# EPR OP SUBETITURIONAL FE ${ }^{3+}$ In A MATURAL CRYSTAL OT BROOKITE $\left(\mathrm{TiO}_{2}\right)$ 

by
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## AESTRECT

EPR spectra of $\mathrm{Fe}^{3+}$ in a natural crystal of brookite have been investigated at X - and C -bend frequencies at room temperature and $573^{\circ} \mathrm{K}$. Part of the paranametic resonance spectrum observed has been interpreted on the assumption that $\mathrm{Fe}^{3+}$ occupies eisht equivalent $\mathrm{Ti}^{4+}$ sites in brookite, with four inequivalent orientations.

The spectra show an "intermediate" zero-field splitine at $X$-band end a "normal" zero field splitting at Q-bend frequencies.

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

$$
\begin{aligned}
& g=2.002 \pm 0.005 \\
& D=(1170 \pm 30) \times 10^{-4} \mathrm{~cm}^{-1} \\
& E=(330 \pm 20) \times 10^{-4} \mathrm{~cm}^{-1} \\
& {[0 a+(1 / 12) \mathrm{n}]_{010}=(13 \pm 10) \times 10^{-4} \mathrm{~cm}^{-1}} \\
& {\left[0 \mathrm{pa}+\left(1 / 1 \chi_{1}\right]\right]_{100}=(-13 \pm 5) \times 10^{-4} \mathrm{~cm}^{-1}} \\
& [0 a+(1 / 12) 1]]_{001}=(-66 \pm 4) \times 10^{-4} \mathrm{~cm}^{-1}
\end{aligned}
$$

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## 1. IMTRODOCTION

It was Klaproth who first recogized a polyworphism in 1798, that is, that the same chemical compound may crystallize in different forms. Klayroth observed the polymorphic forms of calcium carbonate (calcite, aragonite). ${ }^{\text { }}$

That titinium dioxide has several natural polymorphic forms (rutile, anatase and brockite) has been known clready for many years. Recently, a fourth polymorphic form was synthetically produced $\left(\mathrm{TiO}_{2} \mathrm{II}\right)^{2}$.

Rutile, anatase and brookite are often found in nature as good single crystals. Syntinetically one can obtain single crystals of rutile and polycrystalline anatase ${ }^{3}$. To date, all atteapts to produce brookite artificially, even in polycrystalline form have been unsuccessful. As a result most EPR studies have been made witin mutile ${ }^{4-7}$ and some with natural cristals of anatase 8 -13. Ho EPR studies of brookite have been reported.

An EPR comparative study of different polymornhic forms can be interesting from a minerelogical point of view. Only recently, EPR has been acknowledged to be a tool in mineralogy and geology. Reviews by 7 . Ior ${ }^{14}$ and $S$. Ghose ${ }^{15}$ have shown that EPR can be helpiul in clarifing some mineralogicel proolems Such as the relation between the paramabnetic impurity and the mineral host (site preference). Information about coordination and local symmetry (non-equivalent sites, orientation ana values

Of the crystal field paraneters, charee compensation), nature of chemical bonainé, color centens and other lattice defects, order-disorder, and relative abuncence of different paramache tic impurities or difierent valence stetes of a given impurity may be obtained from analysis of ERR ueasureneats.

Since impurities are a factor that determine tine habit formation of the minerals it is also rerotely possible that EPR can be helpful in this geological problew. Remotely since non parancaneic inpurities are impossible to observe or lange concentrations of paramagetic impurities will not be seen or aake analysis extremely dirsicult with EPR.

In the present thesis the results of an EPR study of substitutional iron irourities in a natural single crystal of brookite are described. Fo attempt to analyze other EPR transition lines has been made to date although some speculation has been attemoted.

## 2. RESULTS OF PREUIOUS INVESRIGATIONS ON BROCKITE SQPuc ive or brookice

Brookite has an orthorhombic symetry and belongs to the Pbca ( $D_{2 h}^{15}$ ) space Group. R. Weyl ${ }^{16}$ remeasure $\dot{a}$ the lattice constants of brockite, previously determined by I. Pauline and J.H. Sturdivanily, and found their results to lie within the yrecision limits of 0.1\% attained by his ifeasurements. These values are:

$$
\begin{aligned}
& a=9.184 \AA \\
& b=5.447 \AA \\
& c=5.145 \AA
\end{aligned}
$$

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 equivelent positions for the pbca space Erouplo,l9 one is able to find the projections of the unit cell. Pigure $I$ shows these projections.

Each titanium ion is surrounded by six oxyeen ions at the vertices of an octanedron and it also sheres three edses with other octahedrons. This is shown in Figure 2. These common edges are shorter in comparison with the other edsed of the octahearon mich is in accoráance vith Pauline's Rule ${ }^{20}$. (Rutile shares tuo edges and anatese sheres four ${ }^{19},{ }^{21}$ ).

Wables II and III give the distances between the titanium and the orycens as well as the distances between the oxycens. Clearly, this octahedron is distorted. Purtinermore,



Pigure 2.- Projections in tine (100) plane of scme TiO6 ocianedrons. The cownon edges of the ocivinedrons are diamn heavier.


Pigure j.- Double hexabonal closed pached (DEOP) arrancement
R. Meyl has calculated that the Tio in the octahearon is aisplaced by $0.2 \pm 0.18$ from the center toward $O_{I V}$ and away $O_{\text {II }}$ (in rutile as well as anatase the titanium ion is in tine Midale of the $\mathrm{TiO}_{6}$ octanedman) and that this ion, Tio, is further amay by $0.12 \pm 0.069$ fron the neizhbouring ions, Ti and $\mathrm{Ti}_{2}$ than frow tie third nearest neishbouring ion $\mathrm{Ti}_{3}$, as can be calculated from Tabie IV. (where the subscripts on Ti refer to the ions labelled in Figure 2).

In the brockite structure each octahearon is bound through two comon edzes to tio other octahecrons fozming a chain in the (001I direction and by the third comon ede to another such chain foruing a net, parallel to the (100) plane. The unit cell has tio such nets, one over the other winch are bound by common corners.

The (001) plane in Figure 1 shows distinctively that the unit cell has four empty colums, horever, it is not clear that each such column contains tioo interetitial sites surrouncied by six oxygens at the comers 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 (DHCD) arrangement, i.e. (ABACABAC...) as shown in the Figure 3. The closed nacked plene is the (100) plane, one halî oí the octaneärons are filleá with titaniam 2 .

## QSIE I

##  <br> OT בSUII:G ADSURDIVATM

|  | $\mathrm{O}_{1}$ | $\mathrm{O}_{2}$ | Ti |
| :---: | :---: | :---: | :---: |
| x | $0.008(0.010)$ | $0.229(0.230)$ | $0.128(0.127)$ |
| y | $0.147(0.155)$ | $0.110(0.105)$ | $0.098(0.113)$ |
| z | $0.102(0.180)$ | $0.530(0.535)$ | $0.863(0.873)$ |

## RABLE II

ION COOPDIERES ROP A SEMPIE TIOG OCQSEDPO
(GIVEN IN YRACMTO: OE TEE LSMICE CO:STENSS)

|  | x | y | $\mathbf{z}$ |
| :--- | :---: | :---: | :---: |
| $\mathrm{Ti}_{0}$ | 0,128 | 0,402 | 0,363 |
| $\mathrm{O}_{I}$ | 0,003 | 0,147 | 0,182 |
| $\mathrm{O}_{\text {II }}$ | 0,229 | 0,110 | 0,530 |
| $\mathrm{O}_{\text {III }}$ | 0,271 | 0,610 | 0,530 |
| $\mathrm{O}_{\text {IV }}$ | $-0,008$ | 0,647 | 0,318 |
| $\mathrm{O}_{V}$ | 0,229 | 0,350 | 0,030 |
| $\mathrm{O}_{\mathrm{VI}}$ | 0,008 | 0,353 | 0,682 |

## RASIE III

## ION DISTAMOES MOR A SARPIE

## Tiog OCMEDROE（IOURE 2）

| $\mathrm{Ti}_{0}{ }^{-0} \mathrm{I}$ | $(2,00 \pm 0,05) \AA$ |
| :---: | :---: |
| $\mathrm{Ti}_{0}-\mathrm{O}_{\text {II }}$ | $(2,03 \pm 0,05) ¢$ |
| $\mathrm{Ti}_{0}-\mathrm{O}_{\text {III }}$ | （1，94土0，05）$\AA$ |
| $\mathrm{Ti}-\mathrm{O}_{\text {IV }}$ | （1，84＊0，05） |
| $\mathrm{Ti}_{0}-{ }^{-} \mathrm{V}$ | （1，95 $\pm 0,05)$ ¢ |
| $\mathrm{Ti}_{0}-\mathrm{O}_{\text {VI }}$ | （1．900，05）${ }^{\text {（1）}}$ |
| $0_{i}-0_{I I}$ | $(2,71 \pm 0,08) \AA$ |
| $0_{\text {II }}{ }^{-0}{ }^{\text {VI }}$ | （2，55土0，08）$\AA$ |
| $0^{\text {VI }}{ }^{-0_{\text {III }}}$ | （2，90土0，08）${ }_{\text {a }}$ |
| $0_{\text {III }}{ }^{-}{ }_{\text {IV }}$ | $(2,79 \pm 0,08) \&$ |
| $0^{\text {IV }}{ }^{-0} \mathrm{~V}$ | $(2,98 \pm 0,05) ¢$ |
| $\mathrm{O}_{\mathrm{V}-\mathrm{O}_{\mathrm{I}}}$ | $(2,55 \pm 0,08) \AA$ |
| $0_{\text {II }}{ }^{0}$ III | $(2,75 \pm 0,08) \AA$ |
| ${ }^{\text {IIII }}{ }^{-0} \mathrm{~V}$ | $(2,06 \pm 0,08)$ ¢ |
| $\mathrm{O}_{\mathrm{V}} \mathrm{O}_{\text {II }}$ | （2，99 20,08$) \AA$ |
| $0_{I}-{ }^{-}{ }_{V I}$ | $(2,31 \pm 0,08)$ ¢ |
| $0_{V I}{ }^{-0}{ }^{\text {IV }}$ | $(2,47 \pm 0,08) \AA$ |
| $0^{\text {IV }}{ }^{-0}{ }_{I}$ | $(2,82 \pm 0,05) \AA$ |

## SDIE IV

## Ti-Ti DSGMCS (BEE PTOUP 2)

$$
\begin{array}{ll}
T i_{0}-T i_{1}=T i_{0}-T i & (3,00 \pm 0,03) \AA \\
T i_{0}-T i_{3} & (2,94 \pm 0,03) \AA \\
T i_{0}-T i_{4}=T i_{0}-T i_{5} & (3,70 \pm 0,03) \AA \\
T i_{0}-T i_{6}=T i_{0}-T i_{7} & (3,57 \pm 0,03) \AA \\
T i_{0}-T i=T i_{0}-T i & (3,53 \pm 0,03) \AA
\end{array}
$$

## PFASE TRAESFOREATOE

The topotactic mechanisms for the $\mathrm{TiO}_{2}$ system are based on a princivle of fevoring as much as vossible the maintenance of the oxygen close pacting during the nolymorgic transition (Anatase is pseudo-cubic close packed (CCD) with the close pacted plane (112); Rutile, roush approzimation of an hezagonal close pached (FOP), (100) or (010) planes; TiO II, HCP, (100) olane).

Table $V$ summerizes the observed and proposed topotaxy in the titanium diozide süstem 22 .

At this point, it should be mentioned theit the kinetics and mechanism of the broonite-rutile transformation are very similar to those of the anatase-rutile iransformation ${ }^{23-28}$. The rate of transformetion and its activation energy are Governed by the surface size and $b_{y}$ tie amount of impurities, e.g. the concentration of oxyeen vacancies or inteastitials. But the activation energ, which is mainly for the production or nucleation sites, is higher for the anatase-mitile case and the entropy of activation is large and ne extive for the brookite-muile transformation comered with the small and positive value for the anatase-rutile transformation. This maju be understood in tems of the change of symetry (lower to higier) of the first case and the ajosence of such a change in the second29. rine effect of impurities in ceneral is that onygen vacancies accelerate phereas interstitial ions inhibit the transfomation ${ }^{26}$.

##  TOETAS IT TE TiO2 STSTE

| Reaction | Number of Ovsen Lajers Rearranged | Redistateution of the Titanium Atoms ${ }^{\text {a }}$ | Remarks |
| :---: | :---: | :---: | :---: |
| If - rutile | None |  | Only reaction that has been reversed. Eivierimental evidence inferred from work of Bendeliany el al. (1900) |
| Brookite-II | $1 \text { in } f$ | Every Ti in two consecutive layers altering with two lavers in which there is no Timotion. | Reaciica uithout $\$ R O$ phase formation. Hrowhite ias zig. $2 \mathrm{na} \mathrm{TiO}_{\text {ontah }}$ octeal chains as is found in 11 . |
| Ereokite-rutile | This reaction dors not involve anoxs. gen shearins mechanisn, but there is - shiftine of all oxygen. | Every cther 7i in each layer in order to form strasish Tiociabedral chains. $\begin{array}{ccccccccc} A & B & C & A & B & C & A & B & C \\ : & : & : & : & : & : & : & : \\ 1 / 2 & 1 / 2 & 1 / 2 & 1 / 2 & 1 / 2 & 1 / 2 & 1 / 2 & 1 / 2 \end{array}$ | Experimenta!! ; observed topotaxy. |
| Anatase-rutile | This reaction does not involve an exygen shearing merchanism but all oxygen atoms shift rositions. | Every other Ti in each layer in oruer to form straikht Ti ociejedral chains. $\begin{array}{cccccccc} A & B & A & C & B & A & C \\ : & : & & : & : & : \\ 1 / 2 & 1 / 2 & 1 / 2 & 1 / 2 & 1 / 2 & 1 / 2 & 1 / 2 \end{array}$ | Tomotaxy experimentally of served. A larbe distortion $\propto$ curs in the formation of straight octahedral chains from zizzag chaias. |
| Anatase-II | $\operatorname{tin} 6$ | A repeating sequence of all Ti and no Ti motion beginaing with the Ti between the $A$ and $C$ layers. $\begin{array}{llllllllllll} A & B & C & A & B & C & A & B & C \\ : & : & : & : & : & : & : & : & \\ 1 & 0 & 0 & : & 0 & 1 & 0 \end{array}$ | Reaction always accompanied with SRO plase iormation. |
| Anatase-brookite | e 9 in 12 | Very complex | Reaction ruported only one time. |

- In most cases the movenent of the tiatiun ions is to adjacent tetrahodtal siter which aic in the process of beconing ociahedral site therase of the atcumpanyins oxyern nisi:oa.

The lerend for tie titatum arotima is
1;1 every other titanium chianses site
1 crery titanium changers sise
0 no tilanium chanjers sitc
The liyering sheme is that of the acactant.

## OTEER PROPESTIES

A list oi these properines is given in pable VI. Properties of rutile and awatase have been also included for comparison 30,8 .

## TABIE VI

2POPERTIES
proverty
Density,
Ane.tase
Putile
$3.87-3.95 \% / \mathrm{cil}^{3}$
$4.21-4.25 \mathrm{~g} / \mathrm{cm}^{3}$
Brooritie
5.5-6.0
7.0-7.25
$4.13 \mathrm{c} / \mathrm{cm}^{3}$
Eardness
5.5-6.0

Speciric heat
at R.T.
$13.22 \mathrm{ce} .1 / \mathrm{mol}{ }^{\circ} \mathrm{C}$
$13.16 \mathrm{cal} / \mathrm{mol}{ }^{\circ} \mathrm{C}$
Optical Constants

| $n_{0}^{56938}$ | 2.56 | 2.61 | $n_{\alpha} 2.5831$ |
| :--- | :--- | :--- | :--- |
| $n_{e}^{5693 A}$ | 2.49 | 2.90 | $n_{p} 2.5843$ |
|  |  |  | $n_{r} 2.7004$ |

Static dielectric
constent
48
114
78
Hotice that the values of these physical constants for brookite are bet:ieen those measured for anatase and rutile.
EPR STUDIES
Eamiltonian parameters for substitutional Pe ${ }^{3+}$, where $D, E$, a and $P$ are given in $10^{-4} \mathrm{~cm}^{-1}$, are:

|  | E | D | E | a | F |
| :--- | :--- | :---: | :---: | :---: | :---: |
| hatase $\left(300^{\circ} \mathrm{K}\right)$ | 2.005 | 308.7 | - | 102.8 | 6 |
| Putile $(4.2-300){ }^{\circ} \mathrm{K}$ | 2.00 | 6780 | 690 | -280 | 230 |
| Ho EPR studies in broosite have been reported. |  |  |  |  |  |

## 3. SESEMEITMOIAN

The electronic configuration of the $\mathrm{Fe}^{3+}$ ion is $3 \mathrm{~d}^{5}$ and the iree ion electronic oround state is ${ }^{6} S_{5 / 2}$. The washetic resonance spectrum shoiid be remariably simple. The sextet would have no splitting other then the Reeman interaction, and a single line would be observed, however, experinentally this is far from the truth. Botn fine and hyperfine structures heve been observed for ions with half filled 3 d , $4 f$ and $5 f$ shells. Several mechenisms have been proposed to explein this. 31 Spin-spin and spin-orbit inteactions can produce secund or higher order terms coupling the ground stete through hicher orbital sta.tes to the crystal field.

The multiple fine structure can conveniently be reoresentec by adidng to the Zeeman term in the soin Hamiltonien, terms of nizher powers in $S_{x}, S_{y}$ and $S_{z}$, groupiñ then into combinctions of spin operators, each such operator being the equivalent to a combintion of sherical harmonics. Such equivaleat spin operators denoted as $0_{n}^{m}$ appear extensively in literature.

The acivantage of using equivalent spin operators is that one cen choose imaediately which teras will appear in tine spin Faniltonian. One excluées the equivalent spin operators which are of odd cegree in $\bar{S}$. since taey are not invarient under time reversal. Fron the operators of even degree one chooses only those wich reflect the symetry of the crystel field. Furthermore, the number of such operators is limited by the
fact that operators of highen degree than 25 :ay be owitted since they have zero, watix elements between the states under consideration. Hence for $\mathrm{Ee}^{3^{+}}$one can wite in general

$$
\begin{equation*}
\mathcal{H}=\beta \bar{B} \cdot \tilde{S} \cdot \bar{S}+I / 3 \sum_{i=-2}^{2} b_{2}^{m} O_{2}^{m}+1 / 60 \sum_{i=-4}^{4} i_{i}^{4} O_{4}^{m} \tag{1}
\end{equation*}
$$

Using the mom thensfometion moporties oin when rotetion of the coonhase systen one cen evalunte twe thonsformation properties of the on under these rotations. An apqendix in Bater aw williams ${ }^{33}$ is very helroul for these calcu lations and has been used in fppendix a to calculate the spin Eatailtonian for an arbitrary orientation.

The suin familtonien ney be expressed in an siteraative form. The first suametion in (1) can be uritten as:

$$
\bar{S} \cdot \tilde{D} \cdot \bar{S}
$$

Where $D$ is a tensor quantity. Referred to the principal azes, this becomes

$$
D_{x} S_{x}^{2}+D_{y} S_{y}^{2}+D_{z} S_{z}^{2}
$$

where $i t$ is convenient to set tine sum of the three cocfficients to zero by suestrecting the guantity

$$
1 / 3\left(D_{x}+D_{Y}+D_{z}\right)\left(B_{x}^{2}+\tilde{S}_{y}^{2}+E_{z}^{2}\right)=1 / 3\left(D_{x}+D_{Y}+D_{z}\right) S(S+1)
$$

when is just a constent that zoves all enemay levels up or down by tice same amount.

Whe fact that one can set the trace on tensor $\widetilde{D}$ to be sero, neans that theve are only tro inaependent coefficients

$$
\begin{aligned}
& D_{x} S_{x}^{2}+D_{y} S_{y}^{2}+D_{z} S_{z}^{2}=I / 2\left(D_{z}+D_{y}\right)\left(S_{x}^{2}+S_{y}^{2}\right)+I / 2\left(D_{x}-D_{y}\right) x \\
& x\left(S_{x}^{2}-S_{y}^{2}\right)+D_{z} S_{z}^{2} \\
& D_{X} S_{x}^{2}+D_{y} S_{J}^{2}+D_{z} S_{z}^{2}=D\left\{S_{z}^{2}-1 / j S(S+I)\right\}+I / 2 \mathbb{E}\left(E_{+}^{2}+S_{-}^{2}\right) \\
& \because i \text { 动 } \\
& \begin{array}{l}
D=3 / 2 D_{E} \\
E=I / 2\left(D_{X}-D_{y}\right)
\end{array}
\end{aligned}
$$

Tus the second terin of equation (1) is equal to equation (2) if the axes are chosen to be the principel axes of tine tensor D. These axes are commonly known in EPR literature a.s the magnetic ayes of a paramaznetic center, and are determined experinentally by absolute extreme positions of the EPR spectral lines. By eventual permutation of the axes one cain additionally limit the value of $E / D$ to the range $O \leq E / D \leq I / 3$, where zero is tine purely axial case ${ }^{34}$.

Since there is ao arguaent to suppose that the principal ares of the tensor $b_{4}^{\text {in }}$ coinciae with the principal axes of $b_{2}^{m}$, the latter have been taken as defining the mazhetic axes. Nost work published in this field have included only the $0_{4}^{0}$ and $b_{4}^{4}$ terms of the second summetion in equation ( 1$)^{32}$. Exceptions are made when dealing with cubic or pseuco-cubic crystals (when one cen consicer the first sumation as a small perturbetion of the second). In wich case the machetic axes are taken to be the principal axes of the $b_{4}^{\text {ia }}$ tensor. By includins the two terms described, the Familtonian is elso us:aily mrititen as:

$$
\begin{align*}
& +1 / 6 a_{\{ }\left\{S_{j}^{4}+S_{\eta}^{4}+S_{5}^{2}-1 / 5 S(3+1)\left(33^{2}+35-1\right)\right\}  \tag{3}\\
& 1 / 180 \equiv\left\{355_{z}^{4}-303(3+I) S_{z}^{4}+255_{z}^{2}-03(3+1)+30^{2}(3+1)^{2}\right\}
\end{align*}
$$

mere the coordinate system\} . ~ $\}$, 3 refers to three mutually
 Field. In general, they are not we same as the $x$, $y$, z prinotyal ares of the tensor D. The bin perimeters of the spin \#̈nilunian (I) are related to $D, E$, and $E$ by:

$$
\begin{array}{ll}
b_{2}^{0}=D & b_{4}^{0}=\frac{2}{2}+F / 3 \\
b_{2}^{2}=3 D & b_{4}^{4}=\frac{52}{2}
\end{array}
$$

## WIMURI ORYSTAIS OR 3ROORITE

Several natural crystals of brookite have been used in this work. They orisincted in Naderanerthal, Uri, Switzenlana; Valser Tal, Graubumen, Switzerland; and Nagnet Cove, Araansas, USA. The Fiaderanthal and Valser wal sameles stuaded in this work had the same iabit, they bere translucent flates parallel to the (010) plene, and were either light brown or yellowish in color. The hagnet Cove sample also called Arkansit was elmost e perfect octahedron and black in color.

The EPR spectra of the Raderanertan and Valser Tal samples are undistineuishable, all observed EpR transition lines heve the same relative intensities. Eny comparison with Arkansit mas not possible siace these samples hat a very hien loss factor and hence no EPR spectrum was obtainable.

## X-ETD ADD Q-BED SPDCMOMTTERS

The EPR spectronter mas a conventional balanceù bridée design.

The microwave bridge utilized a maric T at K -onad and a circulator at Q-band. A reflex klystron (K-band: Varien V-I53/6515; mex. cutput 70mv, O-banci: OKI 35V10; mex. actual outout 40 mw ), a one :uay ferrite isoletor, and a flap attenuator were connected to the input arm, a erystal detector, to the outout. In x-benc one ameraded in a pe 102 resonence cavity (Varian militi-puroose cevity $V-4531$ ) coupled throush an
adjustable iris, the other reference am containea a slidescrew tuner and a metched load. In Q-band tiee tinird arui of the circulaton contained a slide-Ecre\# wan and a circular UE 012 resonance cavity (Ventron sample cavity SC-lo-ke) and iics coupled through acjustable teflon spacer 35 . The crystal diode was biased (100-300 PA) by acjusting tie slicie screy tuner.

The klystron was frequency locked to the resonent
 anci using the corresponding phase sensitive detected output from the crystal detector as an error signal. The manatic field was modulated et lookz throuch small modulation coils attacied to the resonant cavity at roon temperature. At Liquid Felium temperature a 400 Hz modilation arrangenent mas used tinough lerger modulation coils attached to the faces of the magnet゙. The moduletion arplitude ueed was 10-15 gauss. This high modilation was safely used since all lines were over 30 gavs wide and hence ro modulation broeciening effects noula be observed.

The pre-amplified output rrom the crestal detector was phase sensitive detected at lookra (400Fz) (PAR Iock in Amplifier/phase aetector, model l21). Whe output mes then connected to a strip chert recoraer.

The frequency of the microwaves at $X$-bend was mecsured withe digitel frequency metea (Eewlett-Deckerd Erecuency counter 5255 A with photin adaptor Fi? 5245 ), eit q-band a mamer
was intrauced (Depry power) to the cavity.

Tre experiments were periommed on a $9.5 "$ Vasmion hachet
 the direct field readings by the sensor..$e r e$ calibrated throngh a ma gansmeter.

Ell measurments were made mith the megetic field yerpenaiculer to the uicrowave mesnetic field at the sample.

Pigure 4 gives a block diagran of the experimental setu.

## SWCUTAR DEPENDENCE OP THE SPECRRA

It is possible, in general, to aetermine experimentally the orincipal axes of the tensor $D$ by finaing the extremum positions of the $\operatorname{PRR}$ spectral lines 32 . To achieve this, one usually measures the EPR transition fielos as a function of tie orientation of the crystel field with respect to the static macketic field.

In the particuler case of brookite, it was found that it mas overctionally very difficult to find the exireme transition fielos since, wat was one line at an orientation parallel to a principal crystallofranic axis becene four lines at a random oricatation. Co try to follow a line by rotating the caystal or megnet in such a randori plane poved to be an impossiole tests.

Tre other possibility was to take the spectre at

ä́Aferent oriextations in the three crystalioaraphic (00l, 010. 100) planes where each transition line split into two and thus hoperuily receive some information on the projections of the magnetic axes in these plenes, then to reconstiuct where the real magnetic axes are, and finally obtain enough infomation to icentify and anclyse the paramanctic centers involved.

The ne: method described by $k$. Horn and C. Schwerdt $\hat{f} \in g e r^{\varepsilon}, 36$ for making ancular plots was used only on a limited basis, since it proved aimost inoperative owing to the large number of lines and their respective cross-overs. However it did prove useful in tris case for the nore eccurate olignmeat of the omstal which was previously owiented wita. a back reflection Laue metinod (Culiity) ${ }^{37}$.

## EIGE TELPERAURE REASURETUTS

In the anguiar plots made in the (001), (010) and (100) planes there are so rany transition lines that iadetification of a Daramachetic center frow sumetry consicerations alone was not possible. Transition lines disapoeared at some orientations, they crossed with other lines and no consistent trends could be founa. A aiscriminatine mechanism was necessary.

The temperature dependence spectra of anatase ${ }^{8}, 9$ showed that spectra due to suostitutional iron could still be seen eesily at temperatures over $900^{\circ} 0$ while suectra of substitutional iron complexes with an oxycen vacancy disapoeared at
zuch lower temperatures. It was e discriminctins device. Zaturaly there res no reason to believe that a charse compensation center was presert. but spin-lattice relaration times For differcht impurity ions are in ceneral always aiffere:so that tinis aiscriminetine tool could very well wora.

EiEh tenpercture measmeements at r-bana mere made mith a flow of heatoc nitrogen ges (Varian V4557), at c-cand a hot brass fingen was used. The discriminating tool proved successful.
5. EXPERTMENTAL PESUIRS

## PREISIMAR OBSERVETIONS

Since brookite has orthornombic symbietry one would expect that its RPR spectra woula also show this symmetry, this was experimentally verified.

EDR spectra at approxirately 36 Giiz are shown in Figures 5, 6 and 7 with the perwent masnetic field pavellel to the principal crystallographic axes, each figure contains ti:\% spectra, one at roon temperature, the other at aporoximately $200^{\circ} \mathrm{C}$. Pigure $\delta$ displays a spectrum slightly off the [010] axis in aporoximately the (101) plane, here each transition line splits into four lines.

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

At first, only spectira at X-band were taken. A preliminary andysis indicated that the zero field splitting was of the order of the frequency used. Since it is easier to analyze the cese for which the zero field splittine is less than the applied frequency, àta were taken and analyzed at Q-band. The X-band measurements, consequentiy, mere only used as a check.


Figure 5.- Wh suectra at a-band of a natural single brookite crystal with $H$ parallel to [100] at yoon temperature and apporimately $200^{\circ} \mathrm{C}$


Pisure 6.- WPR spectra at Q-band oi a naturel single orocirite crystal witin $H$ parailel to $[010]$ at room temperature and aporoximately $200^{\circ} \mathrm{C}$

H $1110011 \quad \frac{-3}{2} \leftrightarrow \frac{-5}{2} \quad \frac{-1}{2} \leftrightarrow \frac{-3}{2}$


MAGNETIC FIELD (Kilogauss)


Figure 7.- ERR spectra at Q-bad of a natural single broorite crystal with II parallel to [001] at roon teuperoture and approximately $200^{\circ} \mathrm{C}$


Figure 0.- ERe sectrum at Q-iand of a natural single brookito crystal with H slightly off [010] in approximately the (101) plane at roon temperature

tomperature in broolite at Q-band with $H$ rotated in the three principal crystal

## 

The first step is to deterinine a set of principai axes for the $D$ tensor. The enguler decenaence of the transition lines in the tinec crystallofremic planes where neasurements were taken :ere carefully recorded.

Frow Figure 9 it can be seen that the anculcn devencence in the (010) plane incicates that there is amemetic axis near the (100) plane, i.e., between zero and lo decrees fromit. rac (IOO) Dane andurn depondences are prosented in the same FEune. The transition lines reach an extremum for two different orientations. The extremur for the [001] direction in the 010 plane is most likely due to the magetic axis mose projection is $\sim 25^{\circ}$ fron the [001] direction in the (100) plane because it is closer to the (010) plene. One lebels this axis Y, noting that this is done only as an aicin this discussion. As yet there are no grounds to assume that this is tine $Y$ nazo netic axis. In the final abiysis, the $Y$ axis setisfies the inequality $0 \leq \frac{\sum}{D} \leq 1 / 3$

Furtien the other projection in the ( 100 ) plene incticates thet there is anctigr magetic axis $\sim 12$ aerees from the 001 plene. Consider tiee (01) plene in the figure. Agein it is most litely that the magnetic axis responsible for tine extremur in the (100) plane near the l010] curstellogranic axis is also
responsiole for the extremum at $\sim 0^{\circ}$ from the [010] axis in the (001) plane, this iskbelled the 2 axis.

If these two axes are near tize planes discussed, one can assume for the moment that the spectrameasured in the Given projectionsare going to be near the spectra, along the true magetic ares. Funthermore, the fine structure splitting is creater in the direction lavelled $Z$, than in the one labelled $Y$, hence the labelling becomes more meaningiul, 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 maxinum fielas for the tranSition lines close to the $Y$ and $Z$ directions respectively. The cifference in wagnetic field betireen transitions $|3 / 2\rangle \leftrightarrow|I / 2\rangle$ and $|-1 / 2\rangle \leftrightarrow|-3 / 2\rangle$ in both directions is nearly the same, this is an indicetion thet the centre under observetion is nearer to a fully orthornombic confiéuretion than it is to a purely axial configuration. Fence $\frac{E}{D}$ "ill be closer to $l / 3$ tian to zero. The data was then compared to the oraphs of Aase ${ }^{30}$, who caiculated for $\mathrm{Fe}^{\bar{J}}$ t the transition fielde $H$ versus $D$ both measured in units of ir using $E / D$ as a parameter. The result is $\mathrm{h} V / \mathrm{D} \cong 12$ for $Q-$ benc with on $E / D$ of 0.25 . (See Apendix B).

Finaily, one can see $b_{j}$ several argunents that the contribution of the term in the Emiltonien with equivalent operators of power four in $S$ is not neslisible. Consider the spectre close to the $Z$ end $Y$ axes. The diference in machetic
fielo between the $|3 / 2\rangle \leftrightarrow|1 / 2\rangle$ anc $|-1 / 2\rangle \leftrightarrow|-3 / 2\rangle$ Uransitions are almost equal, but the difference for the $|5 / 2\rangle \leftrightarrow|3 / \hat{2}\rangle$ and $|-3 / 2\rangle \leftrightarrow|-5 / 2\rangle$ transitions is no longer the same. This can no longer be explained if one does not teke into accomt equivaIent overators of fourth gower in $S$ in the Hamiltonian. The seme is true in one conside:'s three mutually perpendicular directions, say the principal caystallospaphic axes. Second order perturbation theory calculations of the transitions, neslecting fourth order terms show that the aleebreic sum of the differences between $\mid 3 / 2) \leftrightarrow|1 / 2\rangle$ anc $|-1 / 2\rangle \leftrightarrow|-3 / 2\rangle$ for three mutually perpendicular directions siould be zero. In the sum of the aifferences is 300 geuss. Further, using the same celculations the difference betioen $|3 / 2\rangle \leftrightarrow|1 / 2\rangle$ and $|-1 / 2\rangle \leftrightarrow|-3 / 2\rangle$ shoula be half of that for the $|5 / 2\rangle \leftrightarrow|3 / 2\rangle$ and $|-3 / 2\rangle \mapsto|-5 / 2\rangle$ transitions. This is clearly̆ not trie (see e.g. [OIO] direction).

Fron the above discussion, it is clear at this stage that because of the large uncertainty in findine experimentally the orientations of the principal axes of the tensor $\tilde{D}$, and since the $g$ value for $\mathrm{Fe}^{3+}$ in the large variety of host crystals is thet of the free electran torithin a fraction of ly. It will be meaningless in this work to try to fit a correct value for $\varepsilon$ and hence the value of $g=2.002$. was assumed.

Furtienmore, there is no reason to believe thet the vrincipal axes for the tera in the Fewiltonian with equivaleat owerators of degree four in $S$ has the same principal axes as tensor $\widetilde{D}$.

If one assues trat the values of a and $P$ for brokite are of Ghe oncien of those of matase and rutile, one cen calculate thet tiee contribution to first orcer perturvation theory is of the same order as the contribution to second oner perturbation theory fow $E$. Hence it seews only meaningrul to try to fit the transition fields usine first order pertunbation theory for the terus in the meniltonian of degree four in $S$.

The first oner perturbetion theory for this tera is propontionel to $p e+1 / 12$ q ${ }^{2}$ where $p=5 / 2\left(1^{4}+m^{4}+n^{4}-3 / 5\right)$ and $q=35 \cos ^{4} \theta-30 \cos ^{2} \theta+3$. The propoitionality factor for this polynomial is $2,-2.5,0,2.5$ an $\bar{\alpha}-2$ aependine on the tran-
 these promontionality facions are true only if the eicenstates of the unperturbed Hamiltonian are pure.

Since one coes not have an apriori idea of the value of $\underline{p}$, there is no way one can give the values of "e." and "P". The most one can give is tie velue of pat(I) dag(=?) fox any ajrection。

A rough estinate of this value is easily found by celculating the mernetic trenstion fields from second order
 corresponcing provoitionsitity fector,

$$
\begin{aligned}
& h r=8 \beta H_{5 / 2}+2 X+2 R+32 Y-1 Z \\
& h r=8 \beta E_{3 / 2}+1 X-5 / 2 R-4 Y+5 / 4 Z \\
& h r=6 \beta H_{1 / 2}+0 X+0 R-16 Y+2 Z \\
& h r=8 \beta H_{-1 / 2}-1 X+3 / 2 R-4 Y+5 / 4 Z
\end{aligned}
$$

$$
i r=6 \beta-3 / 2^{-2 X}-2 R+52 Y-1 Z
$$

this is a systen of five equations and four unknownsan thus easily solvable for P. Tre unknown $X$, $Y$ and $Z$ are functions of $D, E, \theta$ and $\varphi .^{41}$

## ADUGTGNT OP TEE ROILIOMIAS PARASETERS

An adjustant of the estimated paraneters was then made シi立h a computer prosran Eiven by J. Febden et al. 39 Using a triel and error metnod. This profram colculates for a given $G \times x, G \in V, G z, D$ and $E$, the ERR transition field, the correspondine trensition probability, and plots the enerey levels. t correction mas made to the transition fields by considerinc the contribution of the term R. The proportionclitiy:factors Were taken as true for q-band anaiysis since the transition probabilities at this frequency indicate that the eigenstates are feinly pure in this rence (they are near the 5:0:9:0:5 of the pure cese). The trensition probebility celculation for the $X$-bend rence, on the other hend, incicates a very strong mixture of states, hence no correction was mede to the transition fields and consequently the calculated transition fields cio not fit the experimentel data and in some cases. they are as much as 300 geuss off.

Pigure 10 shows the plots of the encrey levels for the cases "ith H parallel to the thee principal crystallofraphic ases, and Table VII gives the trensition probability calculetions.

## Q3IE VII

## RRWOTMO PROEOMTRIES

Q-End

| nansition | 010 | 100 | 001 |
| :--- | :--- | :--- | :--- |
| $\|5 / 2\rangle^{\prime} \leftrightarrow\|3 / 2\rangle^{\prime}$ | 5.33 | 5.45 | 4.89 |
| $\|=/ 2\rangle \leftrightarrow\|1 / 2\rangle$ | 8.25 | 0.37 | 7.75 |
| $\|1 / 2\rangle \leftrightarrow\|-1 / 2\rangle$ | 8.73 | 8.74 | 8.85 |
| $\|-1 / 2\rangle \leftrightarrow\|-3 / 2\rangle$ | 7.21 | 7.10 | 8.1 .2 |
| $\|-3 / 2\rangle \leftrightarrow\|-5 / 2\rangle$ | 4.20 | 4.05 | 5.27 |

$x-\operatorname{Ean}{ }^{*}$

| $\|5 / 2\rangle^{\prime} \leftrightarrow\|3 / 2\rangle^{\prime}$ | 0.27 | 4.93 | 0.85 |
| :--- | :--- | :--- | :--- |
| $\|3 / 2\rangle^{\prime} \leftrightarrow\|1 / 2\rangle^{\prime}$ | 6.16 | $4.30(0.74)$ | 8.23 |
| $\|1 / 2\rangle^{\prime} \leftrightarrow\|-1 / 2\rangle^{\prime}$ | 6.27 | 5.87 | 4.99 |
| $\|-1 / 2\rangle^{\prime} \leftrightarrow\|-3 / 2\rangle^{\prime}$ | 3.09 | 5.96 | 4.19 |
| $\|-3 / 2\rangle \leftrightarrow\|-5 / 2\rangle$ | 0.68 | 1.06 | 1.33 |

*Several other transitions mich are possible from enerey Gifenences alone have not been includea since the probability ceicuicitions éve values of less tinail 0.10.

## TABIE VITI

## MAILRNIE PARAETERS

$$
\begin{aligned}
& \widetilde{E}=2.002 \pm 0.005 \\
& D=(1170 \pm 30) \times 10^{-4} \mathrm{~cm}^{-1} \\
& E=(330 \pm 20) \times 10^{-4} \mathrm{~cm}^{-1} \\
& (p a+1 / 12 \mathrm{qF})_{010}=(13 \pm 10) \times 10^{-4} \mathrm{~cm}^{-1} \\
& (p a+1 / 12 q F)_{100}=(-13 \pm 5) \times 10^{-4} \mathrm{~cm}^{-1} \\
& (p a+1 / 12 \mathrm{qF})_{001}=(-66 \pm 4) \times 10^{-4} \mathrm{~cm}^{-1}
\end{aligned}
$$

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

|  | $\theta$ | $\varnothing$ |
| :---: | ---: | :---: |
| $z$ | $81^{\circ}$ | 550 |
| y | $149^{\circ}$ | $231^{\circ}$ |
| x | $60^{\circ}$ | $210^{\circ}$ |

Tie direction betmeen the longest and shortest ti-O boné, which are rearly opoosite, comresponds to the $z$ wasnetic axis.

A final least mean square computer calculation of $D, E$, $\alpha, \beta, \gamma, R_{100}, P_{010}$ and $R_{001}$, was made to fit 21115 ER I ines, $j$ ever axis. ( $\alpha, \beta$ and $\gamma$ are tine Euler angles as given by GoIdstein ${ }^{40}$ ). Tais method is discussed in Appendix $C$. The absolute sighs of $D$ and $E$ :reve established with an ERR measurement at liquia heliun temperatures. The resulis are incluced in Table VIII.

It should be pointed out thet low temperature measureBents indicate that the temperature dependence of the paraaeters in the Familtonian vary at nost l\% compred to those Found at room temperature. Fence the temperature behavior of brookite is combarable to thet found in mitile ${ }^{6}$ and not to that founa in anctase? ${ }^{9}$


Figure 10.- Wercy levels of suostitutionel $\mathrm{Fe}^{3+}$ in brookite with H parallel to each of the principal crystallographic axes
6. DISCUSTO: OP DOUTE A: COMTUSTOR

Erom Pable II in Chatter tro, one can calculato the projection of the segments joining the ifo to the neishbouring oryens and the neighcouning titaniuns. Companison with the anculan dependence of the spectra enebles one to identify the menetic aes. The $Z$ aris comesponds to then(Ti. $-O_{I I}$ ) diarection and the $X$ and $Y$ directions coriesmond to the $\sim\left(\mathrm{Hi}_{0}-\mathrm{O}_{I}\right) \operatorname{and} \sim\left(\mathrm{Mi}_{\mathrm{O}}-\mathrm{O}_{V}\right)$ airections meswectively.

The possibility of inon ocapying an interstitiel site has also been explored, but no losical correspondence has been Found, and, on the other hand this mould generate a strong Iocel cherse inequality. In adaition, in rutile one oberves paramagnetic impurities in the laroer interstitial sites only if the impurities are too large to enter the substitutional site. 42 In octahedral coomanation, the ionic racius of $\mathrm{Pe}^{3+}$ is $0.73 \stackrel{\circ}{\mathrm{~A}}$, compared to that of Ti 4 whicn is $0.69{ }^{\circ} 43$. Thus, one cen conclude safely that the $\mathrm{Pe}^{3 t}$ ions go into substitutional sites. The spectina aditionally saow that all eight sites are equally ocuopied by $\mathrm{me}^{3+}$ ions.

A conpanison betucen tho resultu of the ERR syectre of substitutionel Pe in broonito, anetase and muthe is interest ine. The Namitonian paramoters for brookite are found to be between those for amatase and mitile, and contrary to tre case of anatesc, the specta mene found insensitive to temperature. The strons temperatue dependence of the anatase case has been explaneé in teras of a shift of the oryeen ions 8, 9 . Mhis
 naereas it would in rutile.

Wo enalyits has Deen as yet dono on the second or more Grouns of spectre minch heve been also seen at roon temperaGues. Eech one of these lines nas also the characteristic Of splititna in four at a manom orientetions. Replacenent
 one ejenentany chene at the site. mis excess has to be comveaseted to leep the ciystal electrically neutial. mrais may be echieved by other impurities, interstitial ions, on an oneon vacency. The possibility of the first case is unlikely since this impurity ion mould have to be of a positive charge nigher than four. From symuetry considerations of tine spectra the ctiner tuo are possible, the letter case only if tiee oxygen Vaccnoy is not present in the nearest neighbours. Such a case hes been revorted in rutile fon a suvstitutional Cr3+ by Ikebe et al. 43 Tnis Essumption, if true, is interestinc compared With the other colyworphic soms of MiO ${ }_{2}$. Anatese hes a nearest nefonour oyyen vecancyo,9 associated with Fe $3+$ wineme as ruخine ${ }^{6}$ ias none.
$\therefore$ second possibility to esplain tinese lines moula be tio nresesce of othen impurities, on the othen nenc tio $\operatorname{sen}$ seectia of the liderenential and Velsertel samples are incistinuishable;, all observed EPR transition lines have the scare rolative intensities. It is not clear et this stage if ti三s indicates tiat all trensition Iines cen ba attributed to
$\mathrm{Fe}^{3+}$ or that the relative concentration of the paramarnetic impurities is the sare 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 hish loss factor. This leads to another unanswered question. From where coes the hich loss factor come? The possibility of a high concentration of sone impurity is sowhow coubtrul since when the crystal was transformed to rutile by heating, a sharp spectrum was obtained.

At liquid nitrosen and lower temperatures adiditonal spectral lines have been observed centered at $f$ values near two. Any analysis of these spectra will prove-aifificult because of strong overlaping of transition lines in this region.

In conclusion, the high teaperature EPR spectrum is explained by assuainc thet $\mathrm{Fe}^{3+}$ suibstitutes for $\mathrm{Ti}^{4+}$, all eisint equivalent $\mathrm{Ti}^{4+}$ sites being occupied by $\mathrm{Ee}^{3+}$ with equal probability.

The scope of this thesis hes left many questions unanswered which furtner EER investifations can possibly lead to interesinne results.

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## 4PSEMDIX A

The matrix elements of the spin familtonien of equation (1) for an arbitrary orientation of the nachetic field have been calculated by using the general formuae given by Beker and Willians 33 and using the matrix elements for the equivaIent spin operator $O_{n}^{m}$ given by Aoragam and Bleaney ${ }^{2}$. The calculation have been mace oy setiting the $b_{2}^{1}, b \frac{1}{4}, b_{4}^{2}, b_{4}^{3}$ parametors in equation (I) equal to zero. The rotational transformetion of the operators $O_{n}^{m}$ are also given by Thyler et al. ${ }^{44}$ and Vinolurov et al. 45
The result of this calculation is the following:

|  |  | $\left\|\frac{3}{2}\right\rangle$ | $\left\|\frac{1}{2}\right\rangle$ | $\left\|-\frac{1}{2}\right\rangle$ | $\mid$｜－3 ${ }^{-3}$ | $\left\|-\frac{5}{2}\right\rangle$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 〈 ${ }_{2}$ ¢ | $\frac{5 C^{2}}{\frac{5}{2}+\frac{10 K_{1}}{3}+\mathrm{K}_{2}}$ | $\frac{\sqrt{5} K_{3}}{3}+6 \sqrt{5 K_{4}}$ |  | $3 \sqrt{10} \mathrm{~K}_{7}$ | $\frac{2 \sqrt{5}}{120}{ }^{\text {K }}$ | 0 |
| 〈 ${ }_{2}$ ， | $\frac{\sqrt{5} K_{3}}{5}+6 \sqrt{5} K_{4}$ | $\frac{36-2 K_{1}-3 K_{2}}{3}$ | $\frac{\sqrt{2} x_{3}-15 \sqrt{2 \pi} K_{4}}{}$ | $\sqrt{22} 5_{5}-15 \sqrt{2 x_{6}}$ | 0 | $\frac{2}{120} \mathrm{~K}_{8}$ |
| 〈 $\frac{1}{2}$ ， | $\frac{\sqrt{101}}{3} 5+9 \sqrt{1015}$ | $\frac{\sqrt{2} \mathrm{~K}_{5}-15 \sqrt{3} \mathrm{IK}_{4}}{}$ | $\frac{17-8-\frac{8}{3} K_{2}+2 K_{2}}{}$ | 0 | $\sqrt{2} x_{5}-15 \sqrt{2} x_{6}$ | $-3 \sqrt{10} K_{7}$ |
| $\left\langle-\frac{1}{2}\right\|$ | $3 \sqrt{10} \mathrm{~K}_{7}$ | $\sqrt{2} x_{5}-1.5 \sqrt{2} x_{6}$ | 0 | $-\frac{26}{2}-\frac{8 K_{1}}{3}+2 \mathrm{~S}_{2}$ | $-\frac{\sqrt{2} x_{3}+3.5 \sqrt{215}}{4}$ | $\frac{\sqrt{10} x^{3}}{5}+9 \sqrt{10} \mathrm{~K}_{6}$ |
| $\left\langle-\frac{3}{2}\right\}$ | $\frac{2}{1} \frac{\sqrt{5}}{120} \mathrm{~K}_{8}$ | 0 | $\sqrt{2} \times 5-15 \sqrt{2} x_{6}$ | $-\frac{\sqrt{2} x_{3}}{3}+15 \sqrt{2 x_{4}}$ | $-\frac{56-2 K_{1}-3 m_{2}}{3}$ | $-\frac{\sqrt{3} \mathrm{~K}}{3}-{ }^{-6 \sqrt{\overline{2}} \mathrm{~K}_{4}}$ |
| $\left\langle\frac{-\frac{5}{2}}{}\right\|$ | 0 | $\frac{2 \sqrt{5}}{120} x_{8}$ | $-3 \sqrt{10} \mathrm{~K}_{7}$ | $\frac{\sqrt{10} K_{5}}{5}+9 \sqrt{10 K_{6}}$ | $-\frac{\sqrt{5} 5}{5} 5-6 \sqrt{51} K_{4}$ | $\frac{-5 c^{2}+\frac{10 K_{3}}{3}+K_{2}}{}$ |

with
$G=E \mathrm{~F}$
$K_{1}=\frac{b 0}{\delta}\left(3 \cos ^{2} \beta-1\right)+\frac{\dot{b}_{2}^{2}}{2}\left(1-\cos ^{2} \beta\right) \cos 2 \alpha$
$K_{c}=\frac{b_{A}^{0}}{3}\left(35 \cos ^{4} \beta-30 \cos ^{2} \beta+3\right)+\frac{b_{4}^{4}}{8} \sin ^{4} \beta \cos 4 \alpha$
$K_{3}=-600_{2}^{\circ} \sin \beta \cos \beta+2 b_{2}^{2}(\sin \beta \cos \beta \cos 2 \alpha+i \sin \beta \sin 2 \alpha)$
$\mathrm{K}_{4}=\frac{\mathrm{b}_{4}^{0}}{12}\left[6 \sin ^{3} \beta \cos \beta-\sin \beta \cos \beta\left(3+\cos ^{2} \beta\right)\right]+\frac{b^{4}}{60} \sin ^{3} \beta(\cos \beta \cos 4 \alpha+i \sin 4 \alpha)$
$K_{5}=\frac{3 b_{2}^{0}}{2} \sin ^{2} \beta+\frac{b_{2}^{2}}{2}\left[\left(1+\cos ^{2} \beta\right) \cos 2 \alpha+2 i \cos \beta \sin 2 \alpha\right]$
$\mathrm{F}_{6}=-\frac{250_{4}^{0}}{240} \sin ^{4} \beta+\frac{0_{4}^{4}}{240} \sin ^{2} \beta\left[\left(1+3 \cos ^{2} \beta\right) \cos 4 \alpha+i \cos ^{2} \beta\left(3+\cos ^{2} \beta\right) \sin 4 \alpha\right]$
$\mathrm{K}_{7}=-\frac{3 \operatorname{Sin}_{4}^{0}}{60} \sin ^{3} \beta \cos \beta+\frac{0}{60} \sin \beta\left[\cos \beta\left(3+\cos ^{2} \beta\right) \cos 4 \alpha+i\left(1+3 \cos ^{2} \beta\right) x \sin 4 \alpha\right]$
$r_{0}=\frac{350_{4}^{\circ}}{4} \sin ^{4} \beta+\frac{b_{i}^{4}}{4}\left[\left(1+6 \cos ^{2} \beta+\cos ^{4} \beta\right) \cos 4 \alpha+4 i \cos \beta\left(1+\cos ^{2} \beta\right) \sin \alpha\right]$
where $(\alpha, \beta)$ are the azimuthal ana polar angles of the axis of quantization with respect to the crystal field axes, and the following well known reletions hola: $\tan \alpha=\frac{\bar{E}_{y}}{\bar{\sigma}_{Z}} \tan \phi$ and $\tan \beta=$ $\frac{\pi_{\perp}}{G_{Z}} \tan \theta$.

## APROMTVE CLICUISTO: OTDEDE

The ain features of the EDR spectrum of $\mathrm{e}^{3+}$ can be described by neglecting the fourth order ten as of the Zaniliosian in equation ( 5 ) . Tais

$$
\begin{equation*}
\mathscr{H}=\beta(\mathrm{Z} \cdot \mathrm{G} \cdot \mathrm{~S})+D\left\{s_{z}^{2}-1 / 3 s(s+1)\right\}+1 / 2 E\left(s_{+}^{2}+s_{-}^{2}\right) \tag{4}
\end{equation*}
$$

 directions of the acetic axes, are sufficient to characterize the spectrum. These parameters can be estimated with the help of graphs given by Asa 38 if the transition fields along the ascetic axes are measured.

Ease calculates for $5=5 / 2$ the transition fields in as a function of $D$, using $E / D$ as a parameter. $D$ and $E$ are measured in units of inv. Figure ill is a reproduction of those parts $0 f$ hasa's figures I and 2 which correspond to $E / D=0.25$. The transitions for parallel to the directions within the principal crystallographic planes nearest to the $\bar{y}$ and 2 magnoetic awes are show.


Fisure ll. - Fositions of tine Bpr transitions fithin the lower ana upper Kraner doviets of $\mathrm{e}^{3+}$ for $2 / 0=0.25$


## LPDRTIX

## 

## ITEAROW TESEM MEM SQURE BET

As discussed in Chevton 5, the observed EPR tran-

 and emon uethod using a cowbuter progran fiven brineden et al. 39 men all the parameters are inaividualy changed by a small amount pand the new transition fields, which differ by ha from $H_{k}^{O}$ are celculated by diegonalizine with the Hebden computem programe. $\mathrm{H}_{\mathrm{k}}^{\mathrm{Cal}}$ is now definco by

$$
H_{k}^{c a l}=H_{K}^{0}+\sum_{n} p_{n} \cdot \frac{\delta r_{M}}{\delta p_{n}}
$$

This represents a sestem of linecr equations in the unlown $P_{n}$. The best values of $p_{n}$ are determined by minimizing

$$
\sum_{K}\left(\mathrm{H}_{\mathrm{K}}^{\mathrm{EXP}}-\mathrm{H}_{\mathrm{K}}^{\mathrm{caI}}\right)^{2}
$$

Notice must be taken tiat it maj happen that the nem pancmeters \#ill not convemee necessorily to some better values because of unturue Iineanization winich ocours if the ry are not near the $\mathrm{F}_{\mathrm{k}}^{\mathrm{exp}}$ values. It may hence be necessary to reveet the procecure several times.

