EPR analysis of iron(+3) and chromium(+3) in lithium potassium sulphate.

Luigi. Conte

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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS REÇUE
EPR ANALYSIS OF Fe$^{+3}$ AND Cr$^{+3}$ IN LITHIUM POTASSIUM SULPHATE

by

Luigi Conte

A Thesis submitted to the Faculty of Graduate Studies and Research through the Department of Physics in Partial Fulfillment of the requirements for the Degree of Master of Science at the University of Windsor

Windsor, Ontario, Canada 1985
ABSTRACT

The paramagnetic resonance spectra of Cr$^{3+}$ and Fe$^{3+}$ impurity ions in LiKSO$_4$ (single crystal and powder samples), were studied at K- and X-band frequencies as a function of temperature in the range from liquid nitrogen (LN) to room (RT). Spin Hamiltonian parameters were determined at LN and RT. The implication of these results on the crystal structure of LiKSO$_4$ at these temperatures has been fully discussed.
In Memory Of Perino Pasquatonio
ACKNOWLEDGEMENTS

The author wishes to thank Dr. F. Holuj for suggestion of the problem and for guidance and patience during the course of the research. Thanks are also due to Mr. B. Masse and Mr. W. Grewe and their staff for technical assistance and construction of apparatus and also to Bill LaBranche for computer interfacing of apparatus.
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CHAPTER I
INTRODUCTION

LiKSO₄ (LPS) belongs to a class of pseudo-hexagonal crystals which undergo several phase transitions. Their general formula is ABXY₄. Examples are K₂SeO₄, (NH₄)₂SO₄, K₂ZnCl₄, LiNH₄SO₄, LiCsSO₄, LiRbSO₄, and others. The following phases of LPS have been identified: Phase I: P6₃ (hexagonal C₆); Phase II: P6₃mc (hexagonal C₆); Phase III: Cmc2₁ (orthorhombic C₆). We shall refer to phase I as the high temperature (HT) phase, and the phases II and III variously as the low temperature (LT) or the liquid nitrogen (LN) phase. (The phases II and III are not distinguishable in our experiment.)

The existence of each of these phases seems to be dependent not only on the temperature but on the thermal history of the crystal as well as the method used to grow it (Tomaszewski and Lukaszewicz, 1983). Furthermore, wide temperature hysteresis is present. There seems to be an agreement amongst the data that the phase I exists above the temperature -18°C and the phase III below -80°C. The phase II exists either in a mixture of phases II and/or I, or in a pure form in the intermediate temperature range (Tomaszewski et al., 1983). Apart from x-ray study (Tomaszewski et al., 1983) the existence of phase II was confirmed by an NMR study of ⁷Li (Holuj, 1985), and by the neutron diffraction study (Tamhane, Sequeira and Chimbaram, 1985) which claims,
however, that the phase II is P31c (trigonal C_{3v}^4) rather than P6_3mc.

The nature of the structural difference between these phases seems to be connected with the orientation of SO_4 tetrahedra. In phases I and II, these tetrahedra are disordered while in phase III they are ordered (Tomaszewski et al., 1983). One suggestion (Tomaszewski et al., 1983) is that a disorder exists in the position of O_4 (Fig. V.3): in phase II and III it is ordered. Tamhane et al. (1985) claim, however, that the phase between -90 and -20°C is a mixture: [0.45(PI) + 0.55(PII)] and that PII is obtained from PI by a rotation of one of the two SO_4 tetrahedra by 60 degrees about the S-O_4 bond.

Alybakov, Gubanova and Sharsheev (1982) have studied the LPS:Cr^{3+} system by the optical absorption method (at LN) and the EPR method (RT), and claim that the results are consistent with Cr^{3+} entering the K^+ site substitutionally.

Studies using EPR caused by impurity ions hitherto have not been done involving LPS in great detail. Only Cr^{3+} has been studied by Alybakov et al. (1982) but no details of their EPR results were included in their work.

The present work involves the EPR of Fe^{3+} and Cr^{3+} ions as impurities in LPS.

The EPR of Fe^{3+} in LPS was studied at both K- and X-band at room temperature (RT) and LN. These studies enabled the estimation of the crystal field parameters B_{20} and B_{22} at RT
from the K-band data. The low field spectrum at X-band were analyzed and we were able to estimate the values of $\eta \left(= \frac{B_{22}}{B_{20}} \right)$ using the theory of Holuj (1966). Temperature studies were also done using the c-axis orientation and powder spectra at X-band.

The EPR of Cr$^{3+}$ in LPS was also studied at K- and X-bands at RT and LN. The K-band data was used to fit the parameters of the spin Hamiltonian through a multidimensional Newton-Raphson least square minimization method (Fox, Holuj, Baylis, (1973)). The spin Hamiltonian parameters were found at both RT and LN. The X-band data presented no new information. Temperature study was done using the spectral Y-axis orientation at LN in the temperature range LN-RT.
CHAPTER II
THE CRYSTAL STRUCTURE OF LiKSO₄
AND PHYSICAL PROPERTIES

Lithium Potassium Sulphate (LPS) is a hexagonal crystal with two formula units in the unit cell and the SO₄ tetrahedra are related by symmetry. LPS belongs to the space group P6₃ or C₆ with unit cell parameters a=5.1457 Å, b=4.4563 Å and c=8.8298 Å at 25 °C (Wyckooff 1960). The projection of the unit cell in the ⟨001⟩ plane is shown in Fig. II.1a.

In Fig. II.1a the atoms have the following coordinates:

<table>
<thead>
<tr>
<th>Atom</th>
<th># of atoms/group</th>
<th>position</th>
</tr>
</thead>
<tbody>
<tr>
<td>K:</td>
<td>2</td>
<td>0,0,k;0,0,k+1/2 with k=0</td>
</tr>
<tr>
<td>S:</td>
<td>2</td>
<td>1/3,2/3,0,2/3,1/3,k+1/2 with k=0.17</td>
</tr>
<tr>
<td>O(1):</td>
<td>2</td>
<td>with k=0</td>
</tr>
<tr>
<td>O(2):</td>
<td>6</td>
<td>x,y,z;\bar{x},-y,z; y-x,\bar{z},z; \bar{x},\bar{y},z+1/2; \bar{y},-x,z+1/2; x-y,\bar{x},z+1/2 with x=.38, y=.94, z=.25</td>
</tr>
</tbody>
</table>

The largest circles represent the potassium atoms, the oxygen atoms by the intermediate size and sulfur by the smallest size. The possible positions of the lithium atoms are not shown but are presumed to be below (or above) the SO₄ tetrahedra with the value of k greater than 1/2. In Fig. II.1b we show the drawing of the LPS structure viewed
Fig. II.1. a) Represents the projection of the unit cell in the (001) plane and b) is a vertical plane passing through atoms A and C of a).
against a vertical plane passing through atoms A and C. Letters in Fig. II.1a, and II.1b refer to the same atoms.
Lithium are shown as shaded circles in Fig. II.1b.

Temperature studies done on crystals of LPS by Tomaszewski et al. (1983) show that on cooling from room
temperature, LPS transforms to another hexagonal phase,
P6$_3$mc. Further cooling below 180 K it becomes orthorhombic
Cmc$_2$1. Fig II.2 is a pictorial representation of the
temperature transformations of LPS, where temperatures are
in celcius:

```
-190  -86   -18   RT  
```

--- heating

--- cooling

Fig. II.2

LPS crystals were grown isothermally at 315 K by the
dynamical method from aqueous solutions containing the
initial salts at stoichiometric ratio.
CHAPTER III
THEORY

A. Electron Paramagnetic Resonance

The phenomenon of paramagnetism occurs whenever a system of charges has a resultant angular momentum. If the nature of the paramagnetism is electronic, then we talk of electronic paramagnetism.

We can observe such paramagnetism where:

a) Atoms have an odd number of electrons,
b) In ions with partly filled inner electron shells as a paramagnetic impurity,
c) In free radicals; chemical compounds possessing unpaired electrons,
d) In colour centers; produced in solutions or solids by nuclear radiation, etc.

We are concerned with b) namely Cr+3 and Fe+3 as impurities.

If a free ion with resultant angular momentum \( J \) is placed in a magnetic field \( H \), the energy levels of the magnetic dipole are given by

\[
E=g\beta H M_j.
\]

(1)

Where \( g \) is the Lande g factor and \( \beta (=eh/mc) \) is the Bohr magneton, \( M_j \) is the component of the angular momentum \( J \) along the field acting on the free ion. If an alternating field of frequency \( \nu \) is applied at right angles to \( H \), magnetic dipole transitions are produced according to the
selection rule $\Delta M_J = \pm 1$. We then have the following resonance condition

$$h\nu = g_s\mu_B H.$$  \hspace{1cm} (2)

Take a case where we have a single electron whose orbital angular momentum $L$ is zero. The $g$-factor is correspondingly equal to the free electron value $g_s (= 2.0023)$. Energy is absorbed when the electron spin is flipped from a direction parallel to the magnetic field from a direction that was antiparallel to it. Conversely, induced emission will occur. A system which is in thermal equilibrium, the lower state has a greater population. Therefore a net absorption will occur.

B. The Crystal Field

When the paramagnetic ion is placed in a host lattice in our case LPS, there are interactions between it and its surroundings. We are concerned with the interactions between the paramagnetic ion and its diamagnetic neighbours. These neighbours consist of charged ions which set up strong internal electric fields. These fields as a good approximation can be considered static. The effect of the crystal field on the energy levels is a partial lifting of the spin degeneracy where the resulting splittings are Kramers doublets.

C. The Trivalent Chromium and Iron Ions

The ground state for the $S$-state and $F$-state ions $Fe^{+3}$
and Cr$^{3+}$ is $^6S_{5/2}$ and $^4F_{3/2}$, due to the $3d^5$ and $3d^3$
electrons respectively. The ions have a resultant orbital angular momentum given by $L=0$ and $L=3$ and spins given by $S=5/2$ and $S=3/2$ respectively.

The following are the electronic configurations of Cr$^{3+}$ and Fe$^{3+}$ respectively:

Cr$^{3+}$ : $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^3$
Fe$^{3+}$ : $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^5$.

D. The General Hamiltonian

The following is the Hamiltonian which describes the interaction energy of a free paramagnetic atom in zero magnetic field.

$$H_{gen} = U_{TC} + U_{LS} + U_{SS} + U_N + U_Q \tag{3}$$

where,

$$U_{TC} = \frac{N}{K^2} \left( \frac{p_K}{2m} - 2e^2/r_K \right) + \sum_{KJ=1}^{N} e^2/r_{KJ}$$

The first term of the above expression is the total kinetic energy summed over all $K$ electrons. The latter two terms, the coloumb term, is the interaction of the electrons, with the nuclear charge $Ze$ and the mutual repulsion of the electrons.

The $U_{LS}$ term of the Hamiltonian describes the spin-orbit interaction which is written as follows.

$$U_{LS} = \sum_{ij} \frac{\lambda_{ij}}{r_{ij}} I_i I_j S_j$$

Where $i, j$ are summed over all the electrons in the ion. $U_{LS}$ reduces to the following according to the Russell-Saunders scheme.
\[ V_{LS} = \lambda L \cdot S \]

where \( L = \sum_{i} l_i \) and \( S = \sum_{i} s_i \)

and \( \lambda \) is the spin-orbit constant for a given ion.

\( V_{SS} \) is the weak spin-spin interaction. This interaction is given by the following equation

\[ V_{SS} = \sum_{ij} \left[ s_i \cdot s_j / r_{ij}^3 - 3(r_i \cdot s_i)(r_j \cdot s_j) / r_{ij}^5 \right]. \]

If the nucleus has spin \( I \) and a quadrupole moment \( Q \), we then have the final two terms of our Hamiltonian, \( V_N \) which describes the dipole-dipole interaction between the nuclear moment and the magnetic moments of the electron, also includes the anomaly interaction of the s electrons with the nuclear spin. \( V_N \) is mostly referred to as the Hyperfine term.

\( V_Q \) describes the electrostatic interaction with the quadrupole moment \( Q \) of the nucleus.

When a static external magnetic field \( H \) interacts with the free ion we add the following terms to the Hamiltonian, due to the electronic interaction

\[ V_H = \sum_{i} \frac{\mu}{k} (1 + 2s_i \cdot \sigma) \cdot H \]

and nuclear interaction

\[ V_n = -\gamma N H \cdot I \cdot N. \]

E. The Spin Hamiltonian

The previous section introduced the possible interactions involving a free ion in the form of the general Hamiltonian. The general Hamiltonian is not a simple equa-
tion to work with in this form. Therefore for EPR data to be simply analyzed, we make use of a spin Hamiltonian.

Transitions between the lowest energy levels are observed by paramagnetic resonance. Experimentally, if transitions between $2S' + 1$ levels are observed, we can define $S'$ to be the fictitious spin of the system. In the case of Cr+3, we have a $^4F$ ground state. In an external magnetic field a fourfold degeneracy is lifted and transitions between the levels can be induced according to the selection rule $\Delta M = \pm 1$. Therefore the real spin $S$ equals the fictitious spin $S' = 3/2$. The advantage of the spin Hamiltonian is that with the complicated behaviour of the lowest energy levels of the paramagnetic ion in a magnetic field can be described in a simple way by specifying the fictitious spin, together with a small number of parameters which measure the magnitudes of the various terms in the Hamiltonian. The terms of the Hamiltonian are in a form involving appropriate spin angular momentum operators where the effects of the crystal field are represented in the Hamiltonian by higher powers of the fictitious spin.

The interaction terms describing the paramagnetic resonance spectra of Cr+3 ions in the spin Hamiltonian are as follows:

(I) Zeeman Interaction:

The Zeeman term is given by the following equation
\[ H_{\text{zeeman}} = \mathcal{P} S \cdot \mathcal{H} \]
\[ = \mathcal{P} (g_x S_x H_x + g_y S_y H_y + g_z S_z H_z). \quad (4) \]

Equ. (4) in terms of operator equivalents which are given by Buckmaster et al. (1971), can be written as follows:

\[ H_{\text{zeeman}} = \mathcal{P} \hbar \mu T_{10} + \mathcal{P} (h_+ T_{1-1} \sqrt{2} - h_- T_{11} \sqrt{2}) \quad (5) \]
where, \( \hbar \mu = g_z H_z \), \( h_\pm = g_x H_x \pm i g_y H_y \).

(II) Crystalline Electric Field Interaction:

The spin Hamiltonian in terms of operator equivalents for the crystal field with orthorhombic symmetry is

\[ H_{c.f.} = B_{20} T_{20} + B_{22} (T_{22} + T_{2-2}) \quad (6) \]

The form of these operators is given to be:

\[ T_{10} = S_z \]
\[ T_{1\pm1} = \pm \sqrt{1/2} S_\pm \]
\[ T_{20} = \sqrt{1/5} [3S_z^2 - S(S+1)] \]
\[ T_{2\pm2} = 1/2 S_\pm \]

where, \[ S_\pm = S_x \pm i S_y. \]

The matrix elements for the above operators in various manifolds are also given by Buckmaster et al. (1971).

The combined expression for the spin Hamiltonian is

\[ H_S = \mathcal{P} \hbar \mu T_{10} + \mathcal{P} (h_+ T_{1-1} \sqrt{2} - h_- T_{11} \sqrt{2}) \]
\[ + B_{20} T_{20} + B_{22} (T_{22} + T_{2-2}). \quad (7) \]

The matrix formed by equ. (7) in the \( S=3/2 \) manifold is shown in Table III.1.

F. The Strong Crystal Field for Fe+3

(II) The Zero-Field Spin Hamiltonian:
Table III.1. Matrix of the spin Hamiltonian (eq. 7) in the S=3/2 manifold.
The Zeeman term is assumed to be smaller than the remaining terms of the Hamiltonian. The effect of the crystal field on the Kramers doublets is obtained by studying the following zero-field spin Hamiltonian.

\[ H = B_{20} T_{20} + B_{22} \left( T_{22} + T_{2-2} \right) \] (8)

The matrix formed by eqn. (8) in the \( S=5/2 \) manifold is shown in Table III.2 where \( H_z \) is zero. The process of diagonalization of the matrix, whose elements are regarded as functions of the parameters

\[ \eta = \sqrt{2} \frac{B_{22}}{B_{20}} \] (9)

and of \( B_{20} \).

This procedure yields the values of the energy levels,

\[ E_i^0 = \frac{\sqrt{2}}{\Omega_i} B_{20} \],

where \( \Omega_i \) is a function of \( \eta \) and \( i \) represents one of the three Kramers' doublets. Which also yield the following eigenfunctions:

\[ | \pm i \rangle = a_i^{-1} | \pm 1/2 \rangle + a_i^2 | \pm 3/2 \rangle + a_i^3 | \pm 5/2 \rangle \] (10)

Each doublet is assumed isolated and belonging to the effective spin \( S=1/2 \) and each possessing a highly anisotropic effective \( g \) factor, \( g_i \). The effect of the magnetic field on each \( i \)th doublet can be described by the following spin Hamiltonian,

\[ H(S') = g_x H_x S_x' + g_y H_y S_y' + g_z H_z S_z' \] (11)

Eqn. (11) is valid to a first order of approximation (Holuj, 1966). In eqn. (11), \( g_\alpha (\alpha=x,y,z) \) is the true \( g \)-factor of the \( ^6S \) term of Fe\(^{3+} \) (usually close to 2) and \( g_i = g_\alpha \) for \( S_\alpha \).
<table>
<thead>
<tr>
<th></th>
<th>1+5/2⟩</th>
<th>1+3/2⟩</th>
<th>1+1/2⟩</th>
<th>1-1/2⟩</th>
<th>1-3/2⟩</th>
<th>1-5/2⟩</th>
</tr>
</thead>
<tbody>
<tr>
<td>⟨+5/2</td>
<td>5/2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⟩</td>
<td>Ω_{g_z} H_z + 5 \sqrt{2/3} B_{20}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⟨+3/2</td>
<td></td>
<td>3/2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⟩</td>
<td>Ω_{g_z} H_z - \sqrt{2/3} B_{20}</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>⟨+1/2</td>
<td></td>
<td></td>
<td>1/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⟩</td>
<td>Ω_{g_z} H_z - 4\sqrt{2/3} B_{20}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⟨-1/2</td>
<td></td>
<td></td>
<td></td>
<td>-1/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>⟩</td>
<td>Ω_{g_z} H_z - 4 \sqrt{2/3} B_{20}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⟨-3/2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3/2</td>
<td></td>
</tr>
<tr>
<td>⟩</td>
<td>Ω_{g_z} H_z - \sqrt{2/3} B_{20}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⟨-5/2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-5/2</td>
</tr>
<tr>
<td>⟩</td>
<td>Ω_{g_z} H_z + 5 \sqrt{2/3} B_{20}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table III.2. Matrix of the spin Hamiltonian in the S=5/2 manifold. Where the magnetic field is in the z-direction.
the components of the effective spin operator which has an effective eigenvalue of \(\frac{4}{3}\) and \(G^i_\alpha\) are the anisotropic \(g\)-factors of the \(i\)-th doublet. They are given by:

\[
G^i_z = \langle a^i_1 \rangle^2 - 3\langle a^i_2 \rangle^2 + 5\langle a^i_3 \rangle^2
\]

\[
G^i_{x,y} = \pm 2\langle a^i_1 \rangle^2 + 4\langle a^i_1 a^i_2 \rangle \pm 2\langle a^i_2 a^i_3 \rangle
\]

(12)

(13)

When the second-order crystal field parameters are related by:

\[
\frac{B_{20}}{B_{22}} = \frac{1}{\sqrt{3}} = 0.408
\]

which is called an "extreme orthorhombic" case, then the middle doublet \((i = 2)\) has an isotropic \(g\)-factor given by:

\[
G^2_x = G^2_y = G^2_z = 2.143
\]

(15)

and the total \(g\)-factor is \(2 \times 2.143 \approx 4.3\). The remaining doublets, \(i = 1\) and \(3\), have either a very small intensity or are located at very large \((g_i G_i \langle 1 \rangle)\) or very small \((g_i G_i \langle 2 \rangle)\) magnetic fields and are not detected under normal conditions.

G. Estimation of \(B_{20}\) and \(B_{22}\) of Fe+3

The combined spin Hamiltonian is represented by the Zeeman term (equ.(4)) and crystal field interaction (equ.(6)). The matrix formed by the Hamiltonian is shown in Table III.2 with the magnetic field along the \(z\)-direction.

The second-order crystal field parameters \((B_{20} AND B_{22})\) are estimated by diagonalizing the matrix of Table III.2 using perturbation theory. Assuming the Zeeman interaction is larger than the crystal field interaction. The selection
rule being $4 M_s = \pm 1$, the transitions for the $z$-direction are

$$H_{+5/2 \rightarrow 3/2} = H_z + \frac{6 \sqrt{2}}{3} B_{20} - \frac{8}{2 H_z + 9 \sqrt{2}} B_{22}$$

taking $H_z \gg B_{20}$, we have

$$H_{+5/2 \rightarrow 3/2} = H_z + \frac{6 \sqrt{2}}{3} B_{20} - \frac{4}{H_z} (B_{22})^2$$ (15)

similarly the following transitions are found

$$H_{+3/2 \rightarrow 1/2} = H_z + \frac{3 \sqrt{2}}{3} B_{20} + \frac{5}{H_z} (B_{22})^2$$ (16)

$$H_{+1/2 \rightarrow 1/2} = H_z + \frac{6 \sqrt{2}}{3} B_{20} - \frac{4}{H_z} (B_{22})^2$$ (17)

$$H_{-3/2 \rightarrow 1/2} = H_z - \frac{3 \sqrt{2}}{3} B_{20} + \frac{5}{H_z} (B_{22})^2$$ (18)

$$H_{-5/2 \rightarrow 3/2} = H_z - \frac{6 \sqrt{2}}{3} B_{20} - \frac{4}{H_z} (B_{22})^2$$ (19)

where $H_z$ is the magnetic field in gauss of the particular resonance of the corresponding transition. The coefficients $B_{20}$ and $B_{22}$ are in units of electron gauss. Equations 15-19 can be applied to the other two axes, by applying the appropriate rotation group (Tinkam 1964) on the crystal field Hamiltonian (eqn. (16)), to obtain the equivalents for $B_{20}$ and $B_{22}$. These are listed in Table III.3.
Table III.3. Relationship between the parameters of the crystal field Hamiltonian for different orientations of the magnetic field $H$.

<table>
<thead>
<tr>
<th>$H \parallel Z$</th>
<th>$H \parallel X$</th>
<th>$H \parallel Y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{20}$</td>
<td>$-\frac{1}{2} B_{20} + \frac{1}{16} B_{22}$</td>
<td>$-\frac{1}{2} B_{20} - \frac{1}{16} B_{22}$</td>
</tr>
<tr>
<td>$B_{22}$</td>
<td>$\frac{1}{16} B_{20} + \frac{1}{2} B_{22}$</td>
<td>$\frac{1}{16} B_{20} - \frac{1}{2} B_{22}$</td>
</tr>
</tbody>
</table>
CHAPTER IV

INSTRUMENTATION

A. K-Band Spectrometer

The EPR spectrometer used was of balanced bridge design. The microwave frequency was stabilized against the sample cavity. A block diagram of the spectrometer is shown in Fig. IV.1. The microwave generator was a reflex klystron (Varian, type VA-98e) producing thirty milliwatts of power. The external magnetic field was produced by a twelve inch Varian electromagnet with rotating base. It was possible to obtain a linear field sweep of up to fifteen kilogauss.

A Teltronic model KSLP was used to stabilize the klystron against the cavity resonant frequency. Microwaves are prevented from re-entering the klystron by an isolater which is a microwave ferrite device which makes use of the Faraday effect to permit the transmission of microwaves in one direction, and prevents their transmission in the opposite direction.

The microwaves continue to a three port circulator which allows transmission of the klystron power from one terminal to the next in sequence. At resonance the power reflected from the cavity which appears as a 100 KHz amplitude modulated signal with appropriate phase travels to the detector arm. The circulator prevents the klystron power going directly to the detector arm or any reflected power returning to the klystron arm. The signal is then transmitted to a
Fig. IV.1. Block diagram of K-band spectrometer.
100 KHz amplifier via two diodes on each side of the detector or waveguide. The resonant signal is then preamplified. The preamplification simply amplifies the incident signal without adding significant noise to the existing noise which usually accompanies the signal. This signal is then fed into the Princeton Applied Research (PAR) model HR-8 lock-in Amplifier. The PAR only passes signals which have the proper frequency and arrives in phase with the reference 100 KHz modulation signal. This results in a derivative signal proportional to the resonant signal. This signal can be displayed on the oscilloscope or x-y plotter as a function of the magnetic field. For oscilloscope display the magnetic field is modulated at 60 Hz. The horizontal input is connected to a 60 Hz source and a phase shifter. The method of oscilloscope display allows for the observation of the EPR signals when both the directions of the magnetic field and the crystal orientation are varied. This allows for the direct and rapid observation of the angular variation of the EPR lines.

B. X-Band Spectrometer

The spectrometer was of a balanced bridge design with the microwave frequency stabilized against the sample cavity. This spectrometer operated similarly to the K-band spectrometer just previously discussed. Where the magnetic field was modulated at 100 KHz. In this case the modulation
Fig. IV.2. Block diagram of X-band spectrometer.
was applied in the cavity to a single loop of copper wire. The EPR signals were observed in the same fashion as that of the K-band spectra. A block diagram of the X-band spectrometer is shown in Fig. IV.2.

C. K-Band Cavities

Two different cavity arrangements were used at K-band. Both arrangements were used at room and liquid nitrogen temperatures. The difference between the two is that a heater arrangement is employed, where the temperature can be varied from liquid nitrogen temperature to room temperature. This is done very easily by the use of the PDP11-03 computer which is interfaced to a Hewlett-Packard 3478A multimeter for the purpose of the computer to read the thermocouple equivalent temperature. Both arrangements of Fig. IV.3 make use of the same cavity which is cylindrical, operating in the TE_{011} mode. The cavity(b) is lined with silver and gold which is sputtered onto the silver base surface. Microwave power was fed into the cavity through a circular iris(a) located at one end of the cylinder. The cavity system of Fig. IV.3.d allows the crystal to move about a horizontal axis by means of a worm gear arrangement. Plus having the freedom of the magnet base moving about a vertical axis, it is therefore possible to obtain the spectral axes without having to physically disturb the sample.

Fig. IV.3.c shows the cavity system in which the sample is placed on a vertical copper pin which is insulated from
Fig. IV.3. K-band cavity system with c) vertical crystal mount and d) horizontal crystal mount.
the base of the cavity. A thermocouple wire is glued to the side of the pin originating from the base of the cavity. The tip is then attached to the sample by epoxy glue. This arrangement has only the freedom of working in one crystal plane.

D. X-Band Cavities

The X-band cavity was cylindrical and also operated in the TE₀₁₁ mode. This system is similar to that of the cavity in Fig. IV.3.c. The only difference between the two systems is the 100 KHz modulation coil inside the cavity. This is illustrated in Fig. IV.4.c.

E. The Proton Magnetometer

The data was obtained from K-band at liquid nitrogen and room temperature and that of X-band only at liquid nitrogen. We used proton resonance to obtain the magnetic field at which the EPR transitions occurred. These measurements were done by means of a proton magnetic resonance oscillator, tuning circuit and amplifier, including a wide band amplifier and frequency counter. The proton source used was rubber which was then fashioned into probes in the laboratory to cover a wide frequency range. Several probes were constructed to obtain the data at X and K band.

(I) Measurement of Magnetic Field

To obtain a measurement, in conjunction with the x-y plotter, the magnetic field was increased manually and then stopped where the plotter pen indicated the center of the
Fig. IV.4. X-band cavity system with vertical crystal mount.
line to be measured. The frequency of the proton oscillator was varied until the proton resonance signal was observed on the oscilloscope. The frequency of oscillation of the probe is directly measured by an electronic frequency counter. This can be converted to a magnetic field strength using the relation:

\[ H(\text{gauss}) = 234.869 \nu(\text{MHz}). \]

(II) Microwave Frequency Measurement

The microwave frequency can be measured by using a small amount of DPPH (diphenyl picryl hydrazyl) as a reference marker. The DPPH is placed on the crystal in the cavity and its single line is recorded with the EPR lines arising from the crystal. The microwave frequency can be found knowing the magnetic field of the DPPH resonance and using the formula

\[ h\nu = g_D^* H_D. \]

Where \( h \) is Planck's constant \((6.62620 \times 10^{-34} \text{ J-sec})\), \( \nu \) is the required microwave frequency, \( g_D \) is 2.0036 for DPPH, \( g \) is the Bohr magneton \((9.2741 \times 10^{-24} \text{ J T}^{-1})\), and \( H_D \) is the resonant magnetic field of the DPPH.

F. Temperature Controller

The temperature controller is used to adjust and maintain the heating and cooling of a crystal sample originally cooled to liquid nitrogen. A block diagram of this arrangement is shown in Fig. IV.5. It was used in conjunction with the cavity setup of Fig. IV.3.c.
Fig. IV.5. Block diagram of Temperature Controller setup.
The setup of Fig. IV.5 makes use of a number of instruments. Starting at the point where the temperature is being monitored via a Cu-Co thermocouple. The thermocouple voltage enters a digital voltmeter (D.V.M.) model HP 3478A which converts the millivolt reading into a string of ASCII digits. The string is then transmitted to the PDP11/83 minicomputer via an IEEE-488 general purpose instrument bus (G.P.I.B) line. The PDP11 converts the string into binary form, then calculates the appropriate output voltage given the destination temperature. The output voltage then leaves the computer by a programmable D/A (digital to analog) converter. This voltage is then isolated from the computer by the use of a 1:1 "voltage amplifier" where upon via a variable programmable power supply (Lambda KK345A) a voltage related to the destination temperature is applied to the heating coils. The programme written to control the setup of Fig. IV.5 is shown in Appendix 2.
CHAPTER V
EXPERIMENTAL PROCEDURE AND RESULTS

A. Fe$^{3+}$ In Lithium Potassium Sulphate (LPS)

The EPR spectrum of Fe$^{3+}$ were studied as functions of temperature and crystal orientation at room temperature (RT) and liquid nitrogen (LN) at K- and X-band frequencies. The spectrometer systems of Fig. IV.1 and Fig. IV.2 and the cavity systems of Fig. IV.3 and Fig. IV.4 were used at these frequencies.

A spectrum obtained at K-band frequencies at RT showed only a set of lines lying in a narrow band of frequencies on both sides of the DPPH marker in the ab-plane. Along the c-axis, the spectrum consisted of a group of lines lying very close to the DPPH marker, four of which can be assigned to the Fe$^{3+}$ ion. They were characterized by six-fold degeneracy. This clearly indicates that the c-axis is a principal spectral axis. We designate this spectrum as I(Fe) (or simply as I). I at K-band is shown in Fig. V.1, where Table V.1 gives the magnetic field values of the four lines measured by proton resonance.

(I) Temperature variation of I at X-band. The LPS:Fe$^{3+}$ sample was first cooled to LN and allowed to warm up naturally. Recordings were taken at selected temperatures with an error of ± 3 degrees C. Fig. V.2 shows the entire spectrum, at X-band, along the c-axis as a function of temperature. I makes its appearance at -90 °C as a very
Fig. V.1. The EPR spectrum at K-band of Fe$^{3+}$ in LPS along the c-axis. DPPH is a standard marker with $g = 2.0036$. The values of $H$ are given in Table V.1.
Fig. V.2. Temperature variation of the EPR spectrum of Fe$^{3+}$ in LPS along the c-axis at X-band.
broad resonance which becomes narrower and more intense as the temperature is increased. At RT it consists of two peaks (designated as $I_1$ and $I_2$) which are the most prominent feature at this temperature. The LN spectrum consisting of peaks II and III at $138^\circ C$, is the most prominent feature at this temperature. Its frequency changes relatively little but its intensity decreases and at RT it is very small.

Table V.1. Resonant fields of Fe$^{3+}$ EPR lines in LPS along the c-axis.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Field (KG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_1$</td>
<td>7.598</td>
</tr>
<tr>
<td>$H_2$</td>
<td>8.537</td>
</tr>
<tr>
<td>$H_3$</td>
<td>8.616</td>
</tr>
<tr>
<td>$H_4$</td>
<td>8.946</td>
</tr>
</tbody>
</table>

(II) Estimation of $B_{20}$ and $B_{22}$. The spectrum I was analyzed using equ.'s (4) and (6) which combine to become our spin Hamiltonian. The information contained in spectrum I (at X- and K-band) along the c-axis, which corresponds to the spectral X-axis, is sufficient to determine the second-order crystal field parameters $B_{20}$ and $B_{22}$. The Z-axis, which is usually defined as the largest splitting between the outer
satellites resulting from the transitions between the levels \( \pm 5/2 \leftrightarrow \pm 3/2 \), lies in the ab plane and at 18 degrees from the a-axis. Fig. V.3 is offered as a help to visualize this orientation in the unit cell at the K\(^+\) site. The fact that the z-axis points towards one of the oxygens nearest the K\(^+\) ion is offered as corroborating the claim that the Fe\(^{3+}\) ion occupies this site.

The values of the parameters \( B_{20} \) and \( B_{22} \) were found using the values of resonances \( H_2, H_3 \) and \( H_4 \) from Table V.1 and equ.'s (16)-(18). Solving for \( B_{20} \) and \( B_{22} \), these values are summarized in Table V.2 for spectrum I.

Table V.2. Parameters of the EPR of Fe\(^{3+}\) in LPS.

<table>
<thead>
<tr>
<th>Spectra (Temperature)</th>
<th>Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( B_{20} = 0.513 \pm 0.05 \text{ KG} )</td>
</tr>
<tr>
<td>I (20(^\circ))</td>
<td>( B_{22} = 0.059 \pm 0.05 \text{ KG} )</td>
</tr>
<tr>
<td></td>
<td>( (gG)_x ) 3.90 3.53 4.80 0.390</td>
</tr>
<tr>
<td></td>
<td>( (gG)_y ) ( (gG)_z ) ( \eta^{**} )</td>
</tr>
<tr>
<td>II (-195(^\circ))</td>
<td>( (gG)_x ) 3.90 3.53 4.80 0.390</td>
</tr>
<tr>
<td></td>
<td>( (gG)_y ) ( (gG)_z ) ( \eta^{**} )</td>
</tr>
<tr>
<td>III (-195(^\circ))</td>
<td>( (gG)_x ) 4.20 4.01 4.35 0.509</td>
</tr>
<tr>
<td></td>
<td>( (gG)_y ) ( (gG)_z ) ( \eta^{**} )</td>
</tr>
</tbody>
</table>

* Measured from the a-axis in the ab-plane.

** Defined as \( \frac{1}{2} B_{22}/B_{20} \).
Fig. V.3. Unit cell of LPS. Li⁺ (not shown) is above (or below) O₄ at .315. $\Theta_{I,II} = 10^\circ$ denotes the Z-axis of I(Fe) or II(Fe). $\Phi_{I} = 15^\circ$ denotes the Z-axis of I(Cr).
We did not attempt to estimate the other spin Hamiltonian parameters since there are insufficient data.

(III) Estimation of \( \eta \) at LN. The LN spectrum at X-band is shown in Fig. V.4. The recording trace (a) was taken along the \( a \)-axis. It is seen to contain a group of lines at the low-field end of the spectrum. Fig. V.4.b shows the latter lines expanded and in the range of 60 degrees of the ab-plane. This spectrum also has the characteristic of having a 60 degree period shown in spectrum I. For the purpose of analysis the spectrum is broken up into two: one is designated as II(Fe) (or as II). It consists of six lines and they are joined by dashed lines. The second spectrum designated as III(Fe) (or simply as III) also consists of six lines although all lines are bunched more closely together.

To unravel the spectrum we invoke the fact that when the crystal-field is much larger than the Zeeman term, we can regard the three doublets resulting from the action of crystal-field on the \( S = 5/2 \) term as isolated but having very anisotropic g-factors. Fig V.5 are the \( g_{\alpha}^{\perp} \) vs. \( \eta \) curves calculated from eqns. (12) and (13) of Chapter III. Shown on Fig. V.5 are the measured g-factors of spectrum II represented by circles and III represented by triangles. Thus the values of \( \eta \) were found for spectra II and III by reading them off Fig V.5. The above data is summarized in
Fig. V.4. EPR spectrum of Fe$^{+3}$ at X-band at LN. $0^\circ$ corresponds to a-axis. Symbols A and B in (a) and (b) designate identical peaks.
Fig. U.5. A plot of the \( x \), \( y \), and \( z \) components of the effective \( g^i \) tensor as functions of \( \eta \). These curves have been calculated assuming \( g_\alpha = 2 \).
Table V.2.

(IV) Powder EPR spectrum of Fe$^{+3}$. Refer to procedure afore
mentioned in section A.(I). Fig. V.6 shows the EPR of
LPS:Fe$^{+3}$ as a powder at selected temperatures. The spectrum
is dominated by a prominent group of resonances near \( g_G = 4.3 \). It is present at all temperatures in the range \( RT < \) \( LN \).

B. Cr$^{+3}$ In LPS

The EPR spectra of Cr$^{+3}$ were studied as functions of
temperature and crystal orientation at K- and X-band
frequencies. The K-band spectrum was easier to sort out than
the X-band.

(I) Determination of the magnetic axes. We define the
spectral Z-axis as the axis along which the spread of the
\( (\pm 3/2) \leftrightarrow (\pm 1/2) \) pair of resonances are the greatest. This
was done by observing the outer satellite on the scope. Then
rotating magnet and crystal sample until a turning point was
observed. Thus representing the greatest spread. The Y-axis
is the axis being in the plane normal to the Z-axis, and
having the greatest spread of the \( (\pm 3/2) \leftrightarrow (\pm 1/2) \) pair of
resonances in this plane. The remaining X-axis is then
fixed.

(II) LN spectrum. The most prominent spectrum consisted of
three sets which are designated as II$_1^i$ (or II$_1^i$(Cr)), \( i = 1-3 \). The outer satellites which result from the \( m_s = \pm 3/2 \) \( \leftrightarrow \)
\( m_s = \pm 1/2 \) transitions of the \( S = 3/2 \) state were analyzed
Fig. V.6. EPR spectrum at X-band of Fe\(^{3+}\) in powdered LPS.
carefully in the three principal crystallographic planes. This set was found to have an approximate 60 degree period. (But we observed other, smaller, resonances which were not related to one another by the 60 degree period.) This investigation led to the conclusion that the three crystal axis a, b, and c coincide with the spectral Z, Y, and X axes respectively. A plot of one of the sets II in the ab-plane is presented in Fig. V.7 as points.

Table V.3. Resonant fields of Cr$^{3+}$ EPR lines along the spectral axes. Both experimental and calculated values are listed in KGauss.

<table>
<thead>
<tr>
<th>Transition</th>
<th>LN Exper.</th>
<th>LN Calc.</th>
<th>RT Exper.</th>
<th>RT Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1/2→1/2</td>
<td>10.521</td>
<td>10.494</td>
<td>11.735</td>
<td>11.749</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>Y +1/2→1/2</td>
<td>7.348</td>
<td>7.349</td>
</tr>
<tr>
<td>-1/2→3/2</td>
<td>10.354</td>
<td>10.349</td>
<td>8.999</td>
<td>8.999</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>X +1/2→1/2</td>
<td>7.416</td>
<td>7.449</td>
</tr>
<tr>
<td>-1/2→3/2</td>
<td>8.756</td>
<td></td>
<td>8.684</td>
<td></td>
</tr>
</tbody>
</table>

****** not measurable
Fig. V.7. A plot of EPR resonances at K-band of Cr$^{+3}$ in LPS at LH. Points denote experimental values; continuous curves are calculated, using the parameters in Table V.4.
The other members of the set II were omitted from Fig. V.7 for clarity. The magnetic field values of each of the resonances along the three crystal axes were measured by proton resonance and are listed in Table V.3.

(i) Calculation of spin Hamiltonian parameters for Cr$^{3+}$ in LPS. The experimental points were fitted to the parameters of equ. (7) by the least-squares method and the Newton-Raphson procedure (Fox, Holuj, and Baylis 1972). The programme is listed in Appendix I. Table V.4 gives the results of the parameters obtained from II. Fig. V.7 shows also the predicted resonances as continuous curves which were obtained from the parameters in Table V.4. The values of the energy levels were also calculated at small intervals of magnetic field and were plotted for the three spectral axes as shown in Fig. 's V.8, V.9, and V.10.

Table V.4. Spin-Hamiltonian parameters of the EPR spectrum of Cr$^{3+}$ in LPS.

<table>
<thead>
<tr>
<th>Spectra (Temperature)</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
<th>$B_{20}$</th>
<th>$B_{22}$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (RT)*</td>
<td>1.9975</td>
<td>1.9719</td>
<td>1.9751</td>
<td>1.272</td>
<td>0.434</td>
<td>0.293</td>
</tr>
<tr>
<td></td>
<td>± 0.014 ± 0.009 ± 0.011 ± 0.018 ± 0.013</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II (LN)</td>
<td>1.9739</td>
<td>1.9663</td>
<td>1.9794</td>
<td>1.263</td>
<td>0.021</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td>± 0.002 ± 0.001 ± 0.001 ± 0.002 ± 0.002</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Z-axis AT $\phi_1 = 15^\circ$ from a-axis (Fig. V.3).
Fig. V.9. Energy level diagram of Cr-3 with the magnetic field along the z-axis at liquid nitrogen temperature. The vertical solid lines indicate the allowed transitions.
Fig. U.P. Energy level diagram of Cr+3 with the magnetic field along the y-axis at liquid nitrogen temperature. The vertical solid lines indicate the allowed transitions.
Fig. V.10. Energy level diagram of Cr+3 with the magnetic field along the x-axis at liquid nitrogen temperature. The vertical solid lines indicate the allowed transitions.
(III) RT Spectrum of Cr$^{3+}$. The last trace of Fig V.11 was taken at RT. It typifies the problem which this spectrum presented in the investigation: low intensity and a lack of a rigorous 60 degree periodicity. Of the expected three members of this set, only two were intense enough to be analyzed numerically.

Fig. V.12 shows the experimental resonances as points and the predicted resonances as continuous curves. We have included all three members of the set I in Fig. V.12 to emphasize the break-down of crystallographic symmetry. Thus we note that the Z-axis of one member of the set I is approximately reflected about the a-axis as the Y-axis of another member. A similar statement applies to the b-axis. We could not confirm experimentally whether the X-axis of the set I coincide rigorously with the pseudohexagonal c-axis because the satellite signals of the set I fall in the region close to the DPPH marker (i.e., almost free electron) and this region, it should be remembered, contains a large number of resonances of uncertain origin.

(i) Calculation of spin Hamiltonian parameters at RT. The parameters were found using equ. (7). Table V.4 contains the results. The procedure used to obtain these results are the same as was followed in the LN investigation of II. The values of the energy levels were also calculated at small intervals of magnetic field and were plotted for the three spectral axes as shown in Fig.'s V.13, V.14, and V.15.
Fig. V.11. Temperature variation of a portion of Cr$^{+3}$ spectrum at K-band in LPS.
Fig. V.12. A plot of EPR resonances at K-band of Cr$^{+3}$ at RT. See Fig. V.7 for explanation. A complete set of three is plotted to illustrate its relation to the crystallographic a- and b-axis.
(ii) Temperature variation study. The use of the temperature control setup of Fig. IV.5 was used to obtain the following results. The temperature of the LPS:Cr$^{+3}$ sample can be stabilized to within ±1°C for long periods of time. Fig. V.11 shows the EPR spectrum at K-band at selected temperatures along the b-axis which is the Y-axis of II. The low-field satellites of II are indicated as $II_{1,2,3}$. The RT spectrum contains the resonances $I_{1,2,3}$. The spectra in V.11 follow a pattern similar to that in Fig. V.2: The spectrum II persists to about -50°C but in contrast to II(Fe) and III(Fe), it is not detectable at RT.
Fig. V.13. Energy level diagram of Cr⁺³ with the magnetic field along the $z$-axis at room temperature. The vertical solid lines indicate the allowed transitions.
Fig. V.14. Energy level diagram of Cr+3 with the magnetic field along the y-axis at room temperature. The vertical solid lines indicate the allowed transitions.
Fig. V.15. Energy level diagram of Cr+3 with the magnetic field along the x-axis at room temperature. The vertical solid lines indicate the allowed transitions.
CHAPTER VI
DISCUSSION AND CONCLUSIONS

A. Discussion

The effects of the charge compensation are very different in the two cases. The Cr$^{+3}$ compensator is definitely non-local. This is because there are only three sets of spectra and not six as in the case of Fe$^{+3}$. It can therefore be surmised that the Cr$^{+3}$ EPR spectra more closely reflect its undisturbed environment. Unfortunately at RT they turned out to be of poor quality chiefly due to their low intensity and due to the distortion of their line-shape. Furthermore, the latter were too weak to be analyzed in any detail. Nevertheless, the spectrum obtained at LN reflects the pseudo-hexagonal symmetry of LPS since the $60^\circ$ periodicity is maintained and the spectrum is symmetrical about the $a$- and the $b$-axis. The RT spectrum suggests that the site which Cr$^{+3}$ occupies is very distorted in two ways: the first is the apparent lack of its correlation to the point-group of the unit cell, and the second is the very low intensity of one of the components of the set I(Cr). The second effect may be due to the ferroelastic domain structure, but this remains puzzling since an examination of the spectrum under stress produced no visible change in the spectra of both ions. As to the first distortion, we must rule out the misalignment of the sample for the simple reason that the effect is just too large. We also rule out a possibility
that this is due to the twinning of the sample because similar spectra were obtained from several samples. We note, however, that the set I(Cr) is symmetric about a direction in the ab-plane at 45° to the original axes.

Fe³⁺, in contrast, occupies the site in close proximity to its charge compensator. Hence we can surmise that its environment will be distorted. Indeed, the fact that the six members of the sets I(Fe), II(Fe) and III(Fe) exist (and not three as in the case of the Cr³⁺ spectra) is a reflection of this fact. We do not know the identity of this compensator. We note, however, that the EPR of x-rayed sulphates often contains an intense resonance which is usually ascribed to $SO_3^-$ radical. This center would offer a charge compensation we are discussing. However, we must leave this as an open question. The spectra II(Fe) and III(Fe) shown in Fig. V.2 are apparently uncorrelated with one another but seem to give rise to the common RT spectrum I(Fe). One wonders if this fact might be the result of "freezing" of the oxygen $O_4$ alluded to in the Introduction: II(Fe) and III(Fe) originate from the "frozen" units of the $SO_4$ tetrahedra which coexist at LT, while I(Fe) results from the dynamic random disorder in the distribution of the positions of the $O_4$ in the HT phase (Tomaszewski et al, 1983).

EPR spectrum of powders containing ions with $S=1/2$ have peaks at magnetic fields corresponding to the principal
components of the g-factors (Dowsing and Ingram, 1969, and others quoted therein). Additionally, if a paramagnetic ion with \( S=5/2 \) (such as Fe\(^{3+} \)) is incorporated in a glassy substance, there results an intense resonance at \( g = 4.3 \) (Castner, Newell, Holton and Slichter, 1960; Aasa, 1979). The peaks 1-5 in Fig. V.6 correspond to g-factors listed in Table VI.1 and they fall approximately at the \((gG)\)-values of spectra II(Fe) and III(Fe).

Table VI.1. \((gG)_{\alpha,i}\)-Values and magnetic fields of resonances at \( T = -195^\circ C \) (shown in Fig. V.6)

<table>
<thead>
<tr>
<th>Peak</th>
<th>(H(KG))</th>
<th>(\alpha,i)</th>
<th>((gG))-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.83</td>
<td>(y,\text{II})</td>
<td>3.61</td>
</tr>
<tr>
<td>2</td>
<td>1.69</td>
<td>(x,\text{II})</td>
<td>3.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(y,\text{III})</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.57</td>
<td>(x,\text{III})</td>
<td>4.20</td>
</tr>
<tr>
<td>4</td>
<td>1.53</td>
<td>(z,\text{III})</td>
<td>4.31</td>
</tr>
<tr>
<td>5</td>
<td>1.39</td>
<td>(y,\text{II})</td>
<td>4.75</td>
</tr>
</tbody>
</table>

The "glassy" peak at 4.3, however, exceeds the intensity expected of the \((gG)_{z,\text{III}}\)-peak by about 15-20\% at LN and by smaller percentages at higher temperatures. This result can be interpreted that the environment of the Fe\(^{3+}\) ion has a
noticeable random distribution of crystalline field having a mean value centered at the "extreme" orthorhombic symmetry. We note, finally, that the powder samples containing Cr$^3^+$ ion did not reproduce these results, no doubt due to their EPR spectra being much less intense.

8. Conclusions

In this investigation it was possible to obtain and interpret the EPR spectrum of Fe$^3^+$ and Cr$^3^+$ in LPS at X- and K-band frequencies at both LN and RT.

The spectrum of Fe$^3^+$ at X- and K-band were used to obtain the values of $B_{20}$ and $B_{22}$ the second-order crystal field parameters at RT and $\eta (= \frac{12B_{22}}{B_{20}})$ at LN. These results are listed in Table V.2. The spectrum in the ab-plane at X-band was just too complicated. Because the crystal field parameters are of the same order of magnitude as the Zeeman term, we expect that the spin energy levels cross one another frequently. This hindered the interpretation of the spectrum greatly. The powder spectrum of LPS:Fe$^3^+$ showed a prominent group of resonances near $(gG)=4.3$. It is present at all temperatures in the range $(RT)-(LN)$.

The spectrum of Cr$^3^+$ at K-band at both LN and RT were fitted to the spin Hamiltonian of equ. 7. The results are listed in Table V.4. The data at X-band showed no new information since at both X- and K-band frequencies, the transitions fall in the linear regions of the energy levels.
APPENDIX 1

The following programme fits the spin Hamiltonian parameters of eqn. III.7 for G=3 in LPS to the experimental data, using the least squares method and the Newton-Raphson procedure.

```
IMPLICIT REAL*(4,8)
COMPLEX*16
DIMENSION A(21,12),B(21,12),D(21,12),E(21,12),F(21,12),G(21,12),H(21,12),
-J(21,12),K(21,12),L(21,12),M(21,12),N(21,12),O(21,12),P(21,12),Q(21,12),
-R(21,12),S(21,12),T(21,12),U(21,12),V(21,12),W(21,12),X(21,12),Y(21,12),
-Z(21,12)

INPUT FORMAT STATEMENTS

188 FORMAT(212,F6.1)
182 FORMAT(12,F5.1,12,7A8,2A8)
184 FORMAT(16F5.1)
183 FORMAT(8F10.7/2F10.7)
186 FORMAT(8F10.7)
187 FORMAT(5F10.7)
188 FORMAT(5F10.7)

OUTPUT FORMAT STATEMENTS

156 FORMAT(1H1,7G10.2)
154 FORMAT('NUMBER OF ORIENTATIONS=',12,SX,'NUMBER OF ITERATIONS'
154 FORMAT('SIZE OF MATRIX=',12,SX,'SPIN VALUE=',F6.1,'NUMBER'
10F PARAMETERS=',12)
156 FORMAT('DPH PH N2D=',12,F9.4)
150 FORMAT('THETA=',2X,12(F7.1,2X))
158 FORMAT('PHI',':',2X,12(F7.1,2X))
164 FORMAT('SPECTRA(MHZ) XXX')
164 FORMAT('SPECTRA(XXX) XXX')
166 FORMAT('POLE FACE CORRECTION=',F9.4,'GAUSS',',H2=',F8.6,'FREE ELECTRON G VALU'
166 FORMAT('SPECTRA(XXX) XXX')
168 FORMAT('ITERATION #',12//)
178 FORMAT(1X,12,F8.6)
172 FORMAT(1X,12,F8.6)
174 FORMAT(1X,12,F8.6)
176 FORMAT(1X,12,F8.6)
180 FORMAT('PREDICTED DISPLACEMENTS=',12,F8.6)
```

58
Following READ statements initializes the program where:

- LM : The number of orientations
- ITH : The number of iterations
- TEMP : Temperature data was taken from
- N : Size of the matrix
- SPIN : Effective spin of the impurity
- I=3,1,9
- IMAK : Number of parameters to be fitted
- HEADER : Heading line
- HIGNO : Field of the experimental resonance in MHz
- HDP : Field of DPPH in MHz
- THETA : θ in right-handed coordinate system
- PHI : θ
- PG : Proton MHz to gauss conversion = 234.869
- GDP : DPPH g-value = 2.0836
- GFE : Free electron g-value = 2.8829
- P(I) : The initial guess for parameters

READ 188,LM,ITH,TEMP
READ 182,N,SPIN,IMAX,HEADER,GNAME
IH=L(IM-I)
DO 299 I=1,LM
ML=(L-1)*3+1
IH=L33
299 READ 186,((HIGNO,HH=LM,ND,HDP(I),THETA(I),PHI(I))
READ 188,PGH,GDP,GFE
READ 183,(P(I)),I=1,IMAX
CALL DATE (IT,MO,ID)
923 FORMAT(IHX, 'RUN ON ' ,AS,13,15/)

Initialization of the equivalent spin angular momentum operators

T18(1)=1.5D0
T18(2)=.5D0
T18(3)=-.5D0
T10(4)=-1.500
T20(1)=1.22474500
T20(2)=-T20(1)
T20(3)=-T20(1)
T20(4)=T20(1)
T22(1)=1.73205100
T22(2)=1.73205100
T11(1)=-1.22474500
T11(2)=-1.41421400
T11(3)=T11(1)

C Print input data.

PRINT 150, HEADER, GNAME
PRINT 923, MD, ID, IY.
PRINT 152, LM, ITM, TEMP
PRINT 155, N, SPIN, IMAX
PRINT 156, (HDP(L), L=1, LM)
PRINT 158, (THETA(L), L=1, LM)
PRINT 160, (PHI(L), L=1, LM)
PRINT 162,
DO 290 J=1, 3
290 PRINT 164, (HB(INDEO, INDEX=-J, N, M, D)
PRINT 166, PHIM, GDP, GFE
DO2=DOSRT(2, 2)
IMAX2=IMAX1*IMAX
NN=(N+1)*RV2

C Convert field values into gauss

GDP=CA*PHIM
DO 292 L=1, LM
HDP(L)=HDP(L)*PHIM
HD(L)=HDP(L)
LIND=L+1
LIND2=LIND-(N-2)
DO 292 INDEX=LIND, LIND
HB(INDEO)=HB(INDEO)*PHIM
292 CONTINUE

C Iterations loop starts here

DO 294 IT=1, ITM
NL=0

C Initialization of arrays to zero

XLSF=0.08
DO 296 J=1, IMAX2
296 DO2F(J)=0.08
DO 298 L=1, IMAX

288 DIF(1)=0.D0
289 DO 210 IAB=1,NN
290 DO 212 I=1,IMAX
291 212 DH(IAB,1)=ZERO
292 A(IAB)=0.D0
293 B(IAB)=0.D0
294 PRINT 168,IT
295 PRINT 923, MO, ID, IY
296 PRINT 170
297 -PRINT 172,(P(I),I=1,IMAX)

C Setting up field independent components of the matrix elements
C of H(IAB) and field independent matrix elements of DH(IAB,)

IA=1
IB=2
DO 214 K=1,N
A(IAB)=T2B(0)*EP(4)
B(IAB)=T1B(0)*EP(3)
DH(IAB,4)=T2B(0)
IA=IA+1B
214 IB=IB+1
IB=4
IA=4
NX=N-2
DO 215 K=1,NX
A(IAB)=T22(0)*EP(5)
DH(IAB,5)=T22(0)
IA=IA+1B
215 IB=IB+1
IA=2
IB=3
NX=N-1
DO 216 K=1,NX
A(IAB)=P(1)*XT111(0)/DR2
B(IAB)=P(2)*XT111(0)/DR2
IA=IA+1B
216 IB=IB+1

C Calculate energy difference from experimental frequency
C Calculate components of field values

PRINT 176
PRINT 382
382 FORMAT(/, 'EIGENVALUES')
DO 222 L=1,LMX
F(L)=ADP(L)*3D0/GFE
THETAM=THETA(L) 1.8174533
PHIM=PHI(L) 1.8174533
SINTH=65IN(THETAM)
COSTH=65OS(THETAM)
SINPH=DSIN(PHIB0)
COSPH=DCOS(PHIB0)
X=COSPH*SINTH
Y=SINPH*SINTH
Z=COSTH
LIND=LI(N+1)
LIND=LIND+N+2
IF(IT=ITD) 481,481,481
481 PRINT 174,THETA(L),PHI(L)
481 DO 222 INDEX=LIM,LIND
IF(HX(INDEX),LE,8.8) GO TO 248
NL=NL+1
HX=HX(INDEX)X
HY=HX(INDEX)Y
HZ=HX(INDEX)Z
C Setting up field dependent matrix elements of H(IAB)

DO 229 IAB=1,NN
229 H(IAB)=ZERO
IAB=1
N0=N+1
DO 224 IB=2,N0
H(IAB)=A(IAB)+B(IAB)XHZ
224 IAB=IAB+IB
IAB=2
DO 226 IB=3,N0
H(IAB)=-A(IAB)XHK-IMAG(B(IAB)XHY)
226 IAB=IAB+IB
IAB=4
DO 229 IB=5,N0
H(IAB)=A(IAB)
229 IAB=IAB+IB
C Setting up field dependent matrix elements of DH(IAB,I)

IAB=1
IB=2
DO 232 K=1,N
DH(IAB,K)=T1(K)XHZ
IAB=IAB+IB
232 IB=IB+1
IAB=2
IB=3
KX=N-1
DO 234 K=1,NX
DH(IAB,D)=-T11(K)XHK/DR2
DH(IAB,D)=IMAGHYXT11(K)/DR2
IAB=IAB+IB
234 IB=IB+1
The following subroutine CEIGEN computes the eigenvalues and eigenvectors of the Hermitian matrix H(IAB) stored in upper triangular form where:

EVCT: is the unitary transformation which diagonalizes H

N: The size of matrix N x N

MV: Input code if 0 compute eigenvalues and eigenvectors
    1 compute eigenvalues only.

The eigenvalues are returned in the diagonal elements of H where the original elements have been destroyed.

MV=0
CALL CEIGEN (H,EVCT,N,MV)
IAB=1
J=2
DO 236 K=1,N
EN(K)=H(IAB)
IAB=IAB+J
236 J=J+1
IF(IT-IT0) 482,483,483
483 PRINT 383, (EN(IAB),IA=1,N)
383 FORMAT (SX,6F18.8)
482 H=FL(IP)
   CALL SEARCH(DLTA,INHI,INH0,EN,INV,5808.D0,NGQ)
   IF(NGQ.EQ.0)GOTO 1881
   DLTA=EN(INH0)-EN(INH0)-H
   IF(IT-IT0) 488,489,489
489 PRINT 384, INH0,INV,HBD(INDOE),DLTA
384 FORMAT (2I18,2F18.8)

C Transform DH(IAB,I) to new basis

LAMDA=1
DO 241 I=1,2
IAB=1
241 CALL STCM(DH(IAB,I),DHIAB,I),EVCT,N,LAMDA,INH0,INH0
LAMDA=0
DO 242 I=3,4
IAB=1
242 CALL STCM(DH(IAB,I),DHIAB,I),EVCT,N,LAMDA,INH0,INH0
LAMDA=2
I=5
IAB=1
CALL STCM(DH(IAB,I),DHIAB,I),EVCT,N,LAMDA,INH0,INH0
XLSF=XLSF+(DLTA+DELTA)
C Setting up DE(INDEX,I)

KWW=LOW
KHH=HIGH
KHO=(KWW+KHH)/2
KNO=KNGNK+KNO/2
DO 246 I=1,IMAX
   DE(I)=DHT(KWW,I)-DHT(KNO,I)
C
C SETTING UP DIF/DP(I)
C
   DIF(I)=DIF(I)+(2*DELTAXDE(I))
   CONTINUE
   CONTINUE

C Setting up D2E/DP(I)*DP(J)

   DO 258 I=1,IMAX
   DO 258 J=1,IMAX
   IF(HB(INDEX,I.E.8.0)) GO TO 222
   I=I+(J-1)*IMAX
   D2E=8.0D0
   DO 252 ID=1,N
   IF(ID.LT.KW0) GO TO 256
   IF(ID.EQ.KW0) GO TO 258
   KID=KW0*(ID-ID)/2
   DHTI=DCONJG(DHT(KID,I))
   DHTJ=DHT(KID,J)
   IF(ID.EQ.KNO) GO TO 260
   254 IF(ID.LT.KNO) GO TO 259
   KIDA=KW0+(ID-ID)/2
   DHTIA=DCONJG(DHT(KIDA,I))
   DHTJA=DHT(KIDA,J)
   GO TO 262
   256 KID=ID+(KNO-KW0)/2
   DHTI=DHT(KID,I)
   DHTJ=DCONJG(DHT(KID,J))
   KIDA=ID+KNGNK+KNO/2
   DHTIA=DHT(KIDA,I)
   DHTJA=DCONJG(DHT(KIDA,J))
   GO TO 262
   258 KIDA=ID+KNGNK+KNO/2
   DHTIA=DHT(KIDA,I)
   DHTJA=DCONJG(DHT(KIDA,J))
   D2E=D2E+2.0D0*H2IA*H2JA/(ENKNO-EN(ID))
   GO TO 252
   260 D2E=D2E-2.0D0*H2IA*H2JA/(ENKNO-EN(ID))
   GO TO 252
   259 KIDA=ID+KNGNK+KNO/2
   DHTIA=DHT(KIDA,I)
   DHTJA=DCONJG(DHT(KIDA,J))
262 D2E=D2E+2.*DHDXI*DHDXJ/(ENGX0-EN(I)) 2.*DHDXI*DHDXJ/1(ENGX0-EN(I))
252 CONTINUE
   D2F(I,J)=D2F(I,J)+(2.*DHDXI*DHDXJ*DE(J)+D2EDelta)
258 CONTINUE
222 CONTINUE
   NFREE=NL-IMAX
   XLSF=XLSF/NFREE
   DO 264 I=1,IMAX
       D1F(I)=D1F(I)/NFREE
   DO 264 J=1,IMAX
       IJ=I+(J-1)*IMAX
       D2F(I,J)=D2F(I,J)/NFREE
       D2FIN(I,J)=D2F(I,J)
264 CONTINUE
266 FORMAT (18G12.3)
   PRINT 266, (D2FIN(I,J),I,J=1,IMAX2)

C Calculate and print predicted displacements D(I)

484 CONTINUE
   CALL DMINV(D2FIN,IMAX,DETER)
   IF (DETER.EQ.0.) STOP
   DO 298 I=1,IMAX
   DO 298 J=1,IMAX
       IJ=I+(J-1)*IMAX
   298 D2FIN(I,J)=D2FIN(I,J)
   DO 266 I=1,IMAX
       J=1-IMAX
       D(I)=0.08
   DO 266 J=1,IMAX
       IJ=I+J*IMAX
   266 D(I)=D(I)-D2FIN(I,J)*D1F(J)
   PRINT 188
   PRINT 182,(D(I);I=1,IMAX)

C Calculate and print new values for parameters P(I)

268 P(I)=P(I)+D(I)
   PRINT 184
   PRINT 178
   PRINT 172,(P(I),I=1,IMAX)
   XLSHF=XLSF
   II=1-IMAX
   DO 278 I=2,IMAX
       II=(I+IMAX+1
   XLSHF=XLSHF+D1F(I)*D(I)+(D2F(I,J)*D(I)*D(I))/2.08
   JMIN=II+1
   IF(I.IE.IMAX) GO TO 270
   DO 272 J=JMIN,IMAX


LJ=II-I+J
XLSHED=XLShed+D2F(IJ)*LX(IJ)**2
272 CONTINUE
278 CONTINUE

C Check for convergence of P(I)
II=IIMAX
DO 274 I=1,IIMAX
II=II+IIMAX+1
IF (D2F(II).LT.8.D0) PRINT 188,I

C Calculate SIGMA(I)
274 SIGMA(I)=DSORT(DABS(D2FINV(IJ))XLSHED*2.D0/NFRED)
RMS=DSORT(XLSF)
RMSHE=DSORT(DABS(XLSHE))
PRINT 186
PRINT 172,(SIGMA(I),I=1,IIMAX)
PRINT 198,RMS,RMSHE,NL
284 CONTINUE
IF (NCORE) 188,189,188
1881 CONTINUE
END

SUBROUTINE STCM(AP,A,T,N,LAMBDAL,NHI,L0)
C Calculates similarity transform AP=HERMCONJG(T)XAXT of the
C complex matrix a of dimension N, where compact storage is
C used for A and AP.
COMPLEX (16) AP(2J),A(2J),L(36),ZERO,DCONJG
DATA ZERO/(6.D0,8.D0)/
DO 5 J=1,21
5 AP(I,J)=ZERO
LAM=览LAIFDA+1
N0=NJI-L0
DO 20 I=0,NHI,NK
DO 15 J=1,N
I=I+(J-1)/2
IF I.GT.J I=I+(I-1)/2
AP(I,J)=ZERO
DO 18 K=1,LAM,1
L=K-LAMDA
LX=L+(XX-KO)/2
LJ=L+(I-J)*N
KJ=K+(J-1)*N
KI=LI+K-L
LJ=KI+L-K
10 AP(I,J)=DCONJG(T(LI))X(A(LI)X(T(KJ)+T(LJ))XDCONJG(A(LI)X(T(KI)))*AP(I,J)
   IF(LST,J) AP(I,J)=DCONJG(AP(I,J))
   IF(LAMBD.A.EQ.0) AP(I,J)=AP(I,J)/2.0
15 CONTINUE
20 CONTINUE
   DO 30 J=1,N
      I=J
      I=I+(J,J-J-1)/2
      AP(I,J)=ZERO
      DO 25 K=LI+1,L
         L=K-LAMBD.A
         LK=L+(K-K+K-K)/2
         LI=L+(I-I-1)/N
         KJ=K+(J-J-1)/N
         KI=LI+K-L
         LJ=LJ+K-K
      25 AP(I,J)=DCONJG(T(LI))X(A(LI)X(T(KJ)+T(LJ))XDCONJG(A(LI)X(T(KI)))*AP(I,J)
   IF(LAMBD.A.EQ.0) AP(I,J)=AP(I,J)/2.0
30 CONTINUE
RETURN
END

SUBROUTINE SEARCH (DEL, I,HIGH, LOM, XLEVEL, ENERGY, ERROR, NGO)

Search subroutine is used to determine which transition belongs to a specific value of the field H within the error value specified.

IMPLICIT REAL X8 (A-H, O-Z)
DIMENSION XLEVEL(I)
NGO=1
XLEAST=ERROR
DO 3 ILO=1,3
   DO 3 IHI=2,4
      IF(IHI-ILO)/3,3,1
1 X=ABS(XLEVEL(IHI)-XLEVEL(ILO)-ENERGY)
   IF(X-XLEAST) 2,3,3
2 XLEAST = X
   IHIGH=IHI
   LOM=ILO
3 CONTINUE
   IF XLEAST.NE.ERROR GOTO 5
   NGO=0
   PRINT 4
4 FORMAT (26X,'ERROR OUT OF SEARCH RANGE'/ 36X,'RE-ADJUST TRIAL PARAMETERS, OR USE LARGER RANGE')
   RETURN
5 DEL=XLEVEL(IHIGH)-XLEVEL(LOM)-ENERGY
RETURN
END
APPENDIX 2

PROGRAM HFTEMP
C Programme is used to control the temperature of the
C crystal sample using the apparatus of Fig. IV.5
C
C Graph on VT125 home terminal
C text on Televideo out of RS232c port #2. BL’84
C
C
C Part 1)
C The user will be asked to enter a destination temperature in
C degrees Centigrade. (called IDEST)
C This temperature will be looked up on the line in TEMPY1
C (the first lookup table).
C and a corresponding heater voltage will be approximated.
C The approximate slope of the line in TEMPY1 at TMPB.
C Part 2/3)
C The newer version of this program will now interface the
C Hewlett Packard 3478A multimeter and then take temperature
C millivolt readings directly by the IEEE line. The present
C temperature will be displayed on it’s LCD display.
C Part 4)
C The millivolts will then be referenced to temperature by
C The Copper vs. Constantan Thermocouple chart, stored in TEMPY2
C This is the present temperature.
C Part 5)
C The output voltage will be calculated by the differential
C equation derived by Dr. Holuj.
C The output ticks will then be calculated by the equation:
C Outvolt=Outvolt+480+2847 and then the voltage will be set in the D/A
C output port #8 to go to the heater.
C
C Link With:
C
C HFTEMP, REGIS, CONVER, TALK, FORTEX, HPDATA
C
C HFTEMP = This module
C REGIS = Package of subroutines for Regis
C CONVER = A subroutine to convert numbers from integer to ASCII
C TALK = Package of subroutines to "talk & listen" over the
C serial lines
C FORTEX = Package of Fortran extensions
C HPDATA = Subroutine to talk to the IEEE bus (D.U.M.)
C
BYTE NUM(28), JUNK(81), DATA(11)
BYTE ACRLF(18), ACR(3), B(162), INPUT(5), ER
INTEGER TEMPA(38), TEMPB(180)
INTEGER ITIME
REAL TEMPA(38), TEMPB(180)
COMMON /CRLF/ ACRLF
THLAST=-9999
IX=1
FIRST=-1
CALL REGIS(1) ! Clear screen

The following disk access gets the lookup table for
temperatures corresponding to certain heater voltages

TYPEX,' disk access 1 (TEMPY1.DAT)'
CALL ASSIGN(18,'TEMPY1.DAT')
DEFINE FILE 18(100,2,0,IF10)
READ(18,1) SRANGE,SLOPE,LTMP1,TEMP1A(1),TEMP1B(1),I=1,LTMP1
1 FORMAT(F5.2,F5.2,12,E18.10,14,IX,F5.2/I)
CALL CLOSE (18)

The following disk access gets the lookup table for
temperatures versus thermocouple readings

TYPEX,' disk access 2 (TEMPY2.DAT)'
CALL ASSIGN(19,'TEMPY2.DAT')
DEFINE FILE 19(100,2,0,IF19)
READ(19,2) LTMP2,TEMP2A(1),TEMP2B(1),I=1,LTMP2
2 FORMAT(I2,E18.10,14,IX,F6.3/I)
CALL CLOSE (19)

CALL REGIS(1)

IF(FIRST.NE.1) GO TO 51
IX=1

TYPEX,' Do you wish to end (type E (cr))? '
TYPEX,' Or continue with another temperature (type (cr))? '
CALL GETSTR(5,INPUT,2,ER)
IF ((INPUT(1).EQ.'E').OR.(INPUT(1).EQ.'e')) GO TO 4888

TYPEX,' Enter destination temperature (',X TEMP1A(1),', to ',TEMP1A(LTMP1),') '
READ(5,I) IDEST
IF((IDEST.GT.TEMP1A(LTMP1)).OR.(IDEST.LT.TEMP1A(1))) GO TO 3
CALL REGIS(1)

Calculate destination voltage
DO 4 I=1,LTMP1
    IHIGH=I
    IF((IDEST.LE.TEMP1A(I)) GO TO 5
    CONTINUE
    TYPEX,' Temperature not found on lookup table TEMPY1'
    TYPEX,' Something is wrong'
    GO TO 6
4   IF(IHIGH.EQ.1) IHIGH=2
    ILD=IHIGH-1
    SLOPE=(TEMP1B(ILD)-TEMP1B(ILD0))/ ! this \-\ dVolt/
    X (TEMP1A(ILD0)-TEMP1A(ILD)) ! is \-\ /dTemp
C since \[
\frac{T_{\text{dest-Tlow}}}{T_{\text{high-Tlow}}} = \frac{U_{\text{dest-Vlow}}}{U_{\text{high-Vlow}}}
\] therefore a good appromimation for the destination.

Voltage is as follows:

\[
\begin{align*}
\text{AVOLT1} &= \text{FLOAT}(\text{DEST-TEMPA(1L0D)}) \\
\text{AVOLT2} &= \text{AVOLT1}/\text{FLOAT}(\text{HIHOOK-TEMPA(1L0D)}) \\
\text{AVOLT3} &= \text{AVOLT2}/\text{FLOAT}(\text{HIHOOK-TEMPB(1L0D)}) \\
\text{VOLT} &= \text{AVOLT3} + \text{FLOAT}(\text{TEMPB(1L0D)})
\end{align*}
\]

!VOLT is the voltage necessary to the dest temperature.

7 FORMAT(' The slope of the line at the destination temp is'
X ',F10.5,'/" The destination temperature's corresponding',
X ' voltage is,F10.4 //// Please check remote terminal for',
X ' greeting'/'/ From now on, this terminal is being used',
X ' exclusively for Graphing.../'/ Until a new temperature',
X ' is desired'//)

DO 2998 INIT=1,14

2998 ACRFL(INITER)=32 !/

ACRFL(1D)=13 ! This variable is used for producing a carriage
ACRFL(16)=10 ! return and line feed combination on remote terminal
ACRFL(17)=0 ! after padding with blanks.
ACRFL(18)=0 !/
ACR(1)=13 !
ACR(2)=8 ! This one is for just a carriage return (used for
ACR(3)=8 ! multiple striking on one line
CALL SCOPI(' X',JUNO)
JUNK(2)=27
CALL TALK(8,2,JUNO)
IF (FIRST.EQ.1) GO TO 29
FIRST=1
CALL TALK(8,2,' Welcome to TEMPY')
CALL TALK(8,2,ACRFL)
CALL TALK(8,2,'')
CALL TALK(8,2,ACRFL)
CALL TALK(8,2,' This is the text terminal, all the')
CALL TALK(8,2,ACRFL)
CALL TALK(8,2,' important text information will be displayed')
CALL TALK(8,2,ACRFL)
CALL TALK(8,2,' on this terminal while the temperature')
CALL TALK(8,2,ACRFL)
CALL TALK(8,2,' plot will be done on the other terminal (VT125)')
CALL TALK(8,2,ACRFL)
CALL TALK(8,2,ACRFL)
CALL TALK(8,2,' Please press any key to start')
CALL TALK(8,2,ACRFL)
CALL TALK(8,2,'')
CALL TALK(8,2,ACRFL)
CALL TALK(8,2,ACRFL)
CALL TALK(1,2,NUMD)
CALL TALK(2,2,'TIME:')
CALL TALK(0,2,ACRLF)  
15 CALL STIM(TIME)
CALL TIMASC(TIME,B)
CALL TALK(0,2,B)
CALL TALK(0,2,ACRD)
CALL TALK(3,2,B)
IF(B.EQ.0) GO TO 15
CALL RESIS(1)
CALL RESIS(2)
CALL SCOPY(' ','JUNO
JUNK(2)=27
CALL TALK(0,2,JUNO)
99 CALL SCOPY(' ','JUNO
JUNK(2)=27
CALL TALK(0,2,JUNO)
CALL TALK(0,2,'Presently waiting for the clock seconds')
CALL TALK(0,2,' to read a multiple of 85')
CALL TALK(0,2,ACRLF)
CALL TALK(0,2,'To set a new temperature,')
CALL TALK(0,2,' hit a key on this terminal')
CALL TALK(0,2,ACRLF)
ADEST=IDEST
CALL TALK(0,2,'Destination temperature: ') C
CALL CONVR(ADEST,8,8,NUM
CALL TALK(0,2,NUM
CALL TALK(0,2,ACRLF)  
21 CALL STIM(TIME)
DO 12211 IJI=1,188
B(1,J)=0
12211 CONTINUE
CALL TIMASC(TIME,B)
CALL CUTTIM(TIME,IX,IX,ISEC,IT)
CALL TALK(0,2,B)
CALL TALK(0,2,ACRD
CALL TALK(3,2,B)  ! Check for user input to change temperature
IF (B(1).NE.0) 60 TO 35 ! but don't hang up the program.
IF (MOD(180,5).NE.0) GO TO 21
CALL TALK(0,2,ACRLF)

C Get the present voltage on the HP3479A
89979 CALL SCOPY('7E1R-1',JUNO)
CALL HPODATA(JUNO,1) ! Send volt command
CALL SCOPY('K',JUNO
CALL HPODATA(JUNO,0,OUT) ! Fetch voltage
DECODE(11,89978,OUT) A
89918 FORMAT(F11.7)
IF (A.LT.0) GO TO 89911
CALL TALK(0,2,'***Overfl ow condition---CORRECT***')
CALL TALK(0,2,ACRLF)
GO TO 89909

89911 AMILLI=MILLI.
CALL CONVER(MILLI,1,1,NM64)
CALL TALK(8,2,ACRLF)
CALL TALK(8,2,'The HP multimeter would read: '.
CALL TALK(8,2,NM64)
CALL TALK(8,2,ACRLF)
C Look up temperature corresponding to millivolt reading
DO 23 I=1,TMP2
IHIGH=I
IF (AMILLI.LE.TEMP2(IHIGH)) GO TO 26
23 CONTINUE
CALL TALK(8,2,'Can not find millivolt reading... ignoring')
GO TO 18
26 IF (IHIGH.LE.1) IHIGH=2
ILON=IHIGH-1
C As before...
C since Tfind-Tlow = MILLIDest-MILLIow
C
C Thigh-Tlow = MILLIhigh-MILLIow
C
C therefore a good approximation for the seeked
C Temperature is as follows:
C
THERM1=AMILLI-TEMP2(ILO0)
THERM2=THERM1/TEMP2(IHIGH)-TEMP2(ILO0)
THERM3=(THERM2*FLOAT(TEMP2(IHIGH)-TEMP2(ILO0)))
THERMO=THERM3+FLOAT(TEMP2(ILO0))
IF (CHLAST.EQ.-9999) CTHLAST=THERMO
CALL CONVER(CTHAST,1,1,NM64)
CALL TALK(8,2,'(Last temp.)')
CALL TALK(8,2,NM64)
CALL CONVER(THERM1,1,1,NM64)
CALL TALK(8,2,'This temp. is approx.')
CALL TALK(8,2,NM64)
CALL TALK(8,2,ACRLF)
C Send the temp to the Multimeter
CALL CONCAT('7D3TEMP ',NUM,B)
CALL CONCAT(B,ACR,NUM)
CALL HDATA(JUNK,1)
C Find the output voltage
C The differential equation derived by Dr. Holuj suggests that the proper
C output voltage can be determined by the following formula:
C + V(t)=V(to)+ dV/dT(deltaT)
C
Where:
C + V(t)= voltage to be applied to the heater, corresponding to
C present temperature
C + V(to)= voltage corresponding to destination temperature
C + dV/dT= slope of V,T line at destination temp
C + deltaT= the difference in two consecutive temperature readings
C If the temperature is less than RANGE degrees away from the target temperature, the following equation will be used:
C
V(t)=V(t0)+ dV/dT (deltaT) +(to-t) x SCoeff
C
Where:
C
All variables are the same description as before with the
C
addition of:
C
to-t= the difference between the present temperature and the
desired temperature.
C
If the present temp. is higher than the destination temp., this value will be negative.
C
SCoeff= the multiplying coefficient to adjust the heater voltage.
C
C
DELTAT= THERMO- THLAST
THLAST= THERMO
OUTVLT= VOLT+ SLOPE x DELTAT  (VOLT & SLOPE are passed from the main program
SDIFF= FLOAT (DEST) - THERMO
IF (ABS(SDIFF) .GT. RANGE) GO TO 5533  ! If the temp is too far away...
CALL TALK(8,2, 'Fine tuning correction of ')  
SCORR= SDIFF x SCoeff
CALL CONVER(SCORR, 1, 1, NUM0
CALL TALK(8, 2, NUM0
CALL TALK(8, 2, ' Volts')
CALL TALK(8, 2, ACRLF)
OUTVLT= OUTVLT + SCORR
GO TO 5534

5533 CALL TALK(8, 2, 'Fine tuning off...')
   CALL TALK(8, 2, '
   CALL TALK(8, 2, ACRLF)

5534 CALL TALK(8, 2, 'The output voltage should read')
   CALL CONVER(OUTVLT, 1, 1, NUM0
   CALL TALK(8, 2, NUM0
   CALL TALK(8, 2, ACRLF)

C The following equation calculates output D/A ticks
C This equation should be improved with further experimentation

IOUTTK= OUTVLT x 3.483 + 2847
IVALUE= IDOR(1, "178448", -1, IOUTTK,)
CALL TALK(8, 2, 'Output ticks are:')
   ATICK= FLOAT(IOUTTK)
   CALL CONVER(ATICK, 1, 1, NUM0
   CALL TALK(8, 2, NUM0
   CALL TALK(8, 2, ACRLF)
C.........Plot pixel....
   IX= IX+2
   IY= (THERMO+193) x 476/388.
   CALL POINT(IX, IY)
   CALL POINT(IX+1, IY)
GO TO 99

25 CALL REGIS(1)  ! all done with this temperature... reset RegIS
CALL SCOPY(' X',JUNIO) ! and tell the user to look onto the system
JUNK(2)=27 ! terminal for the option to end or enter
CALL TALK(8,2,JUNIO) ! a new temperature.
CALL TALK(8,2,'Please return to the VT125 for')
CALL TALK(8,2,' entering a new temperature')
DO 49 I=1,10
49 CALL TALK(8,2,ACRLF)
GO TO 3

4890 CALL REGIS(1) ! finished program ... ReSET Regis and stop execution
CALL SCOPY(' X',JUNIO)
JUNK(2)=27
CALL TALK(8,2,JUNIO)
CALL EXIT
END

C...

SUBROUTINE POINT(I,IY)
COMMON /CRLF/, ACRLF
LOGICAL : ACRLF(13), BEL(4), ER
LOGICAL : AX(20), AY(20), A1(20), A2(20)
IF (IX.LT.764) GO TO 12
IX=1
CALL REGIS(1)
CALL REGIS(2)
BEL(1)=7
BEL(2)=7
BEL(3)=8
BEL(4)=8
CALL TALK(8,2,BEL)
CALL PUTSTR(7,BEL,43,ER)
CALL TALK(8,2,CRLF)
CALL TALK(8,2,'New graphing page')
CALL TALK(8,2,CRLF)
CALL TALK(8,2,BEL)
12 Y=IY
Y=475-Y
X=IX
CALL REGIS(3)
CALL CONVERX(8,8,AX)
CALL CONVERY(I,IY,AY)
CALL CONCAT(' PI',AX,A1) ! move turtle to desired spot
CALL CONCAT(A1,' ',A1)
CALL CONCAT(A1,AY,A2)
CALL CONCAT(A2,'>',A1)
A1(2)=27
CALL PUTSTR(7,A1,43)
CALL SCOPY(' V1',A1) ! light up pixel
A1(2)=27
CALL PUTSTR(7,A1,43)
CALL REGIS(4)
RETURN
END
REFERENCES


VITA AUCTORIS

I was born in Windsor, Ontario, in 1959 where I received my early education. I completed my secondary school education at F.J. Brennan H.S.. On completion of secondary school I attended the University of Windsor and graduated with a B.Sc. in Physics in 1983. At present I am completing requirements towards my M.Sc. Physics degree at Windsor.