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Shiying Han†§, Jiyang Wang‡, Yunxia Xu†§, Yaogang Liu‡ and Jinqian Wei‡

† Laboratory of Solid State Microstructure, Nanjing University, Nanjing 210008, People's Republic of China
‡ Institute of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China

Abstract. Two groups of EPR hyperfine lines of a V^{4+} ion substituting for a Ti^{4+} ion, corresponding to two kinds of sites which are Ti(1) and Ti(2) sites in the $KTiOPO_4$ single crystal, are observed at room temperature in the X band. The principal values and direction cosines of the principal axes of the **g** and **A** tensors are computed using a least-squares fitting procedure for two kinds of sites, and the principal axes of the **g** tensor of all eight Ti ion sites substituted in a unit cell of $KTiOPO_4$, of which orientations are physically distinct, are revealed.

1. Introduction

The single-crystal $KTiOPO_4$ (hereafter KTP) has been demonstrated to possess superior qualities for applications as a non-linear optical material (Zumsteg *et al* 1976). In some published investigations, considerable effort has been made to attempt to clarify the structural origin of the optical response of KTP and the analogue of composition-modified KTP by means of x-ray analysis (Thomas and Watts 1990, Jacco *et al* 1984). Electron paramagnetic resonance (EPR) can yield much information about the interaction of a paramagnetic ion with its environment. For this purpose the crystal of KTP was grown from a modified flux solution with a small percentage of V_2O_5. In the present paper it is reported that the EPR spectra of the KTP with paramagnetic impurities, V^{4+} ions, have been observed. The principal values of **g** and **A** tensors, as well as the direction cosines of their principal axes for all eight Ti ion sites substituted in a unit cell of KTP have been computed rigorously from EPR experimental data by a general least-squares fitting (LSF) procedure.

2. Experiment

2.1. Sample preparation and crystal structure

Single crystals of V^{4+}-doped KTP were grown by the flux method (Liu *et al* 1986) with a dopant of V_2O_5 in the initial compositions. The crystals are transparent and light

§ Permanent address: Centre of Materials Analysis, Nanjing University, Nanjing 210008, People's Republic of China.

yellow in colour. A crystal sample of size $2 \times 2 \times 1.5$ mm^3 cut along the (100) face was used for the EPR measurement. The crystal structure (Tordjman *et al* 1974) of KTP is orthorhombic and belongs to the acentric point group $mm2$ with the space group $Pn2_1a$. The fundamental skeleton of the KTP structure is characterized by chains of TiO$_6$ octahedra linked at two corners with alternating long and short bonds. The unit cell consists of eight formula KTiOPO$_4$ with $a = 12.814$, $b = 10.616$ and $c = 6.404$ Å. In fact, each two formulae form a unique unit which contains two kinds of TiO$_6$ octahedra with different bond lengths and angles; PO$_4$ tetrahedra and K ion sites also have two kinds. Therefore, there are four unique units in a unit cell of KTP.

2.2. Measurement and spectra details

EPR measurement was performed on a Bruker ER200D-SRC spectrometer in the X band at room temperature for the external magnetic field, B, in three mutually perpendicular planes defined by the x, y and z axes of the experimental system (x, y, z). To simplify the analysis of the EPR spectra, the x axis was chosen to be parallel to the crystallographic c axis and the y and z axes parallel to the a and b axes respectively. EPR spectra were recorded by varying the orientations of the external magnetic field in each plane (zx, zy and xy planes) at 10° intervals. For the single crystal of V^{4+}-doped KTP, eight sets of EPR hyperfine lines were observed in general orientations of the external magnetic field, but each set contains eight hyperfine lines that would be allowed transitions (for the V^{4+} ion electron spin $S = 1/2$ and nuclear spin $I = 7/2$, the number of hyperfine lines $2S \times (2I + 1) = 8$). These eight sets of hyperfine lines can be divided into two groups, say groups I and II, which are related to symmetries of V^{4+} ion sites. The hyperfine line intensity of one of the groups is stronger than that of the other. As far as any one group is concerned, it contains four sets of eight hyperfine lines which arise from four physically equivalent but magnetically non-equivalent V^{4+} ion sites. It should be noted that when B is applied in the crystal principal planes bc, ba and ca (i.e. zx, zy and xy respectively), four sets of eight hyperfine lines merge to become two sets. However, when B is along the crystallographic axes a, b and c, only one set of eight hyperfine lines is observed. The EPR spectrum for $B \| c$ axis is displayed in figure 1, where the set of eight stronger hyperfine lines is assigned to group I and the other set to group II. In fact, two groups of lines with different intensities arise from two kinds of site in KTP that are Ti(1) and Ti(2) sites, say sites I and II. In other words, the hyperfine line sets of groups I and II are related to sites I and II, respectively. An angular variation pattern of EPR hyperfine line positions for B in the bc plane is drawn in figure 2. The two groups of hyperfine lines (a) and (b) shown in figure 2 are connected with site I and site II respectively. The centre of a hyperfine line set corresponds to a fine line position; angular variation patterns of fine line positions in three mutually perpendicular planes for site I are given in figure 3. In addition, the two groups of hyperfine lines have an intensity ratio of 2.

3. Calculation of **g** and **A** tensors

For the V^{4+} ion the effective electronic spin $S = 1/2$ and nuclear spin $I = 7/2$. The spin Hamiltonian appropriate to a V^{4+}-ion site can be expressed as

$$\mathcal{H} = \mu_B S \cdot \mathbf{g} \cdot B + S \cdot \mathbf{A} \cdot I. \tag{1}$$

Figure 1. Observed EPR absorption derivative spectrum of V^{4+}-doped KTP in the X band at room temperature with the magnetic field along the c axis; each line is of quartet degeneration in this axis. (a) Positions of hyperfine lines for site I; (b) positions of hyperfine lines for site II.

The symbols used in equation (1) have their usual meanings. The principal values and direction cosines of the $\mathbf{g}^2$ ($= \mathbf{g}^T \cdot \mathbf{g}$; $\mathbf{g}^T$ is the transpose of a matrix of $\mathbf{g}$) and $\mathbf{A}^2$ ($= \mathbf{A}^T \cdot \mathbf{A}$) matrices, which are real and symmetric and represent true second-rank tensors, were computed by EPR experimental data using the LSF procedure (Misra 1984), yielding the moduli of the principal values of $\mathbf{g}$ and $\mathbf{A}$, as well as their direction cosines.
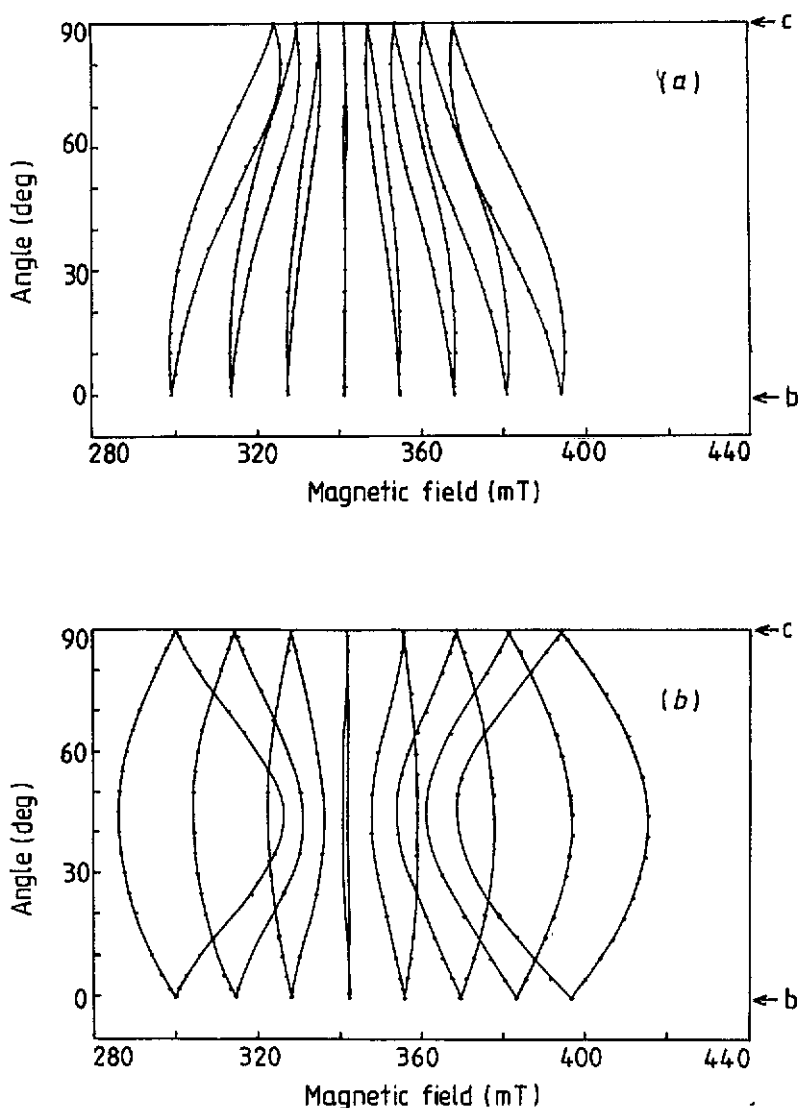
For site I the principal values of the $\mathbf{g}$ tensor and the direction cosines of its principal axes with respect to the experimental system (x, y, z) can be determined from figure 3. It is easy to follow the angular dependence of one molecule site in a plane, but it is difficult to know which curve corresponds to this molecule site in a different plane, since there are two possibilities for choosing a curve in each plane, thus three planes yield eight different combinations. For the four combinations, the principal values of $\mathbf{g}$ are equal, and their direction cosines, lmn, $\overline{l}mn$, $l\overline{m}n$ and $lm\overline{n}$ obviously have a simple relationship. Based on these results by calculation, four physically equivalent but magnetically non-equivalent sites can be shown. The results are given in table 1 for both sites.

We now simultaneously fit all the hyperfine line positions in three mutually perpendicular planes, of which one plane is given in figure 2, and compute the principal values of $\mathbf{A}$ and the direction cosines of its principal axes x'', y'', z'' with respect to the principal axes x', y', z' of $\mathbf{g}$ for the site I. Similar steps can be worked out for site II. The values of these parameters are listed in table 2.

4. Conclusion and discussion

The main results of the present EPR studies on a KTP single crystal with a small dopant of V_2O_5 are as follows.

(i) Eight magnetically non-equivalent V^{4+}-ion sites, consisting of two kinds of V^{4+} site, are observed. It is shown that it is possible to partially substitute the Ti^{4+} ion of TiO_6 octahedra by a V^{4+} ion of the same valency but smaller ionic radius. Moreover, the ratio of substituted amounts for two different Ti ion sites, which are assigned to Ti(1) and Ti(2) sites, has been determined, by average integrated intensities of EPR hyperfine lines, to be about 2; however, it is impossible to determine which Ti site (Ti(1) or Ti(2)) is substituted by more V ions.

Figure 2. Angular dependence of the spectra of V^{4+}-doped KTP with the magnetic field parallel to the (100) face; each curve is of doublet degeneration in this plane. (*a*) For site I; (*b*) for site II.

(ii) The principal values of the **g** and **A** tensors, as well as their direction cosines, have been evaluated.

(iii) These principal values listed in tables 1 and 2 are typical of vanadyl complexes characterized by an axial symmetry of the ligand field, in which two principal values of the **g** and **A** tensors are almost equal, i.e. $g_{x'} \cong g_{y'}$ and $A_{x''} \cong A_{y''}$, for both sites. This means that the V ion enters the lattice to substitute for the Ti ion and to form a V site with tetragonally distorted octahedral symmetry.

(iv) Each kind of site contains four sets of direction cosines (listed in tables 1 and 2): lmn, $\bar{l}mn$, $l\bar{m}n$ and $lm\bar{n}$; they reveal different orientations for four physically
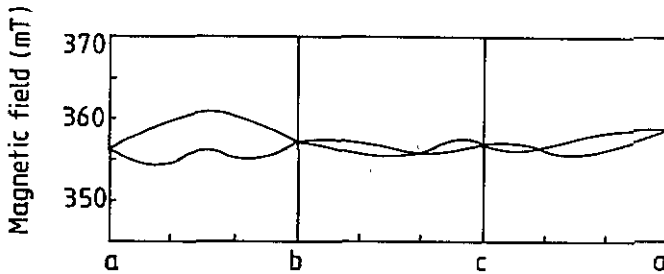
Figure 3. Angular dependence of centre positions of eight hyperfine lines corresponding to the same site with the magnetic field in three crystallographic principal planes for site I, each curve is of doublet degeneration in these planes.

Table 1. Principal values of the **g** tensor and direction cosines of its principal axes (x', y', z') with respect to the coordinate system (x, y, z) for two kinds of site. The direction cosines of another three sets of four physically equivalent but magnetically non-equivalent sites are obtained through the relations: $\bar{l}, m, n; l, \bar{m}, n; l, m, \bar{n}$ for each kind of site.

			Direction cosines		
Sites	Principal values		x	y	z
I	$g_{x'} = 1.9825$	l	0.1969	−0.6816	0.7047
	$g_{y'} = 1.9659$	m	0.9573	0.2887	0.0119
	$g_{z'} = 1.9342$	n	−0.2116	0.6723	0.7094
II	$g_{x'} = 1.9730$	l	0.7975	−0.0542	−0.6009
	$g_{y'} = 1.9596$	m	0.2110	0.9581	0.1936
	$g_{x'} = 1.9369$	n	0.5652	−0.2812	0.7755

Table 2. Principal values of **A** and direction cosines of its principal axes (x'', y'', z'') with respect to the coordinate system (x', y', z') for two kinds of site. Principal values are expressed in GHz.

		Direction cosines		
Sites	Principal values	x'	y'	z'
I	$A_{x''} = 0.1809$	−0.9453	0.3204	−0.0615
	$A_{y''} = 0.1594$	−0.3222	−0.8876	0.3293
	$A_{z''} = 0.4994$	0.0509	0.3311	0.9422
II	$A_{x''} = 0.1828$	−0.9615	−0.1745	0.2125
	$A_{y''} = 0.1610$	0.2486	−0.8817	0.4010
	$A_{z''} = 0.5044$	0.1174	0.4384	0.8911

equivalent but magnetically non-equivalent sites in a unit cell.

(v) It is seen from tables 1 and 2 that the **g** and **A** tensors are almost coincident for both sites.

Acknowledgment

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