EPR OF SUBSTITUTIONAL FE³⁺ IN A NATURAL CRYSTAL OF BROOKITE (TiO₂)

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the Department

of

Physics

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1972

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AES TRACT

EPR spectra of Fe^{3+} in a natural crystal of brookite have been investigated at X- and Q-band frequencies at room temperature and 573°K. Part of the paramagnetic resonance spectrum observed has been interpreted on the assumption that Fe^{3+} occupies eight equivalent Ti^{4+} sites in brookite, with four inequivalent orientations.

The spectra show an "intermediate" zero-field splitting at X-band and a "normal" zero field splitting at Q-band frequencies.

The spin Hamiltonian parameters which fit the spectra are the following:

 $g = 2.002 \pm 0.005$ $D = (1170 \pm 30) \times 10^{-4} \text{ cm}^{-1}$ $E = (330 \pm 20) \times 10^{-4} \text{ cm}^{-1}$ $[pa+(1/12)p]_{010} = (13\pm10) \times 10^{-4} \text{ cm}^{-1}$ $[pa+(1/12)p]_{100} = (-13\pm5) \times 10^{-4} \text{ cm}^{-1}$ $[pa+(1/12)p]_{001} = (-66\pm4) \times 10^{-4} \text{ cm}^{-1}$ TABLE OF CONTENTS

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ACKHOWLEDGEMENTS

I would like to thank Dr. C. F. Schwerdtfeger for his helpful guidance in the preparation of this thesis.

I am also grateful to Dr. M. Horn for the many discussions on the interpretation of the observed spectra. I am also indebted to A. Harnik of the Cristallographic Institute of E.T.H., Zurich, for the supply of many specimens of Brookite.

The research of this thesis was supported financially by the National Research Council, grants number A-2228 and A-7121. Additional financial aid was obtained from the University of British Columbia's 1970-71 President's Committee on Research.

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1. INTRODUCTION

It was Klaproth who first recognized a polymorphism in 1798, that is, that the same chemical compound may crystallize in different forms. Klaproth observed the polymorphic forms of calcium carbonate (calcite, aragonite).¹

That titanium dioxide has several natural polymorphic forms (rutile, anatase and brockite) has been known already for many years. Recently, a fourth polymorphic form was synthetically produced $(\text{TiO}_2\text{II})^2$.

Rutile, anatase and brookite are often found in nature as good single crystals. Synthetically one can obtain single crystals of rutile and polycrystalline anatase³. To date, all attempts to produce brookite artificially, even in polycrystalline form, have been unsuccessful. As a result most EPR studies have been made with rutile⁴⁻⁷ and some with natural crystals of anatase⁸⁻¹³. No EPR studies of brookite have been reported.

An EPR comparative study of different polymorphic forms can be interesting from a mineralogical point of view. Only recently, EPR has been acknowledged to be a tool in mineralogy and geology. Reviews by W. Low¹⁴ and S. Ghose¹⁵ have shown that EPR can be helpful in clarifing some mineralogical problems such as the relation between the paramagnetic impurity and the mineral host (site preference). Information about coordination and local symmetry (non-equivalent sites, orientation and values

of the crystal field parameters, charge compensation), nature of chemical bonding, color centers and other lattice defects, order-disorder, and relative abundance of different paramagnetic impurities or different valence states of a given impurity may be obtained from analysis of EPR measurements.

Since impurities are a factor that determine the habit formation of the minerals it is also remotely possible that EPR can be helpful in this geological problem. Remotely since non paramagnetic impurities are impossible to observe or large concentrations of paramagnetic impurities will not be seen or make analysis extremely difficult with EPR.

In the present thesis the results of an EPR study of substitutional iron impurities in a natural single crystal of brookite are described. No attempt to analyze other EPR transition lines has been made to date although some speculation has been attempted.

2. RESULTS OF PREVIOUS INVESTIGATIONS ON BROOKITE STRUCTURE OF BROOKITE

Brookite has an orthorhombic symmetry and belongs to the Pbca (D_{2h}^{15}) space group. R. Weyl¹⁶ remeasured the lattice constants of brookite, previously determined by L. Pauling and J.H. Sturdivant¹⁷, and found their results to lie within the precision limits of 0.1% attained by his measurements. These values are:

a = 9.184 Åb = 5.447 Åc = 5.145 Å

However he found some discrepancies for the values of the lattice parameters and these are listed in Table I.

Using the values of Table I and the coordinates of equivalent positions for the Pbca space group^{18,19} one is able to find the projections of the unit cell. Figure 1 shows these projections.

Each titanium ion is surrounded by six oxygen ions at the vertices of an octahedron and it also shares three edges with other octahedrons. This is shown in Figure 2. These common edges are shorter in comparison with the other edged of the octahedron which is in accordance with Fauling's Rule²⁰. (Rutile shares two edges and anatase shares four¹⁹, ²¹).

Tables II and III give the distances between the titanium and the oxygens as well as the distances between the oxygens. Clearly, this octahedron is distorted. Furthermore,





Figure 2.- Projections in the (100) plane of some TiO_6 octahedrons. The common edges of the octahedrons are drawn heavier.

					1			
A	0	0	O	0	0	0	0	0
B	0	0	0	0	0	0	0	0
Ā	0	· 0	0	0	0	0	0	0
Ċ	0 0	o c	C) _. 0	C) (o c	C
Ā	0	. 0	Ο.	0	0	0	0	0
₿	0	0	0	0	0	0	0	0
Ā	· O	. 0	0.	· O	ò	, O	0	0
C	0.	o' 0	Ċ) 0	C		с с	0
			5.					

Figure 3.- Double hexagonal closed packed (DHCP) arrangement

R. Weyl has calculated that the Ti_{0} in the octahedron is displaced by 0.2±0.1Å from the center toward 0_{IV} and away 0_{II} (in rutile as well as anatase the titanium ion is in the middle of the TiO₆ octahedron) and that this ion, Ti₀, is further away by 0.12±0.06 Å from the neighbouring ions, Ti₁ and Ti₂ than from the third nearest neighbouring ion Ti₃, as can be calculated from Table IV. (Where the subscripts on Ti refer to the ions labelled in Figure 2).

In the brockite structure each octahedron is bound through two common edges to two other octahedrons forming a chain in the [001] direction and by the third common edge to another such chain forming a net, parallel to the (100) plane. The unit cell has two such nets, one over the other which are bound by common corners.

The (001) plane in Figure 1 shows distinctively that the unit cell has four empty columns, however, it is not clear that each such column contains two interstitial sites surrounded by six oxygens at the corners of a larger distorted octahedron.

Another way of viewing the structure of brookite is the following: the oxygen ions are in approximately double hexagonal closed packed (DHCP) arrangement, i.e. (ABACABAC...) as shown in the Figure 3. The closed packed plane is the (100) plane, one half of the octahedrons are filled with titanium²?.

TABLE I

LADDICE PARAMEDERS (IN BRACKEDS THE VALUES

	OF PAULING		
	ol	°2	Ti
x	0.008 (0.010)	0.229 (0.230)	0.128 (0.127)
у	0.147 (0.155)	0.110 (0.105)	0.098 (0.113)
z	0.182 (0.180)	0.530 (0.535)	0.863 (0.873)

TABLE II

ION	COORDINATES FOR	R A SAMPLE TIO6	OCPANEDRON
(GIVE	N IN FRACTIONS	OF THE LATCICE	CONSTANTS)
	x	у	Z
Ti _o	0,128	0,402	0,363
ΟI	0,008	0,147	0,182
OII	0,229	0,110	0,530
O _{III}	0,271	0,610	0,530
oIN	-0,008	0,647	0,318
٥v	0,229	0,390	0,030
ovi	0,008	0,353	0,682

ovi

TABLE III

ION	DIS TANCES	FOR	<u>A</u>	SAMI	PLE
TiOr	COTAMEDRO) <u>N</u> (I	PI(WRE	2)

Ti _o -0 _I	(2,00±0,05)	8
Tio-OII	(2,03±0,05)	Q A
Tio-OIII	(1,94±0,05)	Å
Tio-OIV	(1,84±0,05)	0 A
Tio-Ov	(1,95±0,05)	0 A
Tio-Ovi	(1,99±0,05)	Q A
0 ₁ -0 ₁₁	(2,71±0,08)	Å
IV ^{O-II} 0	(2,55±0,08)	Å
° _{VI} -° _{III}	(2,90±0,08)	0 A
VIO-UIIIO	(2,79±0,08)	Å
V 0- VI 0	(2,98±0,08)	Q
υ - νο	(2,55±0,08)	Å
O _{II} -O _{III}	(2,75±0,08)	Å
vo_III_0	(2,86±0,08)	0 A
°v-°II	(2,99 <u>+</u> 0,08)	o A
°I-°VI	(2,31±0,08)	<u>Q</u>
° ¹ 0 ¹ V	(2,47±0,08)	0 A
I_O_IO	(2,82±0,08)	o A

TABLE IV

(SEE FIGURE 2) Ti-Ti DISTANCES (3,00[±]0,03) Å $Ti_0 - Ti_1 = Ti_0 - Ti_2$ (2,94±0,03) Å Tio-Ti3 (3,78±0,03) Å $Ti_0 - Ti_4 = Ti_0 - Ti_5$ (3,57±0,03) Å $Ti_0 - Ti_6 = Ti_0 - Ti_7$ (3,53±0,03) Å Tio-Ti₈ = Tio-Ti9

PHASE TRANSFORMATION

The topotactic mechanisms for the TiO₂ system are based on a principle of favoring as much as possible the maintenance of the oxygen close packing during the polymorphic transition (Anatase is pseudo-cubic close packed (CCP) with the close packed plane (112); Rutile, rough approximation of an hexagonal close packed (HCP), (100) or (010) planes; TiO₂II, HCP, (100) plane).

Table V summarizes the observed and proposed topotaxy in the titanium dioxide system²².

At this point, it should be mentioned that the kinetics and mechanism of the brookite-rutile transformation are very similar to those of the anatase-rutile transformation²³⁻²⁸. The rate of transformation and its activation energy are governed by the surface size and by the amount of impurities, e.g. the concentration of oxygen vacancies or interstitials. But the activation energy, which is mainly for the production of nucleation sites, is higher for the anatase-rutile case and the entropy of activation is large and negative for the brookite-rutile transformation compared with the small and positive value for the anatase-rutile transformation. This may be understood in terms of the change of symmetry (lower to higher) of the first case and the absence of such a change in the second²⁹. The effect of impurities in general is that oxygen vacancies accelerate whereas interstitial ions inhibit. the transformation²⁶.

SUMMARY OF THE ATOMIC NOVEMENT IN

TOFOTAXY IN THE TIO2 SYSTEM

Reaction	Number of Oxygen Layers Rearranged	Redistribution of the Titanium Atoms ^a	Remarks
II - rutile	None	One half in each layer $A \ B \ A \ B \ A \ B \ A \ B \ A \ B$: : : : : : : : : $1/2 \ 1/2 \ 1/2 \ 1/2 \ 1/2 \ 1/2 \ 1/2 \ 1/2$	Only reaction that has been reversed. Experimental evi- dence inferred from work of Bendeliany et al. (1966)
Brookite - II	1 in 4	Every Ti in two consecutive layers altering with two layers in which there is no Ti motion. $A \ B \ A \ C \ A \ B \ A \ C$: : : : : : : : 1 1 0 0 1 1 0	Reaction without SRO phase formation. Hrookite has zig- zag TiOs octahedral chains as is found in II.
Brookite - rutile	This reaction does not involve an oxy- gen shearing mech- anism, but there is • shifting of all oxygen.	Every other Ti in each layer in order to form straight Ti octahedral chains. A B C A B C A B C : : : : : : : : : $1/2 \ 1/2 \ 1/2 \ 1/2 \ 1/2 \ 1/2 \ 1/2 \ 1/2$	Experimentally observed topotaxy.
Anatase-rutile	This reaction does not involve an exy- gen shearing mech- anism but all exy- gen atoms shift positions.	Every other Ti in each layer in order to form straight Ti octabedral chains. $A \ B \ A \ C \ A \ B \ A \ C$: : : : : : : $1/2 \ 1/2 \ 1/2 \ 1/2 \ 1/2 \ 1/2 \ 1/2$	Topotaxy experimentally ob- served. A large distortion oc- curs in the formation of straight octahedral chains from zigzag chains.
Anatase—II	4 in 6	A repeating sequence of all Ti and no Ti motion beginning with the Ti be- tween the A and C layers. $A \ B \ C \ A \ B \ C \ A \ B \ C : : : : : : : : : : : : : : : : : : $	Reaction always accompanied with SRO phase formation.
Anatase-brookit	te 9 in 12	Very complex	Reaction reported only one time.

• In most cases the movement of the titanium ions is to adjacent tetrahedral sites which are in the process of becoming octahedral sites because of the accompanying oxygen motion.

The legend for the titanium motion is

1/2 every other titanium changes site 1 every titanium changes site

0 no titanium changes site

The layering scheme is that of the reactant.

OTHER PROPERTIES

A list of these properties is given in Table VI. Properties of rutile and anatase have been also included for comparison^{30,8}.

	TABLE	VI		
PROPERTIES			۰. ۱	
Property	<u>Ana tase</u>	Rutil	e <u>Bro</u>	<u>okite</u>
Density '	3.87-3.958/cm	3 4.21-4.2	5g/cm ³ 4.	13g/cm ³
Eardness	5.5 - б.О	7.0 - 7.	25 5.	5-6.0
Specific heat			•	
at R.T.	13.22cal/mol ⁰	0 13.16cal	/mol ^o C	
Optical Constar n ⁵ 693A	nts 2.56	2.61	n_2	.5831
n5893A	2.49	2.90	n _p 2	•5843
Static dielect:	ric		ⁿ r ²	•7004
constant	48	114	78	
Notice that the	e values of these	physical con	stants for bro	okite
are between the	ose measured for	anatase and r	utile.	
EPR STUDIES				
Hamiltonian par	rameters for subs	titutional Fe	3+, where D, E	, a
and F are given	n in 10 ⁻⁴ cm ⁻¹ , ar	'e:		
Anatase (300°K)	ぎ 2.005	D 308-7	E e - 102.8	F
Rutile (4.2-300) ⁰ K 2.00	6780 6	90 -280	230
No EPR studies	in brookite have	been reporte	đ.	

3. THE SPIN HAMILTONIAN

The electronic configuration of the Fe³⁺ ion is $3d^5$ and the free ion electronic ground state is ${}^{6}S_{5/2}$. The magnetic resonance spectrum should be remarkably simple. The sextet would have no splitting other than the Zeeman interaction, and a single line would be observed, however, experimentally this is far from the truth. Both fine and hyperfine structures have been observed for ions with half filled 3d, 4f and 5f shells. Several mechanisms have been proposed to explain this.³¹ Spin-spin and spin-orbit interactions can produce second or higher order terms coupling the ground state through higher orbital states to the crystal field.

The multiple fine structure can conveniently be represented by adding to the Zeeman term in the spin Hamiltonian, terms of higher powers in S_x , S_y and S_z , grouping them into combinations of spin operators, each such operator being the equivalent to a combination of spherical harmonics. Such equivalent spin operators denoted as 0^m_n appear extensively in literature.³²

The advantage of using equivalent spin operators is that one can choose immediately which terms will appearain the spin Hamiltonian. One excludes the equivalent spin operators which are of odd degree in \overline{S} , since they are not invariant under time reversal. From the operators of even degree one chooses only those which reflect the symmetry of the crystal field. Furthermore, the number of such operators is limited by the

fact that operators of higher degree than 25 may be omitted since they have zero matrix elements between the states under consideration. Hence for Fe^{3+} one can write in general

$$\mathcal{H} = \beta \bar{\mathbb{H}} \cdot \tilde{g} \cdot \bar{\mathbb{S}} + 1/3 \sum_{m=-2}^{2} b_{2}^{m} o_{2}^{m} + 1/60 \sum_{m=-4}^{4} b_{4}^{4} o_{4}^{m}$$
(1)

Using the known transformation properties of Y_n^m under rotation of the coordinate system one can evaluate the transformation properties of the b_n^m under these rotations. An appendix in Baker and Williams³³ is very helpful for these calculations and has been used in Appendix A to calculate the spin Hamiltonian for an arbitrary orientation.

The spin Hamiltonian may be expressed in an alternative form. The first summation in (1) can be written as: $\overline{S} \cdot \widetilde{D} \cdot \overline{S}$

where D is a tensor quantity. Referred to the principal axes, this becomes

 $D_x S_x^2 + D_y S_y^2 + D_z S_z^2$ where it is convenient to set the sum of the three coefficients to zero by substracting the quantity

 $1/3 (D_x + D_y + D_z)(S_x^2 + S_y^2 + S_z^2) = 1/3 (D_x + D_y + D_z)S(S+1)$

which is just a constant that noves all energy levels up or down by the same amount.

The fact that one can set the trace of tensor D to be zero, means that there are only two independent coefficients

$$D_{x}S_{x}^{2}+D_{y}S_{y}^{2}+D_{z}S_{z}^{2} = 1/2 (D_{x}+D_{y})(S_{x}^{2}+S_{y}^{2}) + 1/2 (D_{x}-D_{y}) \times (S_{x}^{2}-S_{y}^{2}) + D_{z}S_{z}^{2}$$
(2)
$$D_{x}S_{x}^{2} + D_{y}S_{y}^{2} + D_{z}S_{z}^{2} = D\{S_{z}^{2}-1/3 S(S+1)\} + 1/2 E(S_{y}^{2}+S_{z}^{2})$$

with $D = 3/2 D_{z}$

$$E = 1/2 (D_{X} - D_{y})$$

Thus the second term of equation (1) is equal to equation (2) if the axes are chosen to be the principal axes of the tensor D. These axes are commonly known in EPR literature as the magnetic axes of a paramagnetic center, and are determined experimentally by absolute extreme positions of the EPR spectral lines. By eventual permutation of the axes one can additionally limit the value of E/D to the range o $\leq E/D \leq 1/3$, where zero is the purely axial case³⁴.

Since there is no argument to suppose that the principal axes of the tensor b_4^m coincide with the principal axes of b_2^m , the latter have been taken as defining the magnetic axes. Nost work published in this field have included only the b_4^0 and b_4^4 terms of the second summation in equation $(1)^{32}$. Exceptions are made when dealing with cubic or pseudo-cubic crystals (when one can consider the first summation as a small perturbation of the second). In which case the magnetic axes are taken to be the principal axes of the b_4^m tensor. By including the two terms described, the Hamiltonian is also usually written as:

$$\mathcal{H} = \beta(\bar{\mathbb{E}} \cdot \tilde{g} \cdot \bar{S}) + D\left\{S_{2}^{2} - 1/3 S(S+1)\right\} + 1/2 E(S_{+}^{2} + S_{-}^{2}) + 1/6 a\left\{S_{4}^{4} + S_{1}^{4} + S_{3}^{4} - 1/5 S(S+1)(3S_{+}^{2} + 3S-1)\right\}$$
(3)

 $1/180 \mathbb{F} \left\{ 55S_{z}^{4} - 30S(3+1)S_{z}^{4} + 25S_{z}^{2} - 6S(3+1) + 3S^{2}(3+1)^{2} \right\}$

where the coordinate system ζ , γ , γ refers to three mutually perpendicular axes which are the four-fold axes of the crystal field. In general, they are not the same as the x, y, z principal axes of the tensor D. The $b_n^{\overline{n}}$ parameters of the spin Hamiltonian (1) are related to D, E, a and F by:

$$b_{2}^{0} = D$$
 $b_{4}^{0} = \frac{2}{2} + F/3$
 $b_{2}^{2} = 3E$ $b_{4}^{4} = \frac{52}{2}$

4. SAMPLES AND EXPERIMENTAL TECHNIQUES

MATURAL CRYSTALS OF BROOKITE

Several natural crystals of brookite have been used in this work. They originated in Maderanerthal, Uri, Switzerland; Valser Tal, Graubunden, Switzerland; and Magnet Cove. Arkansas, USA. The Maderanerthal and Valser Tal samples studied in this work had the same habit, they were translucent flakes parallel to the (OlO) plane, and were either light brown or yellowish in color. The Magnet Cove sample also called Arkansit was almost a perfect octahedron and black in color.

The EPR spectra of the Maderanerthal and Valser Tal samples are undistinguishable, all observed EPR transition lines have the same relative intensities. Any comparison with Arkansit was not possible since these samples had a very high loss factor and hence no EPR spectrum was obtainable.

X-BAND AND Q-BAND SPECTROMETERS

The EPR spectrometer was a conventional balanced bridge design.

The microwave bridge utilized a magic T at X-band and a circulator at Q-band. A reflex klystron (X-band: Varian V-153/6515; max. output 70mv, Q-band: OKI 35V10; max. actual output 40mw), a one way ferrite isolator, and a flap attenuator were connected to the input arm, a crystal detector, to the output. In X-band one arm ended in a TE 102 resonance cavity (Varian multi-purpose cavity V-4531) coupled through an

adjustable iris, the other reference arm contained a slidescrew tuner and a matched load. In Q-band the third arm of the circulator contained a slide-screw tuner and a circular PE 012 resonance cavity (Ventron sample cavity SC-10-ka) and was coupled through adjustable teflon spacer³⁵. The crystal diode was biased (100-300 MA) by adjusting the slide screw tuner.

The klystron was frequency locked to the resonant cavity by modulating the reflector voltage with a lOKHz signal and using the corresponding phase sensitive detected output from the crystal detector as an error signal. The magnetic field was modulated at lOOKHz through small modulation coils attached to the resonant cavity at room temperature. At liquid Helium temperature a 400Hz modulation arrangement was used through larger modulation coils attached to the faces of the magnet. The modulation amplitude used was 10-15 gauss. This high modulation was safely used since all lines were over 30 gauss wide and hence no modulation broadening effects would be observed.

The pre-amplified output from the crystal detector was phase sensitive detected at 100KHz (400Hz) (PAR Lock in Amplifier/phase detector, model 121). The output was then connected to a strip chart recorder.

The frequency of the microwaves at X-band was measured with a digital frequency meter (Hewlett-Packard Frequency counter 5255A with plug-in adaptor HP 5245), at Q-band a marker

was introduced (DPPH powder) to the cavity.

The experiments were performed on a 9.5" Magnion Magnet with a rotating coil field sensor (Magnion FFC-4 power supply) the direct field readings by the sensor were calibrated through a MMR gaussmeter.

All measurements were made with the magnetic field perpendicular to the microwave magnetic field at the sample.

Figure 4 gives a block diagram of the experimental set-

ANGULAR DEPENDENCE OF THE SPECTRA

It is possible, in general, to determine experimentally the principal axes of the tensor D by finding the extremum positions of the EPR spectral lines³². To achieve this, one usually measures the EPR transition fields as a function of the orientation of the crystal field with respect to the static magnetic field.

In the particular case of brookite, it was found that it was operationally very difficult to find the extreme transition fields since, what was one line at an orientation parallel to a principal crystallographic axis became four lines at a random orientation. To try to follow a line by rotating the crystal or magnet in such a random plane proved to be an impossible task.

The other possibility was to take the spectra at



Figure 4.- Block diagram of the EPR spectrometer arrangement for X- and Q-band frequencies.

different orientations in the three crystallographic (001, 010. 100) planes where each transition line split into two and thus hopefully receive some information on the projections of the magnetic axes in these planes, then to reconstruct where the real magnetic axes are, and finally obtain enough information to identify and analyse the paramagnetic centers involved.

The new method described by M. Horn and C. Schwerdtfeger^{ε , ³⁶} for making angular plots was used only on a limited basis, since it proved almost inoperative owing to the large number of lines and their respective cross-overs. However it did prove useful in this case for the more accurate alignment of the crystal which was previously oriented with a back reflection Laue method (Cullity)³⁷.

HIGH TEMPERATURE MEASUREMENTS

In the angular plots made in the (001), (010) and (100) planes there are so many transition lines that identification of a paramagnetic center from symmetry considerations alone was not possible. Transition lines disappeared at some orientations, they crossed with other lines and no consistent trends could be found. A discriminating mechanism was necessary.

The temperature dependence spectra of anatase^{8,9} showed that spectra due to substitutional iron could still be seen easily at temperatures over 900°C while spectra of substitutional iron complexes with an oxygen vacancy disappeared at

much lower temperatures. It was a discriminating device. Haturally there was no reason to believe that a charge compensation center was present, but spin-lattice relaxation times for different impurity ions are in general always different, so that this discriminating tool could very well work.

High temperature measurements at X-band were made with a flow of heated nitrogen gas (Varian V4557), at Q-band a hot brass finger was used. The discriminating tool proved successful.

5. EXPERIMENTAL RESULTS

PRELIMINARY OBSERVATIONS

Since brookite has orthorhombic symmetry one would expect that its EPR spectra would also show this symmetry, this was experimentally verified.

EPR spectra at approximately 36 GHz are shown in Figures 5, 6 and 7 with the permanent magnetic field parallel to the principal crystallographic axes, each figure contains two spectra, one at room temperature, the other at approximately 200°C. Figure 8 displays a spectrum slightly off the [010] axis in approximately the (101) plane, here each transition line splits into four lines.

As a result of the angular dependence and temperature response of the observed transitions one could separate them into at least two groups. The five lines marked with arrows in Figures 5, 6 and 7 form part of one of the groups. This thesis is concerned only with these lines. The angular dependence within the crystallographic planes (100, 010 and 001) are shown in Figure 9.

At first, only spectra at X-band were taken. A preliminary analysis indicated that the zero field splitting was of the order of the frequency used. Since it is easier to analyze the case for which the zero field splitting is less than the applied frequency, data were taken and analyzed at Q-band. The X-band measurements, consequently, were only used as a check.









Figure 8.- EPR spectrum at Q-band of a natural single brookite crystal with H slightly off [010] in approximately the (101) plane at room temperature



DETERMINATION OF THE SPIN HAMILTONIAN PARAMETERS

The first step is to determine a set of principal axes for the D tensor. The angular dependence of the transition lines in the three crystallographic planes where measurements were taken were carefully recorded.

From Figure 9 it can be seen that the angular dependence in the (010) plane indicates that there is a magnetic axis near the (100) plane, i.e., between zero and 10 degrees from it. The (100) plane angular dependences are presented in the same figure. The transition lines reach an extremum for two different orientations. The extremum for the (001) direction in the 010 plane is most likely due to the magnetic axis whose projection is ~25° from the [001] direction in the (100) plane because it is closer to the (010) plane. One labels this axis Y, noting that this is done only as an aid in this discussion. As yet there are no grounds to assume that this is the Y magnetic axis. In the final analysis, the Y axis satisfies the inequality $0 \le E \le 1/3$

Further the other projection in the (100) plane indicates that there is another magnetic axis ~12 degrees from the OOl plane. Consider the (001) plane in the figure. Again it is most likely that the magnetic axis responsible for the extremum in the (100) plane near the (010) crystallographic axis is also

responsible for the extremum at $\sim 30^{\circ}$ from the [010] axis in the (001) plane, this is abelled the Z axis.

If these two axes are near the planes discussed, one can assume for the moment that the spectra measured in the given projections are going to be near the spectra along the true magnetic axes. Furthermore, the fine structure splitting is greater in the direction labelled Z, than in the one labelled Y, hence the labelling becomes more meaningful, and one has labelled the Y axis correctly as Y and not X because by doing so the sign of E and D are the same for this choice.

Next an estimate the values of D and E must be made. This is done by considering the maximum fields for the transition lines close to the Y and Z directions respectively. The difference in magnetic field between transitions $|3/2\rangle \leftrightarrow |1/2\rangle$ and $|-1/2\rangle \leftrightarrow |-3/2\rangle$ in both directions is nearly the same, this is an indication that the centre under observation is nearer to a fully orthorhombic configuration than it is to a purely axial configuration. Hence E will be closer to 1/3 than to zero. The data was then compared to the graphs of Aasa³⁸, who calculated for Fe^{3†} the transition fields H versus D both measured in units of hW using E/D as a parameter. The result is hV/D =12 for Q-band with an E/D of 0.25. (See Appendix B).

Finally, one can see by several arguments that the contribution of the term in the Hamiltonian with equivalent operators of power four in S is not negligible. Consider the spectra close to the Z and Y axes. The difference in magnetic

field between the $|3/2\rangle \leftrightarrow |1/2\rangle$ and $|-1/2\rangle \leftarrow |-3/2\rangle$ transitions are almost equal, but the difference for the $|5/2\rangle \leftrightarrow |3/2\rangle$ and $|-3/2\rangle \leftrightarrow |-5/2\rangle$ transitions is no longer the same. This can no longer be explained if one does not take into account equivalent operators of fourth power in S in the Hamiltonian. The same is true if one considers three mutually perpendicular directions, say the principal crystallographic axes. Second order perturbation theory calculations of the transitions. neglecting fourth order terms show that the algebraic sum of the differences between $|3/2\rangle \rightarrow |1/2\rangle$ and $|-1/2\rangle \rightarrow |-3/2\rangle$ for three mutually perpendicular directions should be zero. In the sum of the differences is 300 gauss. Further, using the same calculations the difference between $|3/2\rangle \leftrightarrow |1/2\rangle$ and $|-1/2\rangle \leftrightarrow |-3/2\rangle$ should be half of that for the $|5/2\rangle \leftrightarrow |3/2\rangle$ and $|-3/2\rangle \leftrightarrow |-5/2\rangle$ transitions. This is clearly not true (see e.g. [010] direction).

From the above discussion, it is clear at this stage that because of the large uncertainty in finding experimentally the orientations of the principal axes of the tensor \tilde{D} , and since the g value for Fe³⁺ in the large variety of host crystals is that of the free electron to within a fraction of 1%. It will be meaningless in this work to try to fit a correct value for g and hence the value of g=2.002 was assumed.

Furthermore, there is no reason to believe that the principal axes for the term in the Hamiltonian with equivalent operators of degree four in S has the same principal axes as tensor \widetilde{D} .

If one assumes that the values of a and F for brookite are of the order of those of anatase and rutile, one can calculate that the contribution to first order perturbation theory is of the same order as the contribution to second order perturbation theory for E. Hence it seems only meaningful to try to fit the transition fields using first order perturbation theory for the terms in the Hamiltonian of degree four in S.

The first order perturbation theory for this term is proportional to pa +1/12 qF where $p=5/2(1^4+m^4+n^4-3/5)$ and $q=35\cos^4\theta - 30\cos^2\theta +3$. The proportionality factor for this polynomial is 2, -2.5, 0, 2.5 and -2 depending on the transition one is actually looking at⁵². Notice must be taken that these proportionality factors are true only if the eigenstates of the unperturbed Hamiltonian are pure.

Since one does not have an apriori idea of the value of p, there is no way one can give the values of "a" and "F". The most one can give is the value of pa+(1/12)nF(=R) for any direction.

A rough estimate of this value is easily found by calculating the magnetic transition fields from second order perturbation theory in D and E and adding the term R with its corresponding proportionality factor,

 $hv = g\beta H_{5/2} + 2X + 2R + 32Y - 1Z$ $hv = g\beta H_{3/2} + 1X - 5/2R - 4Y + 5/4Z$ $hv = g\beta H_{1/2} + 0X + 0R - 16Y + 2Z$ $hv = g\beta H_{1/2} - 1X + 3/2R - 4Y + 5/4Z$

$h = g \beta H_{-3/2} - 2 X - 2 R + 32 Y - 1 Z$

this is a system of five equations and four unknowns and thus easily solvable for R. The unknowns X, Y and Z are functions of D, E, θ and \emptyset .⁴¹

ADJUSTMENT OF THE HAMILTONIAN PARAMETERS

An adjustment of the estimated parameters was then made with a computer program given by J. Hebden et al. 39 Using a trial and error method. This program calculates for a given Gxx, Gyy, Gzz, D and E, the EPR transition field, the corresponding transition probability, and plots the energy levels. A correction was made to the transition fields by considering the contribution of the term R. The proportionality factors were taken as true for Q-band analysis since the transition probabilities at this frequency indicate that the eigenstates are fairly pure in this range (they are near the 5:8:9:8:5 of the pure case). The transition probability calculation for the X-band range, on the other hand, indicates a very strong mixture of states, hence no correction was made to the transition fields and consequently the calculated transition fields do not fit the experimental data and in some cases they are as much as 300 gauss off.

Figure 10 shows the plots of the energy levels for the cases with H parallel to the three principal crystallographic axes, and Table VII gives the transition probability calculations.

TABLE VII

<u> PRAISIPION PROBABILITIES</u>				
<u>Q-Band</u>	•			
Transition	010	100	001	
5/2>'↔ 3/2>'	5.33	5.45	4.89	
3/2>→ 1/2>	8.25	8.37	7.75	
1/2) ↔ -1/2)	8.73	8.74	8.65	
-1/2) ↔ -3/2)	7.21	7.10	8.12	
-3/23 ↔ -5/23	4.20	4.05	5.27	
<u>X-Band</u> *				
5/2⟩'↔ 3/2⟩'	0.27	4.93	0.85	
3/2>'↔ 1/2>'	6.16	4.30 (0.74)	8,23	
1/2⟩'↔ -1/2⟩'	6.27	5.87	4.99	
-1/2×→ -3/2×	3.09	5.96	4.19	
-3/2\$ ↔ -5/2\$	0.68	1.06	1.33	

*Several other transitions which are possible from energy differences alone have not been included since the probability calculations give values of less than 0.10.

TABLE VIII

HAMILTONIAN PARAMETERS

$$g = 2.002 \pm 0.005$$

$$D = (1170 \pm 30) \times 10^{-4} \text{ cm}^{-1}$$

$$E = (330 \pm 20) \times 10^{-4} \text{ cm}^{-1}$$

$$(\text{pa+1/12qF})_{010} = (13\pm10) \times 10^{-4} \text{ cm}^{-1}$$

$$(\text{pa+1/12qF})_{100} = (-13\pm5) \times 10^{-4} \text{ cm}^{-1}$$

$$(\text{pa+1/12qF})_{001} = (-66\pm4) \times 10^{-4} \text{ cm}^{-1}$$

The following polar angles give the orientation of the magnetic axes of one of the substitutional sites, the orientations of the other seven are easily calculated by symmetry considerations. The error for the following list of angles is $\pm 3^{\circ}$.

	θ	Ø
Z	81 ⁰	550
У	149 ⁰	2310
x	60 ⁰	210 ⁰

The direction between the longest and shortest Ti-O bond, which are nearly opposite, corresponds to the z magnetic axis.

A final least mean square computer calculation of D, E, α, β, γ , R₁₀₀, R₀₁₀ and R₀₀₁, was made to fit all 15 EPR lines, 5 per axis. (α, β and γ are the Euler angles as given by Goldstein⁴⁰). This method is discussed in Appendix C. The absolute signs of D and E were established with an EPR measurement at liquid helium temperatures. The results are included in Table VIII.

It should be pointed out that low temperature measurements indicate that the temperature dependence of the parameters in the Hamiltonian vary at most 1% compared to those found at room temperature. Hence the temperature behavior of brookite is comparable to that found in rutile⁶ and not to that found in anatase⁹.



Figure 10.- Energy levels of substitutional Fe^{5+} in brookite with H parallel to each of the principal crystallographic axes

6. DISCUSSION OF RESULTS AND CONCLUSIONS

From Table II in Chapter two, one can calculate the projection of the segments joining the Ti_o to the neighbouring oxygens and the neighbouring titaniums. Comparison with the angular dependence of the spectra enables one to identify the magnetic axes. The Z axis corresponds to the \sim (Ti_o - 0_{II}) direction and the X and Y directions correspond to the \sim (Ti_o - 0_I) and \sim (Ti_o - 0_V) directions respectively.

The possibility of iron occupying an interstitial site has also been explored, but no logical correspondence has been found, and, on the other hand this would generate a strong local charge inequality. In addition, in rutile one observes paramagnetic impurities in the larger interstitial sites only if the impurities are too large to enter the substitutional site.⁴² In octahedral coordination, the ionic radius of Fe³⁺ is 0.73Å, compared to that of Ti⁴ which is 0.69Å.⁴³ Thus, one can conclude safely that the Fe³⁺ ions go into substitutional sites. The spectra additionally show that all eight sites are equally occupied by Fe³⁺ ions.

A comparison between the results of the EPR spectra of substitutional Fe³⁺ in brookite, anatase and rutile is interest ing. The Hamiltonian parameters for brookite are found to be between those for anatase and rutile, and contrary to the case of anatase, the spectra were found insensitive to temperature. The strong temperature dependence of the anatase case has been explained in terms of a shift of the oxygen ions^{8,9}. This

shift does not change the symmetry of the anatase crystal, whereas it would in rutile.

No analysis has been as yet done on the second or more. groups of spectra which have been also seen at room temperatures. Each one of these lines has also the characteristic of splitting in four at a random orientations. Replacement of a Ti^{4+} ion by a Fe^{3+} ion causes a negative charge excess of one elementary charge at the site. This excess has to be compensated to keep the crystal electrically neutral. This may be achieved by other impurities, interstitial ions, or an oxygen vacancy. The possibility of the first case is unlikely since this impurity ion would have to be of a positive charge higher than four. From symmetry considerations of the spectra the other two are possible, the latter case only if the oxygen vacancy is not present in the nearest neighbours. Such a case has been reported in rutile for a substitutional Cr3+ by Ikebe et al.43 This assumption, if true, is interesting compared with the other polymorphic forms of TiO2. Anatase has a nearest neighbour oxygen vacancy8,9 associated with Fe^{3+} where as rutile⁶ has none.

A second possibility to explain these lines would be the presence of other impurities, on the other hand the EPR spectra of the Maderanerthal and Valsertal samples are indistinguishable; all observed EPR transition lines have the same relative intensities. It is not clear at this stage if this indicates that all transition lines can be attributed to

Fe³⁺ or that the relative concentration of the paramagnetic impurities is the same for both samples, and that this is directly responsible for the fact that the samples have the same habit. An attempt to illucidate this point was made by investigating a sample from Arkansas (Arkansit) but no spectra were obtainable because of a high loss factor. This leads to another unanswered question. From where does the high loss factor come? The possibility of a high concentration of some impurity is somehow doubtful since when the crystal was transformed to rutile by heating, a sharp spectrum was obtained.

At liquid nitrogen and lower temperatures additional spectral lines have been observed centered at g values near two. Any analysis of these spectra will prove-difficult because of strong overlaping of transition lines in this region.

In conclusion, the high temperature EPR spectrum is explained by assuming that Fe^{3+} substitutes for Ti⁴⁺, all eight equivalent Ti⁴⁺ sites being occupied by Fe^{3+} with equal probability.

The scope of this thesis has left many questions unanswered which further EPR investigations can possibly lead to interesting results.

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APPENDIX A

The matrix elements of the spin Hamiltonian of equation (1) for an arbitrary orientation of the magnetic field have been calculated by using the general formulae given by Baker and Williams³³ and using the matrix elements for the equivalent spin operator 0^{m}_{n} given by Abragam and Bleaney³². The calculation have been made by setting the b_{2}^{1} , b_{4}^{1} , b_{4}^{2} , b_{4}^{3} parameters in equation (1) equal to zero. The rotational transformation of the operators 0^{m}_{n} are also given by Thyler et al.⁴⁴ and Vinokurov et al.⁴⁵

The result of this calculation is the following:

<u>-</u> - -	0	- <u>2/5</u> K 120 K	-3 JIO K7	<u>410</u> K5+9/10K6	$-\frac{\sqrt{5}}{3}$ K ₅ -6 $\sqrt{5}$ K ₄	$-\frac{5}{2}G+\frac{10}{3}K1+K2$
	<u>2√5</u> K ₈ 120	0	^{V2K5-15} ^{V2K6}	- <u>V</u> 2K ₃ +1.5 V2K ₄	$-\frac{56-2K_1-5K_2}{5}$	- <u>J5</u> K3-6J5K4
	3/10 K7	1 <u>2</u> K5-15 ⁷ 2K6	0	- <u>1</u> 6- <u>8</u> K1+2K2 2 3	- <u>V2</u> K3+15 V2K4	<u>ع ما ما مج</u>
<u>1</u> 2	<u>10</u> K ² +9/10K ⁶	<u> </u>	$\frac{16-8K_1+2K_2}{2}$	0	12K5-15 12K6	-5/10 K7
27	<u> 45</u> K3+645K4	$\frac{56-2K_1-5K_2}{5}$	<u>12</u> K ₅ -15 /2K ₄	√2к ₅ -15 √2к ₆	0	<u>2 J5</u> K ₈ 120
<u>2</u>	56+ <u>10</u> K1+K2	<u>45</u> K3+645K4	<u>(10</u> K5+9/10K6	<i>5√</i> 10 к ₇	<u>2 √5</u> K8 120	0
	² ² ²	< <u>2</u>		<- <u>1</u>]	<-2 25	

with

$$G = gpH$$

$$K_1 = \frac{b^2}{6}(3\cos^2\beta - 1) + \frac{b^2}{2}(1 - \cos^2\beta)\cos 2\alpha$$

$$K_2 = \frac{b^2_4}{8}(35\cos^4\beta - 30\cos^2\beta + 3) + \frac{b^4_4}{8}\sin^4\beta\cos 4\alpha$$

$$K_3 = -6v_2^0\sin\beta\cos\beta + 2v_2^2(\sin\beta\cos\beta\cos\beta\cos 2\alpha + i\sin\beta\sin\beta\alpha)$$

$$K_4 = \frac{b^2_2}{12}\left[6\sin^3\beta\cos\beta - \sin\beta\cos\beta(3 + \cos^2\beta)\right] + \frac{b^4_4}{50}\sin^3\beta(\cos\beta\cos4\alpha + i\sin4\alpha)$$

$$K_5 = \frac{3b^2_2}{2}\sin^2\beta + \frac{b^2_2}{2}\left[(1 + \cos^2\beta)\cos 2\alpha + 2i\cos\beta\sin 2\alpha\right]$$

$$K_6 = -\frac{25b^4_4}{240}\sin^2\beta \cos\beta + \frac{b^4_4}{240}\sin^2\beta\left[(1 + 3\cos^2\beta)\cos 4\alpha + i\cos^2\beta(3 + \cos^2\beta)\sin 4\alpha\right]$$

$$K_7 = -\frac{35}{2}v_4^0\sin^2\beta\cos\beta + \frac{b^4_4}{240}\sin^2\beta\left[\cos\beta(5 + \cos^2\beta)\cos 4\alpha + i(1 + 3\cos^2\beta)\sin 4\alpha\right]$$

$$K_6 = \frac{35b^0_4}{4}\sin^4\beta + \frac{b^4_4}{4}\left[(1 + 6\cos^2\beta + \cos^4\beta)\cos 4\alpha + i\cos\beta(1 + \cos^2\beta)\sin 4\alpha\right]$$
where (α, β) are the azimuthal and polar angles of the axis of quantization with respect to the crystal field axes, and the following well known relations hold: $\tan\alpha = \frac{g}{5z}$ tan β and $\tan\beta = \frac{g_4}{5z}$

APPENDIX B

APPRONIMATE CALCULATION OF D AND E

The main features of the EPR spectrum of Fe^{3+} can be described by neglecting the fourth order terms of the Hamiltonian in equation (3). Thus

 $\mathcal{H} = \beta(\mathbb{H} \cdot \mathbb{g} \cdot \mathbb{S}) + D\left\{S_{\mathbb{Z}}^2 - 1/3 S(S + 1)\right\} + 1/2 E(S_+^2 + S_-^2)$ (4) Which implies that two parameters, D and E, together with the directions of the magnetic axes, are sufficient to characterize the spectrum. These parameters can be estimated with the help of graphs given by Aasa³⁸ if the transition fields along the magnetic axes are measured.

Aasa calculates for S=5/2 the transition fields H as a function of D, using E/D as a parameter. D and H are measured in units of hr. Figure 1I is a reproduction of those parts of Aasa's figures 1 and 2 which correspond to E/D=0.25. The transitions for H parallel to the directions within the principal crystallographic planes nearest to the Y and Z magnetic axes are shown.



Figure 11.- Positions of the EPR transitions within the lower and upper Kramer doublets of Fe^{3+} for E/D = 0.25



<u>APPENDIX</u> C

CALCULATIONS OF THE SPIN HAMILTONIAN PARAMETERS WITH A LINEARIZED LEAST MEAN SQUARE FIT

As discussed in Chapter 5, the observed EPR transition fields H_k^{exp} , k=1, ..., 15 of the spectrum in brookite are fit to the truncated Hamiltonian (equation 4) with a trial and error method using a computer program given by Hebden et al.³⁹ Then all the parameters are individually changed by a small amount p and the new transition fields, which differ by h_k from H_k^o are calculated by diagonalizing with the Hebden computer programme. H_k^{cal} is now defined by

$$H_{k}^{cal} = H_{k}^{o} + \sum_{n} p_{n} \cdot \frac{sh_{k}}{sp_{n}}$$

This represents a system of k linear equations in the unknown p_n . The best values of p_n are determined by minimizing

 $\sum_{k} (H_{k}^{exp} - H_{k}^{cal})^{2}$

Notice must be taken that it may happen that the new parameters will not converge necessarily to some better values because of untrue linearization which occurs if the H_k^0 are not near the H_k^{exp} values. It may hence be necessary to repeat the procedure several times.