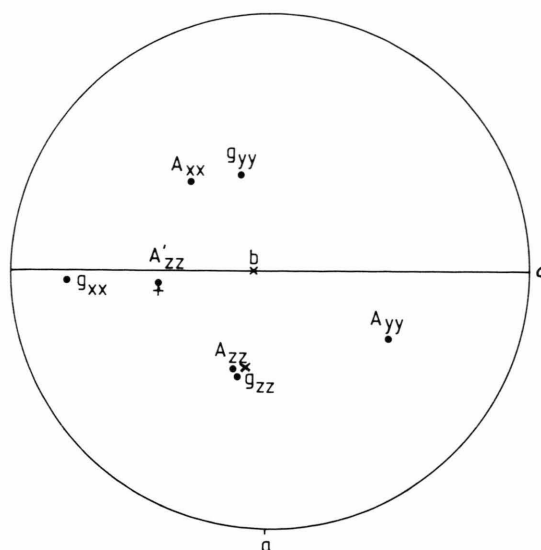


Fig. 4. Stereographic projection of the principal axes of the  $^{51}\text{V}$  hyperfine tensor and  $g$  matrix for  $\text{VO}^{2+}$  in  $\text{Ti}(1)$  site in  $\text{KTiOPO}_4$ . Also included are the directions of  $A'_{zz}$  for the  $\text{Ti}(2)$  site ( $\circ$ ) and of the  $\text{Ti}(1)-\text{O}(\text{T}_2)$  ( $\times$ ) and  $\text{Ti}(2)-\text{O}(\text{T}_1)$  ( $+$ ) short bonds.

Table 1. Spin-Hamiltonian parameters for  $\text{VO}^{2+}$  in  $\text{Ti}(1)$  sites in  $\text{KTiOPO}_4$ .

$i$	$g_{ii}$	$\vartheta/^\circ$	$\varphi/^\circ$	$A_{ii}/10^{-4} \text{ cm}^{-1}$	$\vartheta/^\circ$	$\varphi/^\circ$
$x$	1.975(5)	77.5	87.6	60.8(2)	51.0	137.7
$y$	1.981(3)	43.3	163.7	50.6(2)	57.5	68.2
$z$	1.937(5)	46.4	10.1	175.4(3)	49.3	19.3

$\vartheta$  and  $\varphi$  are the angles to the  $b$  axis and of the projection onto the  $a-c$  plane to the  $a$  axis, respectively. Limits of error for these angles are  $\pm 1.5^\circ$ .

addition to these static differences the dynamical properties of the  $\text{Ti}$  sites are also of influence on the value of  $\Delta H$ , but they should be very similar for these two sites.

Although the principal values of the  $g$  matrix and the hyperfine tensor are not collinear, the directions of their  $z$  components are very similar. From the principal values of the former, estimates for the positions of three of the four excited ligand-field states can be obtained according to the first-order relations

$$\Delta E_{x^2-y^2} = -\frac{8\lambda}{g_{zz}-2.0023} \quad \text{and} \quad E_{iz} = -\frac{2\lambda}{g_{iz}-2.0023} \quad (2)$$

with  $\lambda = 150 \text{ cm}^{-1}$  the spin-orbit coupling constant of  $\text{V}^{4+}$  and  $i = x, y$ . This results in excitation energies of

\* Note added in proof: According to another crystal structure refinement (I. V. Voloshina, R. G. Gerr, M. Y. Antipin, V. G. Tsirel'son, N. I. Pavlova, Y. T. Struchkov, and R. P. Ozerov, Sov. Phys. Crystallogr. **30**, 389 (1985)) it is  $9.4 \pm 1.7 \text{ kJ/mol} \cdot \text{pm}$ .

18 400, 11 000 and 14 100  $\text{cm}^{-1}$ . The first and last one should contribute to optical absorption in the visible range, but the yellow color of the crystals suggests that the contribution from a charge-transfer band in the near UV dominates.

A further splitting of the signals for both centers is clearly evident in Figure 2. It is best resolved for the rotation around the *c* axis, where it results in doublets with intensity ratios of 1:1 and about 0.4 mT separation for the more intense spectra and in triplets with intensity ratios of 1:2:1 and about 0.7 mT separation for the spectra of lower intensity. Undoubtedly it is caused by the  $^{31}\text{P}$  nuclei as next-nearest neighbors. There are two such neighbors for Ti(1) at distances of 326 and 337 pm with their Ti(1)–P directions nearly parallel and perpendicular, respectively, to the *c*-axis. For Ti(2) there are four P at distances between 319 and 326 pm. Two of these Ti(2)–P directions each are closely aligned along the *a* and *b* axes, respectively. More complicated hyperfine splittings from these nuclei at other orientations are qualitatively understandable, but it was not possible to analyze them completely. If they are assumed to be isotropic and

positive, estimates of 3s-electron densities of 0.08 and 0.14%, respectively, result, not unreasonable values for such next-nearest neighbors.

No such  $^{31}\text{P}$  hyperfine splittings could be resolved in wavellite [7], where the most prominent center has two next-nearest P neighbors at slightly shorter distance. They must in this case be hidden in the considerably larger linewidths of 1.3 mT, most likely resulting from additional unresolved hyperfine splitting from  $^{27}\text{Al}$  nuclei with  $I=5/2$ . In contrast, the rather small magnetic moments of  $^{39}\text{K}$  and  $^{41}\text{K}$  in KTP cause a very small hyperfine splitting only. Both can only be resolved by ENDOR or electron-spin echo envelope modulation measurements.

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